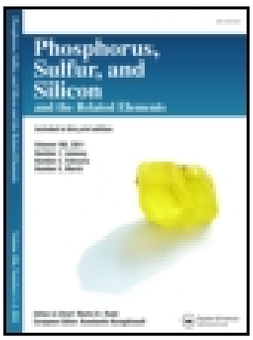

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Enantioselective transfer hydrogenation of pro-chiral ketones catalyzed by novel ruthenium and iridium complexes of well-designed phosphinite ligand

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ABSTRACT

The interaction of [Ru(η^6-arene)(μ-Cl)Cl]$_2$ and Ir(η^5-C_5Me_5)(μ-Cl)Cl]$_2$ with a new Ionic Liquid-based phosphinite ligand, [(Ph_2PO)-$C_6H_9N_2Ph$]Cl, (**2**) gave [Ru((Ph_2PO)-$C_6H_9N_2Ph$)(η^6-*p*-cymene)Cl_2]Cl (**3**), [Ru((Ph_2PO)-$C_6H_9N_2Ph$)(benzene)Cl_2]Cl (**4**) and [Ir((Ph_2PO)-$C_6H_9N_2Ph$)(C_5Me_5)Cl_2]Cl (**5**), complexes. All the compounds were characterized by a combination of multinuclear NMR and IR spectroscopy as well as elemental analysis. Furthermore, the Ru(II) and Ir(III) catalysts were applied to asymmetric transfer hydrogenation of acetophenone derivatives using 2-propanol as a hydrogen source. The results showed that the corresponding alcohols could be obtained with good activity (up to 55% ee and 99% conversion) under mild conditions. Notably, [Ir((Ph_2PO)-$C_6H_9N_2Ph$)(C_5Me_5)Cl_2]Cl (**5**) is more active than the other analogous complexes in the transfer hydrogenation (up to 81% ee).

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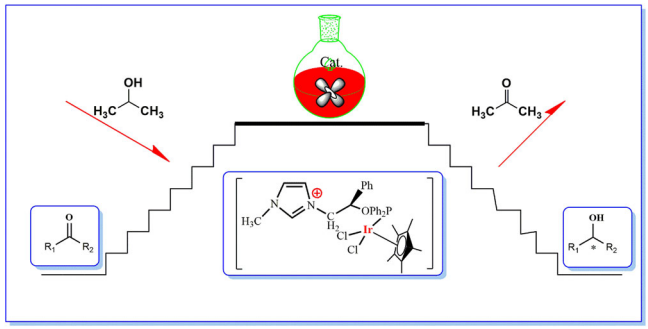
Enantioselective transfer hydrogenation; homogeneous catalysis; chiral phosphinite ligand; ruthenium(II); iridium(III)

GRAPHICAL ABSTRACT



Introduction

An increasing number of chiral compounds and enantiomerically pure drugs are prepared through transition metal-catalyzed asymmetric reactions.[1] Since the reactivity and stereoselectivity of an asymmetric transformation are highly dependent on the structure of the chiral ligand coordinated to the transition metal, the design and synthesis of efficient chiral ligands are important in this area and have attracted a great deal of attention both from academia and industry.[2] Transition metal complexes are effective catalysts for organic transformations and when suitable ligands are associated with the metal center, they can offer chemio-, regio- or stereoselectivity under mild conditions.[3] Many transition metal complexes are known to be catalyzing hydrogen transfer from an alcohol to a ketone.[4,5] Over the last three decades, most effort on asymmetric transfer hydrogenation has been focused on the use of ruthenium, rhodium and iridium catalysts.[6,7]

Alcohols are very important building blocks for the pharmaceutical and fine chemical industries.[8] Although many applications require racemic alcohols, the need for enantiomerically pure products is growing because of their importance as intermediates for the manufacture of pharmaceuticals and advanced materials,[9] 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 perspectives.[10] Extensive efforts have been devoted to their reduction into secondary alcohols especially via hydrogenation.[11] Catalytic transfer hydrogenation (TH) with the aid of a stable hydrogen donor is a

