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Research paper

Catalysts for the asymmetric transfer hydrogenation of various ketones from [3-[(2*S*)-2-[(diphenylphosphanyl)oxy]-3-phenoxypropyl]-1-methyl-1H-imidazol-3-ium chloride] and [Ru(η^6-arene)(μ-Cl)Cl]$_2$, Ir(η^5-C_5Me_5)(μ-Cl)Cl]$_2$ or [Rh(μ-Cl)(cod)]$_2$

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ABSTRACT

The combination of [3-[(2*S*)-2-[(diphenylphosphanyl)oxy]-3-phenoxypropyl]-1-methyl-1H-imidazol-3-ium chloride] with [Ru(η^6-arene)(μ-Cl)Cl]$_2$, Ir(η^5-C_5Me_5)(μ-Cl)Cl]$_2$ or [Rh(μ-Cl)(cod)]$_2$, in the presence of KOH/*iso*PrOH, has been found to generate catalysts that are capable of enantioselectively reducing alkyl, aryl ketones to the corresponding (*R*)-alcohols. Under optimized conditions, when the catalysts were applied to the asymmetric transfer hydrogenation, we obtained the secondary alcohol products in high conversions and enantioselectivities using only 0.5 mol% catalyst loading. In addition, [3-[(2*S*)-2-{[(chloro(η^4-1,5-cyclooctadiene)rhodium)diphenyl phosphanyl] oxy}-3-phenoxypropyl]-1-methyl-1H-imidazol-3-ium chloride], (**6**) complex is much more active than the other analogous complexes in the transfer hydrogenation. Catalyst **6** acts as excellent catalysts, giving the corresponding (*R*)-1-phenyl ethanol in 99% conversion in 30 min (TOF ≤ 396 h^{-1}) and in high enantioselectivity (92% ee).

1. Introduction

The chemistry of *P*-based ligands has been extensively investigated in recent years [1]. These compounds are extremely attractive as potential ligands since various structural modifications are accessible via simple P—N, P—C and P—O bond formation [2]. Many modified *P*-based ligands have significant applications in organometallic chemistry and catalysis, giving selective catalysts for hydroformylation, hydrosilylation and, especially transfer hydrogenation [3,4,5,6]. Although many chiral phosphorus ligands have been synthesized and used in transition-metal-catalyzed asymmetric reactions, a large number of reactions still lack effective chiral ligands, and the enantioselectivities in many reactions are substrate dependent [7]. While much effort has been devoted to the synthesis of aminophosphines and their metal complexes, similar studies on the analogous phosphinites are less extensive [8,9], even though some of their complexes have proved to be efficient catalysts [10,11]. Phosphinites provide different chemical, electronic and structural properties compared to phosphines. The metal-phosphorus bond is often stronger for phosphinites compared to the related phosphine due to the presence of electron-withdrawing P-OR group. In addition, the empty σ*-orbital of the phosphinite $P(OR)R_2$ is stabilized, making the phosphinite a better acceptor [12]. Therefore, the development of effective chiral ligands, especially ligands having novel chiral backbones, is still an important and challenging task for chemists [13].

Many biologically active compounds, such as pharmaceuticals, agrochemicals, flavoring, and functional materials, exhibit “handedness” [14]. The preparation of these “handed” (chiral) compounds in enantiomerically pure form is a challenging goal in modern organic synthesis. Undoubtedly, the use of chiral metal complex catalysis is a powerful, economically feasible tool for the preparation of optically active organic compounds on both laboratory and industrial scales

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[15]. Furthermore, transition metal complexes are influential catalysts for organic transformations and when the suitable ligands are associated with the metal center, they can offer chemio, regio or stereo selectivity under mild conditions [16]. However, the appropriate choice of metal precursors and the reaction conditions are crucial for catalytic properties [17]. A number of transition metal complexes are known to be catalyzing hydrogen transfer from an alcohol to a ketone [18,19]. Ketones are the most widespread corporate precursors used in organic synthesis and reduced ketones, alcohols are very important blocks for the pharmaceutical and fine chemical industries [20]. Although many applications require racemic alcohols, the need for enantiomerically pure products is growing because of their significance as intermediates for the manufacture of pharmaceuticals and advanced materials [21,22], raising great interest in finding new methods for their production. In addition, ketones are one of the most common families of unsaturated substrates, therefore the enantioselective reduction of prochiral ketones leading to optically pure secondary alcohols is a subject of considerable interest from both the academic and the industrial perpectives [23]. Extensive efforts have been devoted to their reduction into secondary alcohols especially via hydrogenation [24]. Catalytic transfer hydrogenation (TH) with the aid of a stable hydrogen donor is a useful alternative process for catalytic hydrogenation by molecular hydrogen for the reduction of ketones [25,26]. In transfer hydrogenation, organic molecules such as primary and secondary alcohols [27] or formic acid and its salts [28] have been employed as the hydrogen source. Over the last three decades, most effort on asymmetric transfer hydrogenation has been focused on the use of ruthenium, rhodium and iridium catalysts [29,30,31].

It is well-known that ionic liquids are potential replacements for organic solvents both on laboratory and industrial scales due to their green characteristics such as thermal stability [32,33,34], lack of vapor pressure, non-flammability, wide liquid range, wide range of solubility and miscibility [35,36,37,38]. Furthermore, they can be readily recycled; have profound effect on the activity and selectivity in reactions and in some cases, facilitate the isolation of products. Therefore, ionic liquids are considered to be viable substitute for volatile organic solvents [39]. An unusual feature of ionic liquids is the tunability of their chemical and physical properties by selection of appropriate anion–-cation combinations [40]. Metal-containing ionic liquids are regarded as promising new materials that combine the properties of ionic liquids with additional intrinsic magnetic, spectroscopic, or catalytic properties, depending on the incorporated metal ion [41]. Furthermore, it has been known that ionic liquids (ILs) can be functionalized flexibly by incorporating functional moieties into the IL structure to develop different functionalized ionic liquids (FILs), which dually possess the characters of the incorporated functionalities as well as those of the ILs [42,43]. The P-based ligands-FILs have long been investigated for the design of the ionic organometallic compounds and applications to catalysis [44,45,46]. It has been found that, while the coordinating P (III) atom is vicinal to the positive charged imidazolium ring, the corresponding P-based ligands-FILs are featured with π-acceptor character as well as σ-donor [47,48]. Hence, the varied coordination behaviors of such P-based ligands-FILs are in great concerns in the coordinating chemistry and catalysis, leading to the significant changes of the complex configurations and catalytic performance [49]. In recent years, we have been synthesized many *P*-based ligands and used them in transition-metal-catalyzed asymmetric transfer hydrogenation reaction [50]. However, *P*-based ligands containing ionic liquid part are rarely used in this reaction. Furthermore, there is still a need for highly effective chiral ligands. Therefore, to develop effective highly active well-designed chiral ligands, the features of ionic liquids are combined with phosphinites. Although some phosphinite ligands and their derivatives have been employed successfully as ligands in the transfer hydrogenation of ketones [51,52,53] references therein), a screening of catalytic activities of ionic liquid based phosphinites in this reaction is not common in the literature. For this reason, we are extending our study to develop useful and magnificent catalysts, in this paper, we report for the first time the synthesis and full characterization of four new half-sandwiches ruthenium, iridium and rhodium-arene complexes based on chiral functionalized ionic liquid, CFIL, and their subsequent application in asymmetric transfer hydrogenation of the various ketones.

2. Experimental

2.1. Materials and methods

Unless otherwise mentioned, all reactions were carried out under an atmosphere of argon using conventional Schlenk glassware, solvents were dried using established procedures and distilled under argon just prior to use. Analytical grade and deuterated solvents were purchased from Merck. The starting materials 1-methylimidazole, (*S*)-2-oxiranylanisole, PPh_2Cl and Et_3N were purchased from Fluka and used as received. $[Ru(\eta^6\text{-}p\text{-cymene})(\mu\text{-Cl})Cl]_2$ [54], $[Ru(\eta^6\text{-benzene})(\mu\text{-Cl})Cl]_2$ [55], $Ir(\eta^5\text{-}C_5Me_5)(\mu\text{-Cl})Cl]_2$ [56] and $[Rh(\mu\text{-Cl})(cod)]_2$ [57] were prepared according to the literature procedures. ^1H (at 400.1 MHz), ^{13}C (at 100.6 MHz) and $^{31}P\text{-}\{^1H\}$ NMR (at 162.0 MHz) spectra were recorded on a Bruker AV 400 spectrometer, with TMS (tetramethylsilane) as an internal reference for ^1H NMR and ^{13}C NMR or 85% H_3PO_4 as an external reference for $^{31}P\text{-}\{^1H\}$ NMR. The infrared spectra was measured by an Agilent Cary 630 FTIR, respectively. The FTIR spectra were recorded using a universal ATR sampling accessory (4000–400 cm^{-1}). Elemental analysis was carried out on a Costech ECS 4010 instrument. Melting points were recorded by a Gallenkamp Model apparatus with open capillaries.

2.2. General procedure for the asymmetric transfer hydrogenation of ketones

Typical procedure for the catalytic hydrogen-transfer reaction: a solution of the complexes **3–6** (0.00125 mmol), KOH (0.00625 mmol) and the corresponding ketone (0.25 mmol) in degassed *iso*PrOH (5 mL) was refluxed until the reaction completed. Then, a sample of the reaction mixture is taken off, diluted with acetone and analyzed immediately by GC, conversions obtained are related to the residual unreacted ketone.

2.3. GC analyses

GC analyses were performed on a Shimadzu GC 2010 Plus Gas Chromatograph equipped with a cyclodex-B (Agilent) capillary column (30 m × 0.32 mm I.D. × 0.25 μm film thickness). Racemic samples of alcohols were obtained by reduction of the corresponding ketones with $NaBH_4$ and used as the authentic samples for ee % determination. The GC parameters for asymmetric transfer hydrogenation of ketones were as follows; initial temperature, 50 °C; initial time 1.1 min; solvent delay, 4.48 min; temperature ramp 1.3 °C/min; final temperature, 150 °C; initial time 2.2 min; temperature ramp 2.15 °C/min; final temperature, 250 °C; initial time 3.3 min; final time, 44.33 min; injector port temperature, 200 °C; detector temperature, 200 °C, injection volume, 2.0 μL.

2.4. Synthesis and characterization of compounds

2.4.1. Synthesis of 3-[(2S)-2-hydroxy-3-phenoxypropyl]-1-methyl-1H-imidazol-3-ium chloride, (1)

To a stirred solution of 1-methylimidazole (1.03 g, 12.5 mmol) in ethanol (2 mL) at room temperature was carefully added concentrated hydrochloric acid (1.05 mL, 12.8 mmol). Caution: neutralization of a base with a strong acid is highly exothermic. After addition of acid, the reaction mixture was cooled to room temperature and (*S*)-2-oxiranylanisole (1.95 g, 13 mmol) was added dropwise with stirring, while maintaining the temperature at 25 °C. The reaction vessel was then

sealed and stirred at room temperature for approximately 30 h. The solvent was removed under reduced pressure on heating at 70 °C, followed by heating under high vacuum, to yield a liquid that became more viscous upon extensive drying, and this was recrystallized from ethylacetate at 0 °C. The precipitated product was filtered and dried in vacuo yielding **1** as an off-white solid. Yield: 2.79 g, 83.0%; M.p.: 121–122 °C; $[\alpha]_D^{20} = +33.6°$ (c 1, $CHCl_3$); ^{1}H NMR $CDCl_3$-d_1, ppm): δ: 9.57 (s, 1H, $(CH_3)NC\underline{H}N$–), 7.41 and 7.33 (2xs, 2H, –$NC\underline{H}C\underline{H}N$–), 7.12–7.16 (m, 2H, –$CH_2O\underline{Ph}$), 6.82–6.86 (m, 1H, –$CH_2O\underline{Ph}$), 6.77–6.79 (m, 2H, –$CH_2O\underline{Ph}$), 6.08 (d, 1H, J = 5.8 Hz, –CHO**H**), 4.53–4.56 (m, 1H, $NC\underline{H}_2$, (a)), 4.36–4.41 (m, 1H, $NC\underline{H}_2$, (b)), 4.27 (br, 1H, –C**H**OH), 4.02–4.05 (m, 1H, –$C\underline{H}_2$OPh, (a)), 3.85 (s, 3H, $C\underline{H}_3N$), 3.77–3.81 (m, 1H, –$C\underline{H}_2$OPh, (b)); ^{13}C NMR (100.6 MHz, $CDCl_3$-d_1, ppm): δ: 36.43 ($\underline{C}H_3N$), 52.55 ($N\underline{C}H_2$), 67.56, 68.40 (–**C**HOH and –$\underline{C}H_2$OPh), 114.45, 121.24, 129.54 (*o*-, *m*-, *p*-carbons of –$CH_2O\underline{Ph}$), 122.90, 123.28 (–$N\underline{C}H\underline{C}HN$–), 137.62 ($(CH_3)N\underline{C}HN$–),158.00 (*i*-carbon of –$CH_2O\underline{Ph}$); ***assignment was based on the ^{1}H–^{13}C HETCOR, DEPT and ^{1}H–^{1}H COSY spectra***; IR: υ 3209 (O—H), 2959 (aliphatic C—H) cm^{-1}; Anal. for $C_{13}H_{17}N_2O_2Cl$ (268.74 g/mol): calcd. C 58.10, H 6.38, N 10.42; found C 57.99, H 6.34, N 10.37%.

2.4.2. Synthesis of [3-[(2S)-2-[(diphenylphosphanyl)oxy]-3-phenoxypropyl]-1-methyl-1H-imidazol-3-ium chloride], (2)

3-[(2*S*)-2-hydroxy-3-phenoxypropyl]-1-methyl-1H-imidazol-3-ium chloride, **(1)** (0.100 gr, 0.37 mmol) and Et_3N (0.038 gr, 0.37 mmol) were dissolved in dry CH_2Cl_2 (30 mL) under an argon atmosphere. Next, PPh_2Cl (0.084 gr, 0.37 mmol) was added dropwise with a syringe to this solution. The mixture was stirred at room temperature for 30 min, and the solvent was removed under reduced pressure. After addition of dry thf, the white precipitate (triethylammonium chloride) was filtered off under argon and dried in vacuo to produce a white viscous oily compound **2**. Yield: 0.160 g, 95.0%. $[\alpha]_D^{20} = +42.5°$ (c 1, $CHCl_3$); ^{1}H NMR (400.1 MHz, $CDCl_3$-d_1, ppm): δ: 9.91 (s, 1H, -$(CH_3)NC\underline{H}N$–), 6.74–7.30 (m, 17H, $P(C_6\underline{H}_5)_2$ + –$NC\underline{H}C\underline{H}N$- + –$CH_2O\underline{Ph}$), 4.84–4.87 (m, 1H, $NC\underline{H}_2$, (a)), 4.62–4.70 (m, 2H, $NC\underline{H}_2$, (b) + -C**H**OP), 4.17 (m, 2H, -$C\underline{H}_2$OPh), 3.72 (s, 3H, $C\underline{H}_3N$); ^{13}C NMR (100.6 MHz, $CDCl_3$-d_1, ppm): *δ* 36.60 ($\underline{C}H_3N$), 52.62 ($N\underline{C}H_2$), 67.64 (–$\underline{C}H_2$OPh), 78.09 (d, J = 22.1 Hz, -**C**HOP), 114.56, 121.35, 122.76, 123.16, 129.61 (–$N\underline{C}H\underline{C}HN$– and *o*-, *m*-, *p*-carbons of –$CH_2O\underline{Ph}$), 128.62 (d, $^3J_{31P–13C}$ = 9.1 Hz, *m*-$P(\underline{C}_6H_5)_2$), 131.53 (*p*-$P(\underline{C}_6H_5)_2$), 135.28 (d, $^2J_{31P–13C}$ = 12.1, *o*-$P(\underline{C}_6H_5)_2$)), 138.21 (-$(CH_3)N\underline{C}HN$–), 158.02 (*i*-carbon of –$CH_2O\underline{Ph}$) (not observed, *i*-P$(\underline{C}_6H_5)_2$); ***assignment was based on the ^{1}H–^{13}C HETCOR, DEPT and ^{1}H–^{1}H COSY spectra***; ^{31}P-{^{1}H} NMR (162.0 MHz, $CDCl_3$-d_1, ppm): *δ* 118.49 (s, O**P**Ph_2); IR: υ 3146, 3053 (aromatic C—H), 2930, 2870 (aliphatic C—H) 1435 (P-Ph), 1044 (O—P) cm^{-1}; Anal. for $C_{25}H_{26}N_2O_2PCl$ (452.92 g/mol): calcd. C 66.30, H 5.79, N 6.19; found C 66.21, H 5.73, N 6.15%.

2.4.3. Synthesis of [3-[(2S)-2-({[dichloro(η^6-p-cymene)ruthenium] diphenyl phosphanyl}oxy)-3-phenoxypropyl]-1-methyl-1H-imidazol-3-ium chloride], (3)