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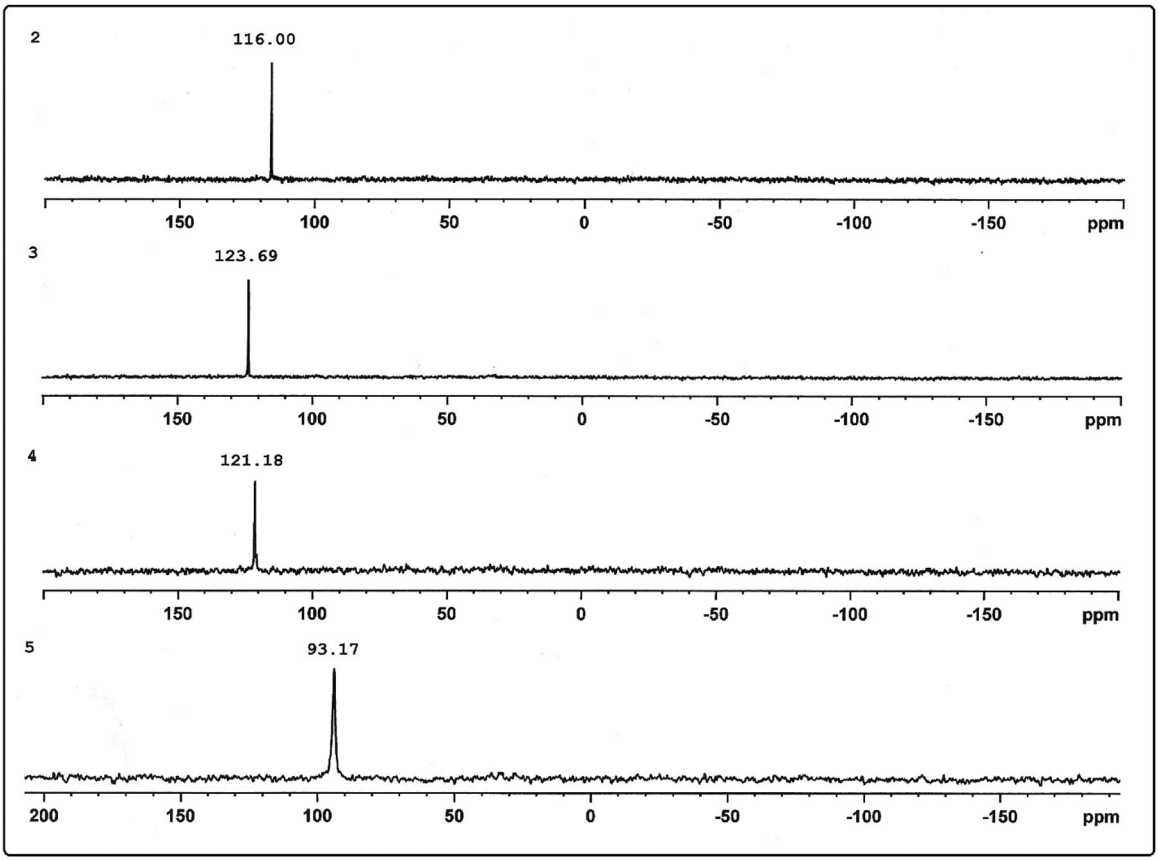


Figure 1. The ^{31}P-{^{1}H} NMR spectra of compounds), [3-[(2*R*)-2-[(diphenylphosphanyl)oxy]-2-phenylethyl]-1-methyl-1H-imidazol-3-ium chloride]], **(2)**, [3-[(2R)-2-({[dichloro(*η*6-*p*-cymene)ruthenium]diphenyl phosphanyl}oxy)-2-phenylethyl]-1-methyl-1H-imidazol-3-ium chloride]] **(3)**, [3-[(2*R*)-2-({[dichloro(*η*6-benzene)ruthenium]diphenylphosphanyl}oxy)-2-phenylethyl]-1-methyl-1H-imidazol-3-ium chloride]] **(4)**, [3-[(2*R*)-2-{[(dichloro(η^5–pentamethylcyclopentadienyl)iridium)diphenyl phosphanyl]oxy}-2-phenylethyl]-1-methyl-1H-imidazol-3-ium chloride], **(5)**.