$[Ru(\eta^6$-*p*-cymene)(μ-Cl)Cl$]_2$ (0.068 g, 0.110 mmol) and [(Ph_2P)-$C_{13}H_{16}N_2O_2$]Cl, **2** (0.100 g, 0.221 mmol) were dissolved in dry CH_2Cl_2 (25 mL) under argon atmosphere and stirred for 1 h at room temperature. The volume was concentrated to ca. 1–2 mL under reduced pressure and addition of petroleum ether (20 mL) gave the corresponding ruthenium(II) complex as a red solid. The product was collected by filtration and dried in vacuo. Yield:150 mg, 89.5%; m.p.:127–128 °C; $[\alpha]_D^{20} = +39.1°$ (c 1, $CHCl_3$); ^{1}H NMR (400.1 MHz, $CDCl_3$, ppm): *δ* 9.89 (s, 1H, -$(CH_3)NC\underline{H}N$–), 6.42–7.95 (m, 17H, P$(C_6\underline{H}_5)_2$ + –$NC\underline{H}C\underline{H}N$- + –$CH_2O\underline{Ph}$), 5.50 (s, 2H, aromatic protons of *p*-cymene), 5.16 (d, J = 5.2 Hz, 1H, aromatic protons of *p*-cymene), 4.93 (d, J = 5.2 Hz, 1H, aromatic protons of *p*-cymene), 4.69 (br, 1H, -C**H**OP), 4.60 (br, 2H, $NC\underline{H}_2$), 3.95 (br, 4H, -$C\underline{H}_2$OPh, (a) + $C\underline{H}_3N$), 3.60 (br, 1H, -$C\underline{H}_2$OPh, (b), 2.45 (m, 1H, –C**H**– of *p*-cymene), 1.85 (s, 3H, $C\underline{H}_3$Ph of *p*-cymene), 1.05 (d, J = 6.8 Hz, 3H, $C\underline{H}_3)_2$CHPh of *p*-cymene), 0.72 (d, J = 6.8 Hz, 3H, $C\underline{H}_3)_2$CHPh of *p*-cymene); ^{13}C NMR (100.6 MHz, $CDCl_3$-d_1, ppm): *δ* 17.22 ($\underline{C}H_3$Ph of *p*-cymene), 20.25, 22.56 (($\underline{C}H_3)_2$CHPh of *p*-cymene), 30.05 (–**C**H– of *p*-cymene), 36.60 ($\underline{C}H_3N$), 50.50 ($N\underline{C}H_2$), 66.55 (–$\underline{C}H_2$OPh), 73.73 (d, J = 9.1 Hz, -**C**HOP), 85.29 (s, aromatic carbons of *p*-cymene), 88.26 (s, aromatic carbons of *p*-cymene), 89.91 (d, J = 8.0 Hz, aromatic carbons of *p*-cymene), 94.23 (s, aromatic carbons of *p*-cymene), 96.41, 110.35 (quaternary carbons of *p*-cymene), 114.27, 121.15, 122.55, 124.18, 129.33 (–$N\underline{C}H\underline{C}HN$– and *o*-, *m*-, *p*-carbons of –$CH_2O\underline{Ph}$), 128.30 (d, $^3J_{31P–13C}$ = 10.1 Hz, *m*-$P(\underline{C}_6H_5)_2$), 131.30 (*p*-$P(\underline{C}_6H_5)_2$), 134.50 (d, $^2J_{31P–13C}$ = 12.1, *o*-$P(\underline{C}_6H_5)_2$)), 137.78 (-$(CH_3)N\underline{C}HN$–), 157.18 (*i*-carbon of –$CH_2O\underline{Ph}$), (not observed, *i*-$P(\underline{C}_6H_5)_2$); ***assignment was based on the ^{1}H–^{13}C HETCOR, DEPT and ^{1}H–^{1}H COSY spectra***; ^{31}P-{^{1}H} NMR (162.0 MHz, $CDCl_3$, ppm): *δ* 124.61 (s, O**P**Ph_2); IR: υ 3146, 3056 (aromatic C—H), 2960, 2870 (aliphatic C—H) 1435 (P-Ph), 1044 (O—P) cm^{-1}; Anal. for $C_{35}H_{40}N_2O_2PRuCl_3$ (759.12 g/mol): calcd. C 55.38, H 5.31, N 3.69; found C 55.31, H 5.27, N 3.64%.

2.4.4. Synthesis of [3-[(2S)-2-({[dichloro(η^6-benzene)ruthenio] diphenylphosphanyl}oxy)-3-phenoxypropyl]-1-methyl-1H-imidazol-3-ium chloride], (4)

$[Ru(\eta^6$-benzene)(μ-Cl)Cl$]_2$ (0.055 g, 0.110 mmol) and [(Ph_2P)-$C_{13}H_{16}N_2O_2$]Cl, **2** (0.100 g, 0.221 mmol) were dissolved in dry CH_2Cl_2 (25 mL) under argon atmosphere and stirred for 1 h at room temperature. The volume was concentrated to ca. 1–2 mL under reduced pressure and addition of petroleum ether (20 mL) gave the corresponding ruthenium (II) complex as a red solid. The product was collected by filtration and dried in vacuo. Yield:138 mg, 88.9%; m.p.:131–132 °C; $[\alpha]_D^{20} = +28.8°$ (c 1, $CHCl_3$); ^{1}H NMR (400.1 MHz, $CDCl_3$, ppm): *δ* 9.26 (s, 1H, -$(CH_3)NC\underline{H}N$–), 6.63–7.95 (m, 17H, P$(C_6\underline{H}_5)_2$ + –$NC\underline{H}C\underline{H}N$- + –$CH_2O\underline{Ph}$), 5.50 (s, 6H, aromatic protons of benzene), 5.11 (br, 1H, -C**H**OP), 4.60 (br, 2H, $NC\underline{H}_2$), 3.97 (br, 5H, -$C\underline{H}_2$OPh + $C\underline{H}_3N$)); ^{13}C NMR (100.6 MHz, $CDCl_3$-d_1, ppm): δ (not observed, $\underline{C}H_3N$), 52.12 ($N\underline{C}H_2$), 67.88 (–$\underline{C}H_2$OPh), 75.32 (d, J = 16.1 Hz, -**C**HOP), 90.49 (s, aromatic carbons of benzene), 114.68, 121.14, 124.62, 124.84, 129.43 (–$N\underline{C}H\underline{C}HN$– and *o*-, *m*-, *p*-carbons of –$CH_2O\underline{Ph}$), 128.58 (d, $^3J_{31P–13C}$ = 10.1 Hz, *m*-$P(\underline{C}_6H_5)_2$), 131.59 (*p*-P$(\underline{C}_6H_5)_2$), 133.38 (d, $^2J_{31P–13C}$ = 35.2*o*-$P(\underline{C}_6H_5)_2$)), 137.69 (-$(CH_3)N\underline{C}HN$–), 157.37 (*i*-carbon of –$CH_2O\underline{Ph}$), (not observed, *i*-$P(\underline{C}_6H_5)_2$); ***assignment was based on the ^{1}H–^{13}C HETCOR, DEPT and ^{1}H–^{1}H COSY spectra***; ^{31}P-{^{1}H} NMR (162.0 MHz, $CDCl_3$, ppm): *δ* 121.85 (s, O**P**Ph_2); IR: υ 3142, 3056 (aromatic C—H), 2952 (aliphatic C—H) 1435 (P-Ph), 1044 (O—P) cm^{-1}; Anal. for $C_{31}H_{32}N_2O_2PRuCl_3$ (703.01 g/mol): calcd. C 52.96, H 4.59, N 3.99; found C 52.88, H 4.55, N 3.94%.

2.4.5. Synthesis of [3-[(2S)-2-{[(dichloro(η^5–pentamethylcyclopentadienyl) iridio)diphenyl phosphanyl]oxy}-3-phenoxypropyl]-1-methyl-1H-imidazol-3-ium chloride], (5)

$Ir(\eta^5$-$C_5Me_5)$(μ-Cl)Cl$]_2$ (0.088 g, 0.110 mmol) and [(Ph_2P)-$C_{13}H_{16}N_2O_2$]Cl, **2** (0.100 g, 0.221 mmol) were dissolved in dry CH_2Cl_2 (25 mL) under argon atmosphere and stirred for 1 h at room temperature. The volume was concentrated to ca. 1–2 mL under reduced pressure and addition of petroleum ether (20 mL) gave the corresponding Iridium (III) complex as an orange microcrystalline solid. The product was collected by filtration and dried in vacuo. Yield:160 mg, 85.1%; m.p.:152–153 °C; $[\alpha]_D^{20} = +46.7°$ (c 1, $CHCl_3$); ^{1}H NMR (400.1 MHz, $CDCl_3$, ppm): *δ* 9.72 (s, 1H, -$(CH_3)NC\underline{H}N$–), 6.46–7.88 (m, 17H, P$(C_6\underline{H}_5)_2$ + –$NC\underline{H}C\underline{H}N$- + –$CH_2O\underline{Ph}$), 5.13 (br, 1H, -C**H**OP), 4.67 (d, J = 17.2 Hz, 2H, $NC\underline{H}_2$), 4.00 (s, 3H, $C\underline{H}_3N$), 3.97 (br, 1H, -$C\underline{H}_2$OPh, (a), 3.86 (br, 1H, -$C\underline{H}_2$OPh, (b), 1.33 (s, 15H, $C\underline{H}_3$ of $\underline{Cp}$*(C_5Me_5); ^{13}C NMR (100.6 MHz, $CDCl_3$-d_1, ppm): *δ* 8.24 ($C_5\underline{Me}_5$), 36.90 ($\underline{C}H_3N$), 50.63 ($N\underline{C}H_2$), 67.58 (–$\underline{C}H_2$OPh), 74.44 (d, J = 6.0 Hz, -**C**HOP), 94.12 ($\underline{C}_5Me_5$), 114.29, 120.96, 122.67, 123.76, 129.22 (–$N\underline{C}H\underline{C}HN$– and *o*-, *m*-, *p*-carbons of –$CH_2O\underline{Ph}$), 128.29 (d, J = 11.1 Hz, *m*-$P(\underline{C}_6H_5)_2$), 131.57 (s, *p*-$P(\underline{C}_6H_5)_2$), 134.67 (br, *o*-$P(\underline{C}_6H_5)_2$)), 138.37 (-$(CH_3)N\underline{C}HN$–), 157.42 (*i*-carbon of –$CH_2O\underline{Ph}$) (not observed, *i*-$P(\underline{C}_6H_5)_2$);

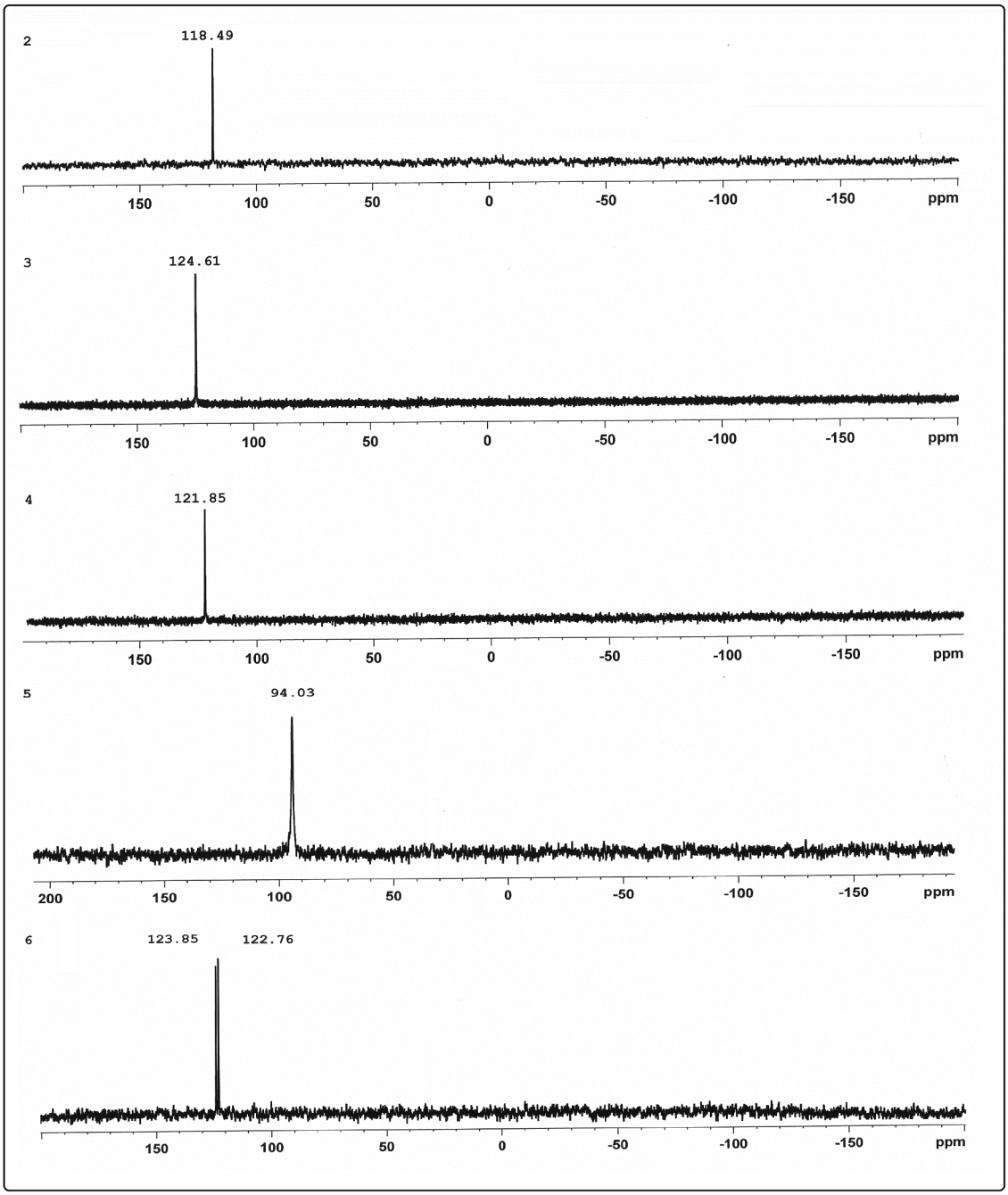


Fig. 1. The ^{31}P-{^{1}H} NMR spectra of compounds [3-[(2S)-2-[(diphenylphosphanyl)oxy]-3-phenoxypropyl]-1-methyl-1H-imidazol-3-ium chloride]], **(2),** [3-[(2S)-2-({[dichloro(η^6-*p*-cymene)ruthenio]diphenyl phosphanyl}oxy)-3-phenoxypropyl]-1-methyl-1H-imidazol-3-ium chloride]] **(3),** [3-[(2S)-2-({[dichloro(η^6-benzene)ruthenio]diphenylphosphanyl}oxy)-3-phenoxypropyl]-1-methyl-1H-imidazol-3-ium chloride]] **(4)**, [3-[(2S)-2-{[(dichloro(η^5–pentamethylcyclopentadienyl)iridio)diphenyl phosphanyl]oxy}-3-phenoxypropyl]-1-methyl-1H-imidazol-3-ium chloride]] **(5),** [3-[(2S)-2-{[(chloro(η^4-1,5-cyclooctadiene)rhodio)diphenylphosphanyl] oxy}-3-phenoxypropyl]-1-methyl-1H-imidazol-3-ium chloride]] **(6).**

***assignment was based on the ^{1}H–^{13}C HETCOR, DEPT and ^{1}H–^{1}H COSY spectra*;** ^{31}P-{^{1}H} NMR (162.0 MHz, $CDCl_3$, ppm): δ 94.03 (s, O**P**Ph_2); IR: υ 3056 (aromatic C—H), 2960 (aliphatic C—H) 1435 (P-Ph), 1044 (O—P) cm^{-1}; Anal. for $C_{35}H_{41}N_2O_2PIrCl_3$ (851.27 g/mol): calcd. C 49.38, H 4.85, N 3.29; found C 49.29, H 4.81, N 3.26%.

2.4.6. Synthesis of [3-[(2S)-2-{[(chloro(η^4-1,5-cyclooctadiene)rhodium) diphenyl phosphanyl] oxy}-3-phenoxypropyl]-1-methyl-1H-imidazol-3-ium chloride], (6)

[Rh(μ-Cl)(cod)]$_2$ (0.054 g, 0.110 mmol) and [(Ph_2P)-$C_{13}H_{16}N_2O_2$]Cl, **2** (0.100 g, 0.221 mmol) were dissolved in dry CH_2Cl_2 (25 mL) under argon atmosphere and stirred for 1 h at room temperature. The volume was concentrated to ca. 1–2 mL under reduced pressure and addition of petroleum ether (20 mL) gave the corresponding Rhodium (I) complex as a yellow microcrystalline solid. The product was collected by filtration and dried in vacuo. Yield: 130 mg, 84.2%; m.p.:124–125 °C; $[\alpha]_D^{20} = +33.2°$ (c 1, $CHCl_3$); **^{1}H NMR (400.1 MHz, $CDCl_3$, ppm)**: δ 10.41 (s, 1H, -(CH_3)NC**H**N–), 6.84–7.52 (m, 17H, P(C_6**H**$_5$)$_2$ + –NC**H**C**H**N- + –CH_2O**Ph**), 5.76 (br, 1H, C**H** of cod), 5.69 (br, 1H, C**H** of cod), 5.03 (m, 1H, NC**H**$_2$ (a)), 4.85 (m, 1H, NC**H**$_2$ (b)), 4.57–4.64 (m, 2H, -C**H**$_2$OPh), 4.27 (br, 1H, -C**H**OP), 3.93 (s, 3H, C**H**$_3$N), 3.42 (br, 1H, C**H** of cod), 2.96 (br, 1H, C**H** of cod), 2.38 (br, 2H, C**H**$_2$ of

cod), 2.28 (d, J = 7.2 Hz, 2H, C**H**$_2$ of cod), 1.96 (br, 2H, C**H**$_2$ of cod), 1.67 (d, J = 8.0 Hz, 2H, C**H**$_2$ of cod) ; ^{13}C NMR (100.6 MHz, $CDCl_3$-d_1, ppm): δ 27.82, 29.08, 32.12, 34.04 (**C**H$_2$ of cod), 36.65 (**C**H$_3$N), 50.63 (N**C**H$_2$), 68.97 (–**C**H$_2$OPh), 71.32 (d, J = 15.1 Hz, **C**H of cod), 71.81 (d, J = 13.1 Hz, **C**H of cod), 77.58 (d, J = 12.1 Hz, -**C**HOP), 111.85 (d, J = 11.1 Hz, **C**H of cod), 114.74, 121.49, 122.20, 123.12, 129.76 (–N**C**H**C**HN– and *o*-, *m*-, *p*-carbons of –CH$_2$O**Ph**), 128.77 (d, J = 13.1 Hz, *m*-P(**C**$_6$H$_5$)$_2$), 131.65 (s, *p*-P(**C**$_6$H$_5$)$_2$), 133.18 (d, J = 15.1 Hz, *o*-P(**C**$_6$H$_5$)$_2$)), 138.94 (-(CH$_3$)N**C**HN–), 158.08 (*i*-carbon of –CH$_2$O**Ph**) (not observed, *i*-P(**C**$_6$H$_5$)$_2$); ***assignment was based on the ^{1}H–^{13}C HETCOR, DEPT and ^{1}H–^{1}H COSY spectra***; ^{31}P-{^{1}H} NMR (162.0 MHz, $CDCl_3$, ppm): δ 123.31 (d, $^1J_{(103Rh-31P)}$ = 176.6 Hz, O**P**Ph$_2$); IR: υ 3146, 3053 (aromatic C—H), 2937, 2874 (aliphatic C—H) 1435 (P-Ph), 1044 (O—P) cm^{-1}; Anal. for $C_{33}H_{38}N_2O_2PRhCl_2$ (699.46 g/mol): calcd. C 56.67, H 5.48, N 4.05; found C 56.56, H 5.44, N 4.01%.