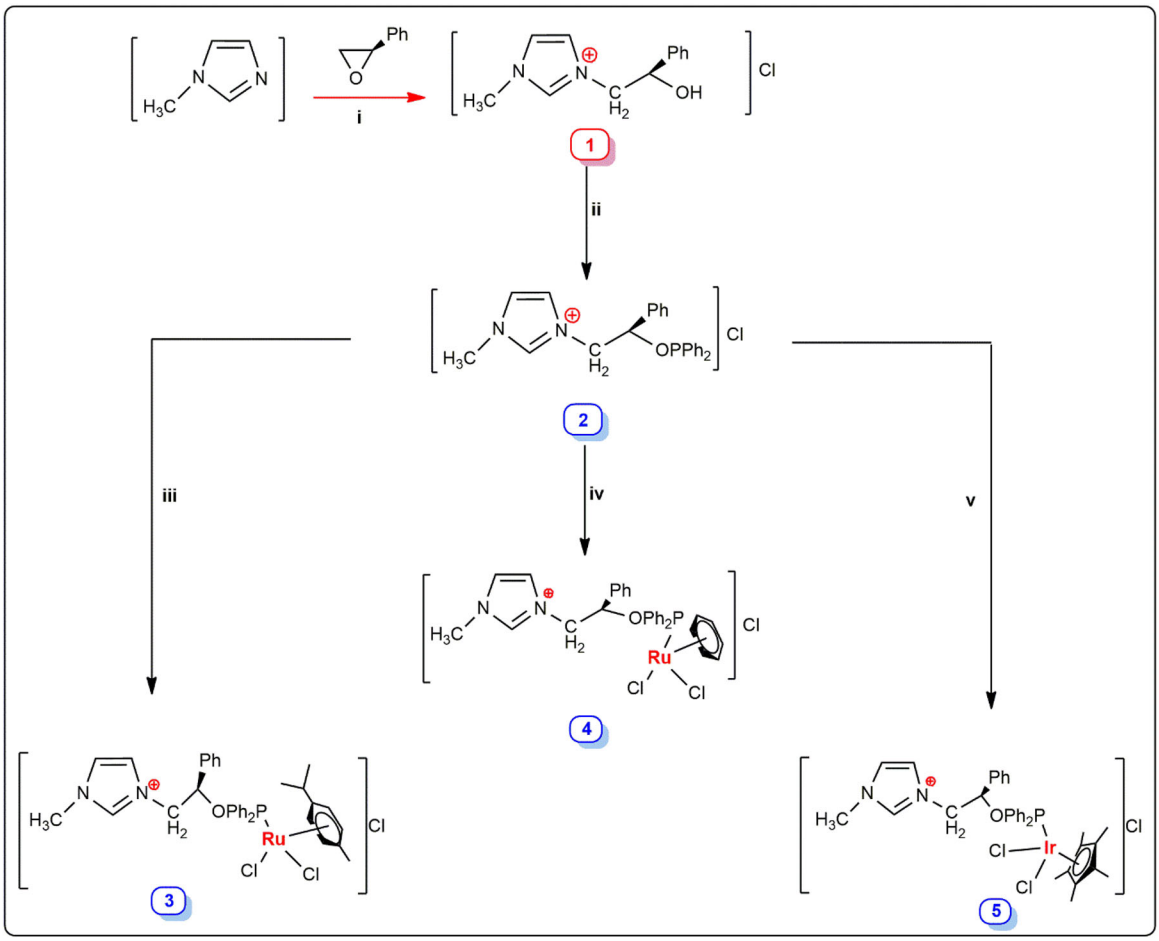
useful alternative process for catalytic hydrogenation by molecular hydrogen for the reduction of ketones.[12] In transfer hydrogenation, organic molecules such as primary and secondary alcohols [13] or formic acid and its salts [14] have been employed as the hydrogen source.

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,[15] lack of vapor pressure, non-flammability, wide liquid range, wide range of solubility and miscibility.[16] 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 a viable substitute for volatile organic solvents.[17] 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.[18] 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 ILs (FILs), which dually possess the characters of the incorporated functionalities as well as those of the ILs.[19] The P-based ligands-FILs have long been investigated for the design of the ionic organometallic compounds and applications to catalysis.[19,20] It has been found that, while the coordinating P(III) atom is vicinal to the positively charged imidazolium ring, the corresponding P-based ligands-FILs are featured with π-acceptor character as well as σ-donor.[21,22] Hence, the changing coordination behaviors of such P-based ligands-FILs are of great concerns in the coordination chemistry and catalysis, leading to the significant changes in the complex configurations and catalytic performance.[23] In this regard, our study to develop useful and efficient catalysts, and in this paper is extended. Reported for the first time are the synthesis and full characterization of three half-sandwich ruthenium and iridium-arene complexes from a new ionic liquid based ligand, and their subsequent application in asymmetric transfer hydrogenation of the acetophenone derivatives.

Results and discussion

Synthesis of the new complexes

It is well-known that the regioselective ring-opening of epoxides by amines is an important way for the preparation of *β*-aminoalcohols.[24] The synthesis of a novel ionic liquid, 3-[(2*R*)-2-hydroxy-2-phenylethyl]-1-methyl-1H-imidazol-3-ium chloride [$C_6H_{10}OPh$]Cl, **(1)**, was accomplished in one step from the reaction of 1-methylimidazole and (*R*)-styrene oxide, according to a reported procedure.[25] The precipitated product was filtered and dried in vacuo to obtain **1** as an off-white solid with a good yield (78.0%). The ^{1}H NMR spectrum of



Scheme 1. Synthesis of 3-[(2R)-2-hydroxy-2-phenylethyl]-1-methyl-1H-imidazol-3-ium chloride, **(1)**, [3-[(2R)-2-[(diphenylphosphanyl)oxy]-2-phenylethyl]-1-methyl-1H-imidazol-3-ium chloride]], **(2)**, [3-[(2R)-2-({[dichloro(η6-p-cymene)ruthenio]diphenyl phosphanyl}oxy)-2-phenylethyl]-1-methyl-1H-imidazol-3-ium chloride]] **(3)**, [3-[(2R)-2-({[dichloro(η6-benzene)ruthenio]diphenylphosphanyl}oxy)-2-phenylethyl]-1-methyl-1H-imidazol-3-ium chloride]] **(4)**, [3-[(2R)-2-{[(dichloro(η5–pentamethylcyclopentadienyl)iridio)diphenyl phosphanyl]oxy}-2-phenylethyl]-1-methyl-1H-imidazol-3-ium chloride]] **(5)**, (*i*) 1 equiv. (*R*)-Styrene oxide, 1 equiv. HCl, C_2H_5OH; (*ii*) 1 equiv. Ph_2PCl, 1 equiv. n-BuLi, CH_2Cl_2; (*iii*) 1/2 equiv. $[Ru(\eta^6\text{-}p\text{-cymene})(\mu\text{-Cl})Cl]_2$; (*iv*) 1/2 equiv. $[Ru(\eta^6\text{-benzene})(\mu\text{-Cl})Cl]_2$, CH_2Cl_2; (*v*) 1/2 equiv. $[Ir(\eta^5\text{-}C_5Me_5)(\mu\text{-Cl})Cl]_2$, CH_2Cl_2.