3. Results and discussion

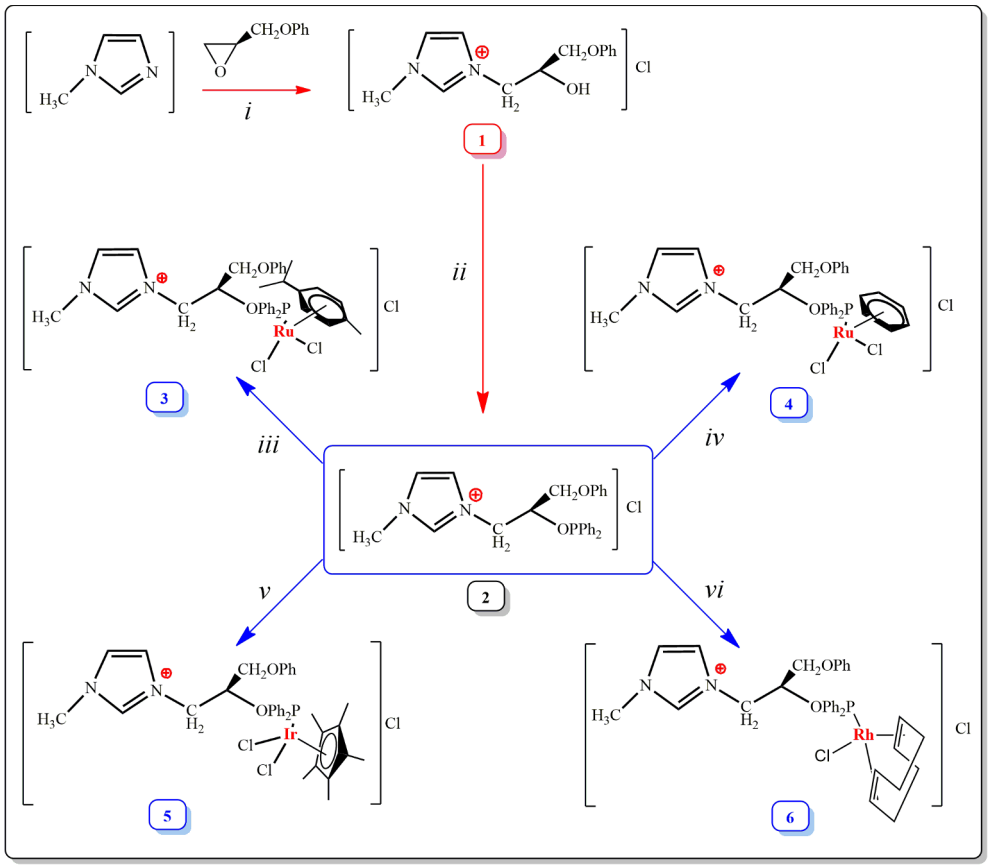
3.1. Synthesis of the new complexes

The reaction of imidazole with epoxide derivatives has been described [58] and we have also recently reported the preparation of a new imidazolium-based phosphinite ionic liquid (**IL-OPPh$_2$**) and its application as a reagent for transfer hydrogenation of ketones [59,60,61]. The regioselective ring opening of epoxides constitutes one of the most general methods for synthesis of functionalized imidazole derivatives [62]. Based on this methodology, here, the reaction between 1-methylimidazole and (*S*)-2-oxiranylanisole in ethanol leads to formation of new 3-[(2*S*)-2-hydroxy-3-phenoxypropyl]-1-methyl-1H-imidazol-3-ium chloride, **(1)** according to a reported procedure [63]. The precipitated product, **1** was filtered and dried in vacuo to obtain it as an off-white solid with a good yield (83.0%). The ^{1}H NMR spectrum of compound **1** shows characteristic features: the imidazolium ring protons at δ 9.57 (s, 1H, (CH$_3$)NC**H**N–), 7.41 and 7.33 (2xs, 2H, –NC**H**C**H**N–) ppm. The magnetic non-equivalence of protons as well as carbon atoms of the imidazolium ring (123.28 (–N**C**H**C**HN–), 137.62 ((CH$_3$)N**C**HN–),158.00 ppm) was also observed. The structure for this compound is consistent with the data obtained from a combination of multinuclear NMR spectroscopy, IR spectroscopy and elemental analysis (for details see experimental section and **SI**). In the next step, [3-[(2*S*)-2-[(diphenylphosphanyl)oxy]-3-phenoxypropyl]-1-methyl-1H-imidazol-3-ium chloride], **(2)** was prepared from the commercially available starting material chlorodiphenylphosphine and **1**, in the presence of triethylamine [64,65,66]. The evolution of this reaction was conveniently monitored by ^{31}P-{^{1}H} NMR spectroscopy [67,68,69]. The signals of the starting material PPh$_2$Cl at δ 81.0 ppm disappeared and new singlet appeared downfield at δ 118.49 (s, O**P**Ph$_2$) ppm due to the corresponding phosphinite ligand, in line with the values previously observed for similar compounds [Fig. 1] [70,71,72]. The appropriate assignment of the ^{1}H chemical shifts was derived from 2D HH-COSY spectra and that of the ^{13}C chemical ones from DEPT and 2D HMQC spectra. Furthermore, characteristic $J_{(31P-13C)}$ coupling constants of the carbons of the phenyl ring are observed in the ^{13}C NMR spectra (including *i*-, *o*-, *m*-, *p*- carbons of phenyl rings, for details see experimental section), which are consistent with the literature values [73]. The structure for this ionic based monodendate phosphinite ligand is also consistent with the data obtained from IR spectrum and elemental analysis.

Because **(2)** is not stable enough in solution, the Ru(II) complexes **3** and **4** were synthesized *in-situ*. Reactions of **(2)** with metal precursors [Ru(η^6-*p*-cymene)(μ-Cl)Cl]$_2$ and [Ru(η^6-benzene)(μ-Cl)Cl]$_2$ are depicted in Scheme 1. Firstly, [Ru(η^6-*p*-cymene)(μ-Cl)Cl]$_2$ was initially chosen as a starting material, which was prepared from the reaction of the commercially available α-phellandrene(5-*iso*prophyl-2-methylcyclohexa-1,3-diene) with $RuCl_3$ [74]. The reaction of [Ru(η^6-*p*-cymene)(μ-Cl)Cl]$_2$ with 1/2 equivalent of **(2)** affords only the corresponding monodendate [3-[(2*S*)-2-({[dichloro(η^6-*p*-cymene)ruthenium]diphenyl phosphanyl} oxy)-3-phenoxypropyl]-1-methyl-1H-imidazol-3-ium chloride], **(3)** as the main product. Complexation reaction was straightforward, with coordination to ruthenium being carried out at room temperature. The initial color change, i.e., from clear orange to deep red [75], attributed to the dimer cleavage most probably by the functionalized phosphinite ligand based on ionic liquid (FILs-OPPh$_2$). The ^{31}P-{^{1}H} NMR spectrum is fairly consistent with the structure of **3** showing a single resonance at δ 124.61 ppm as shown in Fig. 1. Furthermore, ^{1}H NMR spectral data of compound **3** are consistent with the structure suggested. The signals consisting of a doublet and two different singlet centered at 5.50, 5.16 and 4.93 ppm are due to the presence of the aromatic protons in the *p*-cymene group, this information is complemented by the presence of signals at 2.45 and 1.05, 0.72 ppm due to the CH and CH_3 of the isopropyl groups of the *p*-cymene moiety. The *p*-cymene ligand is particularly informative with respect to the symmetry of the three legged fragment. Especially, one of the most available arene ligands in ruthenium chemistry is *p*-cymene, whose NMR signals are very sensitive to the symmetry of organometallic compound. Thus, when it is η^6-coordinated to a ML_2L' metal fragment (C*s* symmetry), the ^{1}H and ^{13}C NMR spectra are very different from that of η^6-coordinated to a ML_1L_2L' fragment (C_1 symmetry) [76,77,78]. Finally, a signal due to the presence of the methyl in the *p*-cymene group is observed at 1.85 ppm. In the ^{13}C-{^{1}H} NMR spectrum of **3**, J(^{31}P-^{13}C) coupling constants of the carbons of the phenyl rings were observed (***for details see experimental section***), which are consistent with the literature values [79,80,81]. The most relevant signals of ^{13}C-{^{1}H} NMR spectrum of complex **3** are those corresponding to *p*-cymene ligands. Carbon atoms of the arene rings in *p*-cymene ligands are observed as four singlets at 94.23, 89.91, 88.26 and 85.29 ppm for complex **3**. The structural composition of the complex was also confirmed by IR and elemental analysis. Although, single crystals of both complexes were obtained by slow diffusion of diethylether into a solution of the compound in dichloromethane over several days, unfortunately we were not able to protect them from rapid decomposition in air.

The reaction of stoichiometric amounts of [Ru(η^6-benzene)(μ-Cl)Cl]$_2$ and [(Ph$_2$PO)$_2$-C$_{24}$H$_{16}$N$_4$], **2** affords the complex **(4)** in good yield as a dark red microcrystalline powder. Ligand **2** was expected to cleave the [Ru(η^6-benzene)Cl$_2$]$_2$ dimer to give the corresponding **(4)** via monohapto coordination of the phosphinite group. Complex **4** was isolated as indicated by a singlet in the ^{31}P-{^{1}H} NMR spectrum at δ 121.85 ppm, in line with the values previously observed for similar compounds [82]. Analysis by ^{1}H NMR reveals this compound to be diamagnetic, exhibiting signals corresponding to the imidazole ring at 9.26 (s, 1H, -(CH$_3$)NC**H**N–), ppm and the C$_6$H$_6$ protons as a singlet 5.50 ppm. In the ^{13}C NMR spectrum of **4**, the (-(CH$_3$)N**C**HN–) carbon signal was observed at 137.69 ppm and the C$_6$H$_6$ carbon resonance occurred at 90.49 (s) ppm. Furthermore in the ^{13}C-{^{1}H} NMR spectrum of **4**, J(^{31}P-^{13}C) coupling constants of the carbons of the phenyl rings was detected, which is consistent with the literature values [83]. In the ^{13}C-{^{1}H} NMR spectrum, J(^{31}P-^{13}C) coupling constants of the carbons of the phenyl rings were observed, which are consistent with the literature values. The structure of **4** was further confirmed by IR spectroscopy and microanalysis, and found to be in good agreement with the theoretical values.

Reactions of the functionalized ionic based monodendate phosphinite (FILs-OPPh$_2$) with metal [Ir(η^5-C$_5$Me$_5$)(μ-Cl)Cl]$_2$ precursor is also depicted in Scheme 1. Synthesis of compound **5** was achieved by the reaction of ligand (**2**) with [Ir(η^5-C$_5$Me$_5$)(μ-Cl)Cl]$_2$ in a molar ratio of 2/1 at room temperature for 1 h. In the ^{31}P-{^{1}H} NMR spectrum, resonance at δ 94.03 ppm may be attributed to complex **5** (Fig. 1). The ^{1}H NMR spectra are consistent with the anticipated structure. Analysis by ^{1}H NMR reveals this compound to be diamagnetic, exhibiting signal consisting of a singlet centered at 1.33 ppm due to the presence of the methyl protons in the Cp* group, this information is complemented by



Scheme 1. Synthesis of the 3-[(2*S*)-2-hydroxy-3-phenoxypropyl]-1-methyl-1H-imidazol-3-ium chloride, **(1),** [3-[(2*S*)-2-[(diphenylphosphanyl)oxy]-3-phenoxypropyl]-1-methyl-1H-imidazol-3-ium chloride]], **(2),** [3-[(2*S*)-2-({[dichloro(η^6-*p*-cymene)ruthenio]diphenyl phosphanyl}oxy)-3-phenoxypropyl]-1-methyl-1H-imidazol-3-ium chloride]] **(3),** [3-[(2*S*)-2-({[dichloro(η^6-benzene)ruthenio]diphenylphosphanyl}oxy)-3-phenoxypropyl]-1-methyl-1H-imidazol-3-ium chloride] **(4),** [3-[(2*S*)-2-{[(dichloro(η^5–pentamethylcyclopentadienyl)iridio)diphenyl phosphanyl]oxy}- 3-phenoxypropyl]-1-methyl-1H-imidazol-3-ium chloride]] **(5),** [3-[(2*S*)-2-{[(chloro(η^4-1,5-cyclooctadiene)rhodio)diphenylphosphanyl]oxy}-3-phenoxypropyl]-1-methyl-1H-imidazol-3-ium chloride] **(6)** (**i**) 1 equiv. (*S*)-2-Oxiranylanisole, 1 equiv. HCl, C_2H_5OH; (**ii**) 1 equiv. Ph_2PCl, 1 equiv. Et_3N, CH_2Cl_2; (**iii**) 1/2 equiv. [Ru(η^6-*p*-cymene)(μ-Cl)Cl]$_2$; (**iv**) 1/2 equiv. [Ru(η^6-benzene)(μ-Cl)Cl]$_2$, CH_2Cl_2; (**v**) 1/2 equiv. [Ir(η^5-C_5Me_5)(μ-Cl)Cl]$_2$, CH_2Cl_2; (**vi**) 1/2 equiv. [Rh(μ-Cl)(cod)]$_2$, CH_2Cl_2.

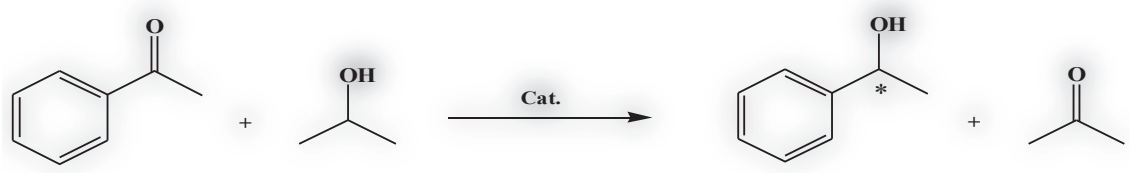
the presence of a signal at 9.72 ppm (-(CH_3)NC**H**N–). Furthermore, the ^{13}C NMR spectrum of the complex **3** displays a singlet at δ 8.24 ppm attributable to methyl carbons of Cp* and doublet at δ 94.12 due to carbons of Cp* ring. We also examined simple coordination chemistry of [Rh(μ-Cl)(cod)]$_2$ with ligand **(2) .** Reactions of [Rh(μ-Cl)(cod)]$_2$ with ligand **2** in CH_2Cl_2 in a ratio of 1/2:1 at room temperature for 1 h gave micro-crystalline precipitate of complex **6**. Complexation reactions were straightforward, with coordination to rhodium being carried out at room temperature. This ligand was expected to cleave the [Rh(μ-Cl)(cod)]$_2$ dimer to give the corresponding complex via monohapto coordination of the phosphinite ligand based ionic liquid (FILs-$OPPh_2$). The coordination of the ligand through the P donor was confirmed by the ^{31}P-{^{1}H} NMR spectroscopy. Complex **6** was isolated as indicated by a doublet in the ^{31}P-{^{1}H} NMR spectrum at δ 123.31 (d, $^1J_{RhP}$: 176.6 Hz), [84,85] (Fig. 1), indicating that ionic liquid based phosphinite ligand acting as monodendate ligand. ^{1}H and ^{13}C NMR spectra of compound **6** display all the signals of coordinated ligands. The structural compositions of the complexes **5** and **6** were further confirmed by IR spectroscopy and microanalysis, and found to be in good agreement with the theoretical values (***for details see experimental section***).

3.2. Catalytic transfer hydrogenation of ketones

Transfer Hydrogenation method has been extensively studied because of the low cost and favorable properties of the hydrogen donor as well as the operational simplicity. However, a problem of the transfer hydrogenation reaction in *iso*PrOH is the reversibility of the process. Not only to overcome this problem, but also to develop highly active well-designed catalysts, our studies have been continuing and our group has been reported some metal complexes with phosphinite ligands based on ionic liquid in recent years [59,60,61]. Especially, we have shown that several rhodium, iridium and ruthenium complexes with phosphinite ligand based on functional ionic liquid (FILs) are higly active in the transfer hdrogenation of ketones. This prompted us to investigate the asymmetric version of this reaction by using rhodium, iridium or ruthenium complexes with (CFILs).

Initially, complexes **3–6** were evaluated as precursors for the catalytic asymmetric transfer hydrogenation of acetophenone by *iso*PrOH. A comparison of metal complexes based on chiral fuctionalized ionic liquid as precatalysts for the asymmetric hydrogenation of acetophenone by *iso*PrOH is summarized in Table 1. Catalytic experiments were carried out under inert (Ar) atmosphere using standard Schlenk-line techniques. These systems catalyzed the reduction of acetophenone to corresponding alcohol ((*R*)-1-phenylethanol) in the presence of KOH. To an *iso*PrOH solution of M – CFILs {M: Ru(II), Ir(III), Rh(I)} complex, an appropriate amount of acetophenone and KOH/*iso*PrOH solutions were added, at room temperature. At this temperature, transfer hydrogenation of acetophenone occurred very slowly, with low conversion (up to 17%, 24 h) and moderate to high enantioselectivity (up to 86% ee) in the reactions (Table 1, entries 1–4). As a result of the reversibility at room temperature, the prolonging the reaction time (96 h) led to a decreasing of enantioselectivity, as indicated by the catalytic results collected with catalysts, [86,87]. One typical problem with transfer hydrogenation reactions (that exploit alcohols as the sacrificial reductants) is that the initial ee % can be degraded as the reaction is allowed to proceed to higher conversion. This occurs because oxidation of (*S*)-1-phenyl ethanol is thermodynamically favored over reduction relative to the oxidation of 2-propanol [88] Therefore, we were not surprised to find that a slight decrease in ee % occurred at higher conversion with the currently described system [89]. In addition, to obtain the chiral alcohol in a high yield without significant deterioration of the enantiomeric purity, the reaction has to be performed with a substrate concentration as low as 0.1 M and an unnecessarily long exposure of the reaction mixture to the catalyst should be avoided. The reversibility of these reactions results in 'back transfer' of hydrogen

Table 1
Transfer hydrogenation of acetophenone with 2-propanol catalyzed by [3-[(2*S*)-2-({[dichloro(η^6-*p*-cymene)ruthenium]diphenyl phosphanyl}oxy)-3-phenoxypropyl]-1-methyl-1H-imidazol-3-ium chloride], **(3),** [3-[(2*S*)-2-({[dichloro(η^6-benzene)ruthenio]diphenylphosphanyl}oxy)-3-phenoxypropyl]-1-methyl-1H-imidazol-3-ium chloride]] **(4),** [3-[(2*S*)-2-{[(dichloro(η^5–pentamethylcyclopentadienyl)iridio)diphenyl phosphanyl]oxy}-3-phenoxypropyl]-1-methyl-1H-imidazol-3-ium chloride], **(5)** and [3-[(2*S*)-2-{[(chloro(η^4-1,5-cyclooctadiene)rhodio)diphenyl phosphanyl] oxy}-3-phenoxypropyl]-1-methyl-1H-imidazol-3-ium chloride]] **(6)**.