compound **1** shows characteristic features: the imidazolium ring protons at δ 8.41 (s, 1H, $(CH_3)NC\mathbf{H}N$–), 7.19–7.35 (m, 7H, –NCHCHN+–CHPh) ppm. The magnetic nonequivalence of protons as well as carbon atoms of the imidazolium ring 123.17, 122.97 (–NCHCHN–), 136.41 ($(CH_3)NCHN$–), was observed. The structure for this ionic based monodendate phosphinite ligand is also consistent with the data obtained from its IR spectrum and elemental analysis. As shown in Scheme 1, [3-[(2R)-2-[(diphenylphosphanyl)oxy]-2-phenylethyl]-1-methyl-1H-imidazol-3-ium chloride], **(2)** was prepared from the commercially available starting material PPh_2Cl and $[C_7H_{12}N_2OCl]Cl$, **(1)** in the presence of *n*-BuLi.[26–28] The LiCl salt was separated by filtration and the ligand was obtained by removal of the solvent *in vacuo* in good yields. The progression of this reaction was conveniently monitored by $^{31}P\text{-}\{^1H\}$ NMR spectroscopy.[29–31] The signal of the starting material PPh_2Cl at δ 81.0 ppm disappeared and a new singlet appeared downfield at δ 116.00 (s, $O\mathbf{P}Ph_2$) ppm due to the corresponding phosphinite ligand, in line with the values previously observed for similar compounds (Figure 1).[32,33] The appropriate assignment of the ^1H chemical shifts was derived from 2D HH-COSY spectrum and that of the ^{13}C chemical ones from DEPT and 2D HMQC spectra. Furthermore, characteristic $J_{(31P\text{-}13C)}$ coupling constants of the carbons of the phenyl ring are observed in the ^{13}C NMR spectrum (including *i*-, *o*-, *m*-, *p*- carbons of phenyl rings, for details, see experimental section), which are consistent with the literature values.[34] The structure for this compound is consistent with the data obtained from a combination of multinuclear NMR spectroscopy, IR spectroscopy and elemental analysis.

Because **(2)** is not stable enough in solution, Ru(II) complexes **3** and **4** were synthesized in-situ. Reactions of **(2)** with metal precursors $[Ru(\eta^6\text{-}p\text{-cymene})(\mu\text{-Cl})Cl]_2$ and $[Ru(\eta^6\text{-benzene})(\mu\text{-Cl})Cl]_2$ are depicted in Scheme 1. $[Ru(\eta^6\text{-}p\text{-cymene})(\mu\text{-Cl})Cl]_2$ was initially chosen as a starting material, which was prepared from the reaction of the commercially available α-phellandrene(5-*iso*propyl-2-methylcyclohexa-1,3-diene) with $RuCl_3$.[35] The reaction of $[Ru(\eta^6\text{-}p\text{-cymene})(\mu\text{-Cl})Cl]_2$ with 1/2 equivalent of **(2)** affords only the corresponding monodentate [3-[(2R)-2-({[dichloro(η^6-p-cymene)ruthenium]diphenyl phosphanyl}oxy)-2-phenylethyl]-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,[36] attributed to the dimer cleavage

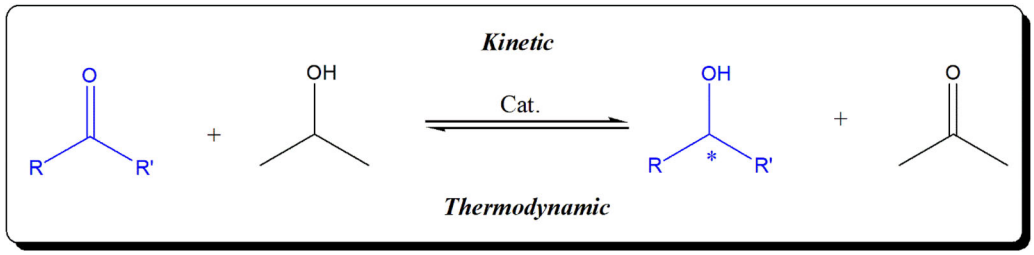


Figure 2. Equilibria between the kinetic and thermodynamic products (R is aryl).