Entry	Complex	S/C/KOH	Time	Conversion(%)[c]	% ee[d]	Conf.[e]	TOF(h^{-1})[f]
1	3 [a]	200:1:5	48 h	15	68	*R*	< 5
2	4 [a]	200:1:5	48 h	14	67	*R*	< 5
3	5 [a]	200:1:5	48 h	10	76	*R*	< 5
4	6 [a]	200:1:5	48 h	21	86	*R*	< 5
5	3 [b]	200:1:5	1 h	98	72	*R*	192
6	4 [b]	200:1:5	1 h	99	70	*R*	196
7	5 [b]	200:1:5	2 h	99	80	*R*	99
8	6 [b]	200:1:5	1/2h	99	92	*R*	396
9	5	200:1:3 [g]	1/2h	94	89	*R*	376
10	5	200:1:5 [g]	1/2h	98	92	*R*	392
11	5	200:1:7 [g]	1/2h	95	88	*R*	380
12	5	200:1:9 [g]	1/2h	91	87	*R*	364

Reaction conditions:[a] At room temperature; acetophenone/Cat./KOH, 200:1:5; [b] Refluxing in 2-propanol; acetophenone/Cat./KOH, 200:1:5; [c] Determined by GC (three independent catalytic experiments); [d] Determined by capillary GC analysis using a chiral cyclodex B (Agilent) capillary column (30 m × 0.32 mm I.D. × 0.25 μm film thickness); [e] Determined by comparison of the retention times of the enantiomers on the GC traces with the literature values, *(R)* configuration was obtained in all experiments; [f] TOF = (mol product/mol Cat.) × h^{-1}; [g] Refluxing in 2-propanol.

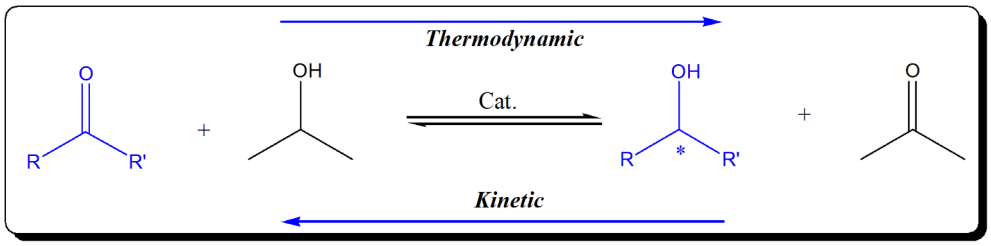


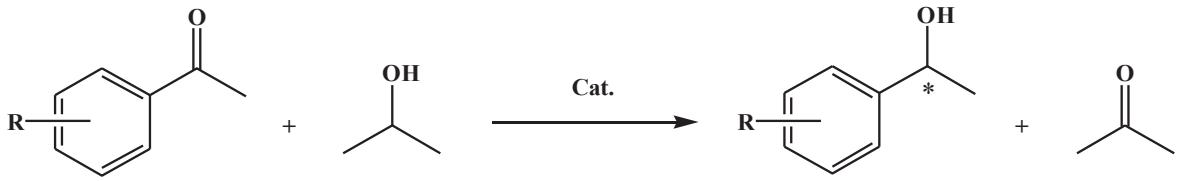
Fig. 2. Equilibria between the kinetic and thermodynamic products (R is aryl).

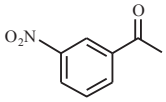
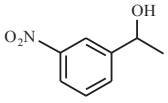
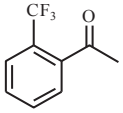
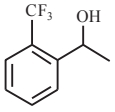
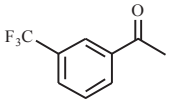
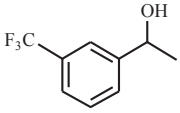
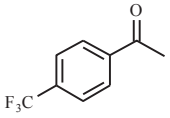
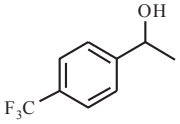
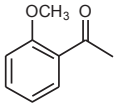
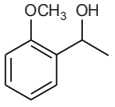
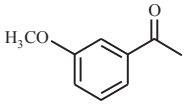
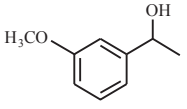
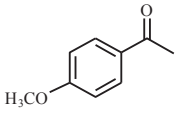
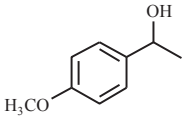
(from the enantioenriched alcohol) to the generated ketone as depicted in Fig. 2. However, the extent of degradation of enantiomeric purity was only found to be at approximately 4% when the reaction times were extended from 48 to 96 h for the various case. As such the reactions were not allowed to reach full conversion, and data were acquired for all cases at 48 h [90]. As seen from Table 1, the reactions proceeded to give (*R*)-1-phenyl ethanol in 10–21% conversion with 67–86% ee's after stirring at room temperature for 48 h. An increase in the reaction time to 96 h resulted in 19–43% conversion with 62–83% *ee*'s. Due to the reversibility at room temperature, the prolonging the reaction time led to a slight decrease in enantioselectivity.

When the reactions were carried out at 82 °C, all catalysts showed satisfying catalytic activities (up to 396 TOF values) and enantioselectivities since almost conversions to the total corresponding alcohol were observed (Table 1, entries 5–8). Although the lower reaction temperatures should have a beneficial effect on the enantioselectivities, higher asymmetric inductions (70–92% ee's) were observed at 82 °C. This may attributed to the shorter reaction times and these results indicate that the reaction temperature plays an important role on the catalytic activity and enantioselectivity. Furthermore, the complexes were very active catalysts, leading to quantitative conversions of (*R*)-1-phenyl ethanol with a catalyst/base ratio of 1:5. Increase or decrease of the base:Cat. ratio from 5:1 to 9:1 or 3:1 slightly decreased the reaction rate with a slight loss of enantiomeric purity of the product (Table 1, entries 9–12). In addition, replacing KOH with NaOH slightly decreased both the reaction rate and enantioselectivity. A control experiment in the absence of base did not lead to meaningful conversion (< 3%). As seen from Table 1, the higher conversion and ee % obtained for initial reduction of acetophenone motivated us to keep employing **(6)**. These results clearly indicate that the skeleton of the ligands and the fragment attached to the Rhodium(I) center are responsible for the high conversion (up to 98%) and enantioselectivity (up to 92 ee %).

The catalytic reduction of acetophenone derivatives were conducted with a substrate/catalyst molar ratio (S/C) of 200 using 0.05 M solution in *iso*PrOH. Examples of the asymmetric reaction of acetophenone derivatives with the complexes are listed in Table 2. The rate and stereoselectivity are delicately influenced by reaction conditions as well as steric and electronic properties of the substituents of the ketones. As seen from Table 2, aromatic ketones are hydrogenated with high enantioselectivity and the same mode face selection. One can easily see from the results that a range of acetophenone derivatives can be hydrogenated from good to high enantioselectivities. It is well-known that the introduction of electron withdrawing substituents to the aryl ring of the ketone decreases the electron density of the C═O bond so that the activity was improved resulting in easier hydrogenation [91]. Thus, the introduction of electron-withdrawing substituents, such as CF_3 or NO_2, to the aryl ring of the ketone, resulted in improved activity with good enantioselectivity (Table 2, entries 1–16). On the contrary, the

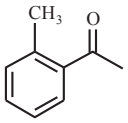
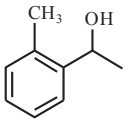
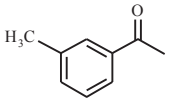
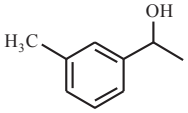
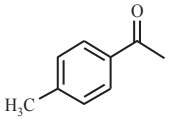
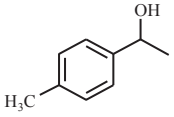
Table 2
Transfer hydrogenation results for substituted acetophenones with the catalyst systems prepared from [3-[(2*S*)-2-({[dichloro(η^6-*p*-cymene)ruthenium]diphenyl phosphanyl}oxy)-3-phenoxypropyl]-1-methyl-1H-imidazol-3-ium chloride], **(3),** [3-[(2*S*)-2-({[dichloro(η^6-benzene)ruthenio]diphenylphosphanyl}oxy)-3-phenoxypropyl]-1-methyl-1H-imidazol-3-ium chloride]] **(4),** [3-[(2*S*)-2-{[(dichloro(η^5–pentamethylcyclopentadienyl)iridio)diphenyl phosphanyl]oxy}-3-phenoxypropyl]-1-methyl-1H-imidazol-3-ium chloride], **(5)** and [3-[(2*S*)-2-{[(chloro(η^4-1,5-cyclooctadiene)rhodio)diphenyl phosphanyl] oxy}-3-phenoxypropyl]-1-methyl-1H-imidazol-3-ium chloride]] **(6).**[a]