Table 1. Transfer hydrogenation of acetophenone with *iso*-PrOH catalyzed by [3-[(2R)-2-({[dichloro(*η*6-*p*-cymene)ruthenium]diphenyl phosphanyl}oxy)-2-phenylethyl]-1-methyl-1H-imidazol-3-ium chloride], **(3)**, [3-[(2*R*)-2-({[dichloro(*η*6-benzene)ruthenium]diphenylphosphanyl}oxy)-2-phenylethyl]-1-methyl-1H-imidazol-3-ium chloride], **(4)**, [3-[(2*R*)-2-{[(dichloro(η5–pentamethylcyclo pentadienyl)iridium)diphenyl phosphanyl]oxy}-2-phenylethyl]-1-methyl-1H-imidazol-3-ium chloride], **(5)**.

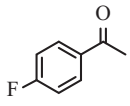
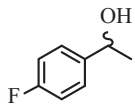
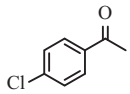
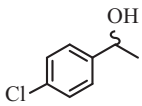
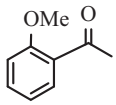
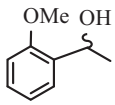
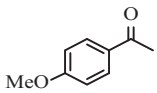
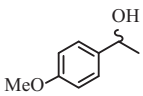
Entry	Catalyst	S/C/KOH	Time	Conversion (%)[a]	% ee[b]	Configuration[c]
1	3[d]	100:1:5	48 h	12	23	R
2	4[d]	100:1:5	48 h	11	26	R
3	5[d]	100:1:5	48 h	7	42	R
4	3[e]	100:1	3 h	trace	… …	… …
5	4[e]	100:1	3 h	trace	… …	… …
6	5[e]	100:1	3 h	trace	… …	… …
7	3[f]	100:1:5	24 h	98	32	R
8	4[f]	100:1:5	24 h	99	35	R
9	5[f]	100:1:5	40 h	99	56	R

Reaction conditions: [a]Determined by GC (three independent catalytic experiments),[b]Determined by capillary GC analysis using a chiral cyclodex B (Agilent) capillary column, [c]Determined by comparison of the retention times of the enantiomers on the GC traces with literature values, (*R*) configuration was obtained in all experiments, [d]At room temperature; acetophenone/Ru/KOH, 100:1:5, [e]Refluxing in *iso*-PrOH; acetophenone/Ru, 100:1, in the absence of base, [f]Refluxing in *iso*-PrOH; acetophenone/Ru/KOH, 100:1:5.

most probably by the functionalized phosphinite ligand based on ionic liquid (IL-OPPh$_2$). The ^{31}P-{^{1}H} NMR spectrum is fairly consistent with the structure of **3** showing a single resonance at δ 123.69 ppm as shown in Figure 1. Furthermore, ^{1}H NMR spectral data of compound **3** are consistent with the structure suggested. The signals consisting of two different doublets and one singlet centered at 5.45, 5.38 and 5.01 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 2.52 and 1.20, 1.03 ppm due to the CH and CH$_3$ of the *iso*-propyl 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$_2$L ▫ metal fragment (*Cs* symmetry) the ^{1}H and ^{13}C NMR spectra are very different from that of η^6-coordinated to a ML^{1}L^{2}L ▫ fragment (*C*$_1$ symmetry).[37] It is very well-known that the presence of one (broad) or two signals due to aromatic CH *p*-cymene protons in the ^{1}H NMR spectrum of **3** is consistent with a *Cs* symmetry of complexes and a free rotation of the arene (*p*-cymene) ligand.[38] In this case, the steric hindrance of ionic liquid-based phosphinite ligands seems to prevent free rotation of *p*-cymene ligand around the arene-Ru axis.[39] Finally, a signal due to the presence of the methyl in the *p*-cymene group is observed at 1.91 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.[40–42] The most relevant signals of ^{13}C-{^{1}H} NMR spectrum of complex **3** are those corresponding to *p*-cymene ligands. Signals for carbon atoms of the arene rings in *p*-cymene ligands are observed as four singlets at 93.29, 89.43, 88.88 and 86.56 ppm in the spectrum of complex **3**. The structural composition of the complex was also confirmed by IR spectroscopy and elemental analysis.

The reaction of stoichiometric amounts of [Ru(η^6-benzene)(μ-Cl)Cl]$_2$ and [C$_{24}$H$_{24}$N$_2$OPCl], **2** affords the complex, [3-[(2*R*)-2-({[dichloro(η^6-benzene)ruthenium]diphenylphosphanyl}oxy)-2-phenylethyl]-1-methyl-1H-imidazol-3-ium chloride], **(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 [3-[(2R)-2-({[dichloro(η^6-benzene)ruthenium]diphenylphosphanyl}oxy)-2-phenylethyl]-1-methyl-1H-imidazol-3-ium chloride]], **(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 121.18 ppm, in line with the values previously observed for similar compounds.[43] Analysis by ^{1}H NMR reveals this compound to be diamagnetic, exhibiting signals corresponding to the imidazole ring at 9.14 (br, 1H, -(CH$_3$)NC**H**N-), ppm and the C$_6$H$_6$ protons as a singlet 5.39 ppm. In the ^{13}C NMR spectrum of **4**, the (-(CH$_3$)N**C**HN–) carbon signal was observed at 137.37 ppm and the C$_6$H$_6$ carbon resonance occurred at 90.39 (s) ppm. Furthermore, in the ^{13}C-{^{1}H} NMR spectrum of **4**, J(^{31}P-^{13}C) coupling constants for the carbons of the phenyl rings were detected, which are consistent with the literature values.[44] The structure of **4** was further confirmed by IR spectroscopy and microanalysis, and found to be in good agreement with the theoretical values. In addition, reactions of the functionalized ionic based monodentate 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 [3-[(2*R*)-2-{[(dichloro(η5–pentamethylcyclopentadienyl) iridium)diphenyl phosphanyl]oxy}-2-phenylethyl]-1-methyl-1H-imidazol-3-ium chloride], **(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 24 h. In the ^{31}P-{^{1}H} NMR spectrum, resonance at δ 93.17 ppm may be attributed to complex **5** (Figure 1). The ^{1}H NMR spectrum is consistent with the anticipated structure. Analysis by ^{1}H NMR reveals this compound to be diamagnetic, exhibiting signal consisting of a singlet centered at 1.35 ppm due to the presence of the methyl protons in the Cp* group, this information is complemented by the presence of a signal at 9.08 ppm (-(CH$_3$)NC**H**N-). Furthermore, the ^{13}C NMR spectrum of the complex **5** displays a singlet at δ 8.21 ppm

Table 2. Asymmetric Transfer Hydrogenation results for substituted acetophenones with the catalyst systems, [3-[(2R)-2-({[dichloro(η6-*p*-cymene)ruthenium]diphenyl phosphanyl}oxy)-2-phenylethyl]-1-methyl-1H-imidazol-3-ium chloride], **(3)**, [3-[(2*R*)-2-({[dichloro(η6-benzene)ruthenium]diphenylphosphanyl}oxy)-2-phenylethyl]-1-methyl-1H-imidazol-3-ium chloride], **(4),** [3-[(2*R*)-2-{[(dichloro(η^5–pentamethylcyclopentadienyl)iridium)diphenyl phosphanyl]oxy}-2-phenylethyl]-1-methyl-1H-imidazol-3-ium chloride], **(5).**[a]

Entry	Cat.	Substrate	Product	Time	Conversion (%)[b]	% ee[c]	Configuration[d]
1	3			18 h	98	30	*R*
2	4			20 h	99	31	*R*
3	5			32 h	98	53	*R*
4	3			22 h	92	27	*R*
5	4			22 h	90	27	*R*
6	5			36 h	98	49	*R*
7	3			32 h	95	48	*R*
8	4			32 h	94	51	*R*
9	5			38 h	92	72	*R*
10	3			48 h	97	28	*R*
11	4			48 h	96	27	*R*
12	5			72 h	95	49	*R*

[a]Catalyst (0.005 mmol), substrate (0.5 mmol), *iso*PrOH (5 mL), KOH (0.025 mmol %), 82 °C, the concentration of acetophenone is 0.1 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]Determined by comparison of the retention times of the enantiomers on the GC traces with literature values; [e]Referred at the reaction time indicated in column; TOF = (mol product / mol Ru(II) Cat.) × h^{-1}.

attributable to methyl carbons of Cp* and doublet at δ 94.00 due to carbons of Cp* ring. The structural composition of the complex **5** was further confirmed by IR spectroscopy and microanalysis and found to be in good agreement with the theoretical values.

Catalytic transfer hydrogenation of ketones

Asymmetric Transfer Hydrogenation method has been extensively studied because of the lower price and satisfactory properties of the hydrogen donor as well as the operational simplicity. However, a problem of the transfer hydrogenation reaction in 2-propanol is the reversibility of the process (Figure 2). Not only to overcome this problem but also to develop highly active catalysts, we have been working on designing novel complexes for transfer hydrogenation. A few groups have reported some metal complexes with phosphinite ligands based on ionic liquid in recent years.[43–45] Especially, we have shown that several transition metal, such as rhodium, iridium and ruthenium complexes with phosphinite ligand based on functional ionic liquid (FILs) are highly active in the transfer hydrogenation of ketones. This encouraged us to investigate the asymmetric version of this reaction by using iridium or ruthenium complexes with chiral functionalized ionic liquids (CFILs).

Primarily, we studied the effect of complexes **3–5** on the asymmetric transfer hydrogenation of acetophenone. Our purpose here is to compare the organizing abilities of various functionalized transition metal complexes in the catalytic asymmetric transfer hydrogenation. A comparison of complexes **3–5** as precatalysts for the asymmetric hydrogenation of acetophenone by 2-propanol in the presence of NaOH is summarized in Table 1. Each catalytic experiment was repeated three times for precision. These systems catalyzed the reduction of acetophenone to corresponding alcohol ((*S*)-1-phenylethanol) in the presence of NaOH as a

promoter. To an *iso*PrOH solution of ruthenium complex and chiral ligand, an appropriate amount of acetophenone and NaOH/*iso*PrOH solutions were added, respectively, at room temperature. The solution was stirred for several hours, and then examined with capillary GC analysis. At room temperature, transfer hydrogenation of acetophenone occurred very slowly [45] with low conversion (up to 12%) and moderate enantioselectivity (up to 42% ee) in all reactions.