Entry	Cat.	Substrate	Product	Time	Conv.(%)[b]	% ee[c]	TOF(h^{-1})[d]	Config.[e]
1	**3**			20 min	98	**63**	588	***R***
2	**4**			20 min	99	**65**	594	***R***
3	**5**			45 min	97	**76**	259	***R***
4	**6**			10 min	99	**86**	1188	***R***
5	**3**			45 min	99	**65**	264	***R***
6	**4**			45 min	99	**66**	264	***R***
7	**5**			3/2 h	98	**78**	131	***R***
8	**6**			20 min	98	**85**	588	***R***
9	**3**			30 min	98	**61**	392	R
10	**4**			30 min	97	**60**	388	R
11	**5**			1 h	99	**71**	198	R
12	**6**			15 min	99	**84**	792	R
13	**3**			15 min	99	**58**	792	***R***
14	**4**			15 min	99	**57**	792	***R***
15	**5**			30 min	97	**70**	388	***R***
16	**6**			10 min	99	**82**	1188	***R***
17	**3**			8 h	99	**72**	25	***R***
18	**4**			8 h	98	**73**	25	***R***
19	**5**			14 h	99	**84**	14	***R***
20	**6**			5 h	98	**93**	39	***R***
21	**3**			5 h	97	**60**	39	***R***
22	**4**			5 h	99	**62**	40	***R***
23	**5**			8 h	99	**69**	25	***R***
24	**6**			3 h	98	**80**	65	***R***
25	**3**			3 h	98	**53**	65	***R***
26	**4**			3 h	99	**50**	66	***R***
27	**5**			6 h	98	**62**	33	***R***
28	**6**			3/2h	99	**75**	132	***R***

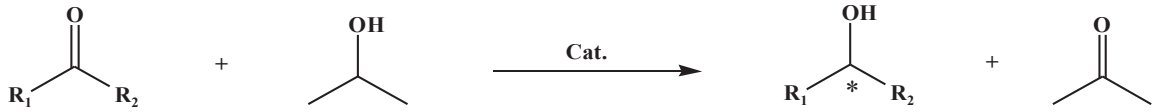
(*continued on next page*)

Table 2 (*continued*)

Entry	Cat.	Substrate	Product	Time	Conv.(%)[b]	% ee[c]	TOF(h^{-1})[d]	Config.[e]
29	**3**			6 h	98	**67**	33	***R***
30	**4**			6 h	97	**66**	32	***R***
31	**5**			10 h	99	**78**	20	***R***
32	**6**			3 h	98	**87**	65	***R***
33	**3**			5 h	99	**57**	40	***R***
34	**4**			5 h	99	**55**	40	***R***
35	**5**			8 h	97	**64**	24	***R***
36	**6**			2 h	98	**81**	98	***R***
37	**3**			3 h	98	**50**	65	***R***
38	**4**			3 h	99	**49**	66	***R***
39	**5**			6 h	98	**57**	33	***R***
40	**6**			1 h	98	**70**	196	***R***

Reaction conditions: [a] Catalyst (0.00125 mmol), substrate (0.25 mmol), 2-propanol (5 mL), KOH (0.0625 mmol %), 82 °C, the concentration of acetophenone derivatives are 0.05 M; [b] Purity of compounds is checked by NMR and GC (three independent catalytic experiments), yields are based on aryl ketone; [c] Determined by capillary GC analysis using a chiral cyclodex B (Agilent) capillary column (30 m × 0.32 mm I.D. × 0.25 μm film thickness); [d] TOF = (mol product/mol Cat.) × h^{-1}; [e] Determined by comparison of the retention times of the enantiomers on the GC traces with literature values, *(R)* configuration was obtained in all experiments.

Table 3
Transfer hydrogenation of various ketones with 2-propanol catalyzed [3-[(2*S*)-2-{[(chloro(η^4-1,5-cyclooctadiene)rhodio)diphenyl phosphanyl] oxy}-3-phenoxypropyl]-1-methyl-1H-imidazol-3-ium chloride], **(6).**[a]



Entry	Cat.	R_1	R_2	Time	Conv.(%)[b]	ee(%)[c]	TOF(h^{-1})[d]	Conf.[e]
1	**6**	CH_3	**CH_2CH_3**	1 h	98	**90**	196	***R***
2	**6**	CH_3	**$CH_2CH_2C_6H_5$**	3/2h	99	**84**	132	***R***
3	**6**	CH_3	**$CH(CH_3)_2$**	4 h	98	**83**	55	***R***
4	**6**	CH_3	**$CH_2CH(CH_3)_2$**	3 h	97	**81**	65	***R***
5	**6**	CH_3	**1-naphthyl**	3/4h	99	**96**	264	***R***
6	**6**	CH_3	***n*-C_4H_9**	5/2h	97	**79**	78	***R***
7	**6**	CH_3	**C_6H_{11}**	3/2h	98	**70**	131	***R***
8	**6**	C_6H_5	**C_6H_{11}**	3 h	98	**77**	65	***R***

Reaction conditions:[a] Catalyst (0.00125 mmol), substrate (0.25 mmol), 2-propanol (5 mL), KOH (0.00625 mmol %), 82 °C, the concentration of acetophenone derivatives are 0.05 M; [b] Purity of compounds is checked by NMR and GC (three independent catalytic experiments), yields are based on aryl ketone; [c] Determined by capillary GC analysis using a chiral cyclodex B (Agilent) capillary column (30 m × 0.32 mm I.D. × 0.25 μm film thickness); [d] TOF = (mol product/mol Cat.) × h^{-1}; [e] Determined by comparison of the retention times of the enantiomers on the GC traces with literature values, (*S*) or (*R*) configuration was obtained in all experiments.

introduction of an electron-donating group such as methyl or methoxy group tends to lower the rate with nearly similar enantioselectivities (Table 3, entries 17–40). It can be seen from Table 2, *ortho*-substituted acetophenones can dramatically increase the enantioselectivity, while *meta*- and *para*- substitution to acetophenones have detrimental effect. As expected, the lowest enantioselectivity was observed in transfer hydrogenation of *p*-methoxyacetophenone, whereas the highest one was found in that of *o*-methoxyacetophenone (93% ee) [92].

Due to the efficiency in higher enantioselectivity (approximately 12 ee%) of **(6)** in the transfer hydrogenation of aromatic ketones, a variety of simply aryl alkyl (S/C = 200) can be transformed to the corresponding secondary alcohols with high enantiomeric purity under the optimization conditions, as exemplified in Table 1. The rate and stereoselectivity are delicately affected by the bulkiness and electronic properties of the alkyl group and aryl substituent. With the using complex **6** as catalyst, the reaction of methyl/alkyl and methyl/aryl ketones gave the chiral alcoholic products in an acceptable chemical yield and enantiomeric purity. Primarily, we carried out further experiments to study the influence of bulkiness of the alkyl groups on the catalytic activity and selectivity (Table 3, entries 1–4). For this aim, a variety of simple methyl/steric-alkyl ketones were transformed to the corresponding secondary alcohols, and it was found that the activity and selectivity are highly dependent on the steric hindrance of the alkyl group. As seen from Table 3, reaction of methyl/steric-alkyl ketones possessing a bulky alkyl substituent proceeded rather sluggish and led a decrease in enantioselectivity. As the bulkiness of the alkyl group

increases from ethyl to *sec*butyl, the extent of enantioselectivity lowers. Indeed, lower activity and enantioselectivity were obtained in case of methyl *sec*butyl ketone (81% ee, TOF: 65) as expected (Table 3, entry 4) [93]. Furthermore, as seen from Table 3, the best result in terms of enantioselectivity was observed with 1-naphtyl methyl ketone. In that case, high TOF value (TOF: 264) and the highest enantioselectivity, up to 96% ee, were obtained for catalyst **(6)**. In addition, the hydrogenation of ketones including cyclohexyl group was very slow and the enantioselectivities were incredible lower (Table 3, entries 7–8).

4. Conclusions

Several catalytic systems with metal complexes based on CFILs for asymmetric transfer hydrogenation of prochiral ketones have now reached high levels of efficiency in term of activity and enantioselectivity. High conversion and enantioselectivity were obtained in the catalytic reaction. The high catalytic activity and enantioselectivity for this kind of ligands show great potential for further exploring similar system and achieving outstanding stereoselectivity for a wider scope of ketone substrates. Furthermore, the simplicity and efficiency clearly make it an excellent choice of catalyst for the practical preparation of highly valued alcohols via catalytic asymmetric transfer hydrogenation of ketones. Further studies are in progress to explain the improvement of both activity and enantioselectivity related to this CFILs group and to extend the use of these new phosphinite ligands in other asymmetric catalytic reactions.

Acknowledgements

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ica.2019.04.016.

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