As can be inferred from Table 1 (Entries 4–6), the presence of a base is necessary to observe appreciable conversions. However, the choice of base, such as KOH and NaOH, had little influence on the conversion and enantioselectivity. In addition, optimization studies of the catalytic reduction of acetophenone in 2-propanol showed that good activity was obtained with a base/catalyst ratio of 5:1. Reduction of acetophenone into (*S*)-1-phenylethanol could be achieved in high yield by increasing the temperature up to 82 °C (Table 1, entries 7–9).

As shown in Table 1, it is noteworthy that the complexes display the differences in reactivity. The examination of the results indicates clearly that the best enantioselectivity was achieved when iridium complex **(5)** was used as a catalyst. The highest enantioselectivity (56%) was reached with complex **5** as shown in Figure S1 in Supplemental Materials, although it should be noted that with **3** and **4** a slightly lower level of induction was observed (32 and 35 ee %), respectively. In the context of the results, it could be reasonably argued that the absolute configuration of the product is governed by the carbon-centered chirality.

Encouraged by the enantioselectivities obtained in these preliminary studies, we next extended our investigations to include asymmetric hydrogenation of substituted acetophenone derivatives. The results in Table 2 prove that a range of acetophenone derivatives can be hydrogenated with moderate to good enantioselectivities. The catalytic reductions of acetophenone derivatives were all tested with the conditions optimized for acetophenone. Complexes **3–5** showed good activity for most of the ketones. The introduction of electron withdrawing substituents, such as F and Cl to the *p*-position of the aryl ring of the ketone decreased the electron density of the C = O bond so that the activity was improved giving rise to easier hydrogenation.[46,47] An electron-withdrawing group such as fluoro group to the *p*-position was helpful to obtain high conversion and moderate to good enantioselectivity (up to 53% ee, Table 2, entries 1–6), while the introduction of an electron-donating substituents such as methoxy group to the *p*-position tended to lower activity while maintaining low enantioselectivity (Entries 7–9). Among all selected ketones, the best result was obtained in the reduction of *o*-methoxyacetophenone giving up to 72% ee in Figure S2 (Table 2, entry 12). Conversely, the most electron donating substituent to the *p*-position (-OCH_3) led to lower conversion with lower ee%, exceptionally electron donating substituent to the *o*-position (Table 2).

As a result of their efficiency in the transfer hydrogenation of acetophenone derivatives, complexes **3–5** were further investigated in transfer hydrogenation of a variety of ketones to be converted to the corresponding chiral alcohols under the optimization conditions. Table 3 shows several examples of the asymmetric reductions tried using this method. The reaction of methyl/alkyl and methyl/aryl ketones gave the chiral alcoholic products in an adequate chemical yield and enantiomeric purity. Initially, we carried out further experiments to study the influence of bulkiness of the alkyl groups on the catalytic activity and selectivity (Table 3, entries 1–12). For this aim, a variety of simple aryl/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. The reaction of methyl/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 (Entries 10–12, 25–47% ee). As expected, when the size of alkyl group increased, the activity and selectivity decreased.[48–51]

In addition, as seen in Table 3, the best result in terms of enantioselectivity was observed with 1-naphthyl methyl ketone (Entries 13–15). In that case, the highest enantioselectivity, up to 81% ee, was obtained for catalyst **(5)** (Figure S3). Furthermore, the hydrogenation of ketones including cyclohexyl group was very slow and the enantioselectivities were remarkable lower (Table 3, entries 16–18).

Table 3. Asymmetric Transfer Hydrogenation results for various ketones catalyzed by, [3-[(2R)-2-({[dichloro(*η*6-*p*-cymene)ruthenium]diphenyl phosphanyl}oxy)-2-phenylethyl]-1-methyl-1H-imidazol-3-ium chloride], **(3)**, [3-[(2*R*)-2-({[dichloro(*η*6-benzene)ruthenium]diphenylphosphanyl}oxy)-2-phenylethyl]-1-methyl-1H-imidazol-3-ium chloride], **(4)**, [3-[(2*R*)-2-{[(dichloro(η^5–pentamethyl cyclopentadienyl)iridium)diphenyl phosphanyl]oxy}-2-phenylethyl]-1-methyl-1H-imidazol-3-ium chloride], **(5)**.[a]

Entry	Cat.	R_1	R_2	Time	Conversion (%)[b]	ee (%)[c]	Configuration[d]
1	3	CH_3	CH_2CH_3	24 h	98	33	*R*
2	4			24 h	98	34	*R*
3	5			40 h	97	55	*R*
4	3	CH_3	$CH_2CH_2C_6H_5$	28 h	99	30	*R*
5	4			28 h	98	31	*R*
6	5			45 h	99	54	*R*
7	3	CH_3	$CH(CH_3)_2$	32 h	99	26	*R*
8	4			32 h	99	26	*R*
9	5			32 h	98	50	*R*
10	3	CH_3	$CH_2CH(CH_3)_2$	30 h	97	25	*R*
11	4			30 h	96	24	*R*
12	5			32 h	97	47	*R*
13	3	CH_3	1-naphthyl	26 h	99	67	*R*
14	4			26 h	98	66	*R*
15	5			42 h	98	81	*R*
16	3	CH_3	C_6H_{11}	48 h	98	33	*R*
17	4			48 h	99	32	*R*
18	5			72 h	99	45	*R*

Reaction conditions: [a]Catalyst (0.005 mmol), substrate (0.5 mmol), 2-propanol (5 mL), KOH (0.025 mmol %), 82 °C, the concentration of acetophenone derivatives are 0.1 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]Determined by comparison of the retention times of the enantiomers on the GC traces with literature values, (*R*) configuration was obtained in all experiments.

Experimental

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, (*R*)-styrene oxide, PPh_2Cl and Et_3N were purchased from Fluka and used as received. $[Ru(\eta^6\text{-}p\text{-cymene})(\mu\text{-Cl})Cl]_2$,[52] $[Ru(\eta^6\text{-benzene})(\mu\text{-Cl})Cl]_2$,[53] and $Ir(\eta^5\text{-}C_5Me_5)(\mu\text{-Cl})Cl]_2$ [54] 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 AV400 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 were measured by a Perkin Elmer Lambda 25 instrument using a universal ATR sampling accessory (4500–500 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.

General procedure for the asymmetric transfer hydrogenation of ketones

Typical procedure for the catalytic hydrogen-transfer reaction: a solution of the complexes 3–5 (0.0025 mmol), KOH (0.0125 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 (Gas Chromatograpy), conversions obtained are related to the residual unreacted ketone.

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.

Synthesis of compounds

Synthesis of 3-[(2R)-2-hydroxy-2-phenylethyl]-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 the acid, the reaction mixture was cooled to room temperature and (*R*)-styrene oxide (1.56 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 ethyl acetate at 0 °C. The precipitated product was filtered and dried in vacuo yielding **1** as an off-white solid. Yield: 2.32 g, 78%; M.p.: 201–202 °C $[\alpha]_D^{20}$= +41.8° (c 1, $CHCl_3$); ^1H NMR D_2O, ppm): δ: 8.44 (s, 1 H, $(CH_3)NCHN$–), 7.26–7.33 (m, 7H, –NCHCHN+–CHPh), 5.08 (br, 1H, –C**H**OH) 4.38 (m, 2H, NCH_2), 3.75 (s, 3H, CH_3N); ^{13}C NMR (100.6 MHz, D_2O, ppm): δ: 35.59 (CH_3N), 55.40 (NCH_2), 71.41 (–CHOH), 128.90, 128.67, 125.44 (*o*-, *m*-, *p*-carbons of –CHPh), 123.17, 122.97 (–NCHCHN–), 136.41 ($(CH_3)NCHN$–), 139.00 (*i*-carbon); assignment was based on the $^1H\text{-}^{13}C$ HETCOR, DEPT and $^1H\text{-}^1H$ COSY spectra; IR: υ 3227 (O-H), 3068, 3037 (aromatic C–H), 1563 (C = N), 1167 (C–N); Anal. for $C_{12}H_{15}N_2OCl$ (238.71 g/mol): calcd. C 60.37, H 6.33, N 11.73; found C 60.05, H 6.23, N 11.51%.

Synthesis of [3-[(2R)-2-[(diphenylphosphanyl)oxy]-2-phenylethyl]-1-methyl-1H-imidazol-3-ium chloride], (2)

A dry and degassed CH_2Cl_2 (20 ml) solution of 3-[(2*R*)-2-hydroxy-2-phenylethyl]-1-methyl-1H-imidazol-3-ium chloride, (1) (0.100 g, 0.42 mmol) under an argon atmosphere was cooled to −78 °C in an acetone and dry ice bath. To the cooled solution was added dropwise a hexane solution of *n*-BuLi (0.262 ml, 0.42 mmol). After the addition, the mixture was stirred at −78 °C for 1 h and then for another 30 min at room temperature. The reaction solution was cooled to −78 °C again and a solution of diphenylchlorophosphine (0.094 g, 0.42 mmol) in CH_2Cl_2 (10 ml) was added dropwise to the reaction medium. Stirring was continued for a further 1 h at −78 °C, then the cooling bath was removed and the mixture was stirred for another 4 h at room temperature. Precipitated lithium chloride was removed by filtration under argon and then the volatiles were evaporated in vacuo to leave a viscous oil of the phosphinite ligand **2**. Yield 0.165 g, 93%, $[\alpha]_D^{20}$= +22.8° (c 1, $CHCl_3$); ^1H NMR (400.1 MHz, $CDCl_3$, ppm): δ: 10.31 (s, 1H, -$(CH_3)NCHN$-), 7.73–7.75 (m, 17H, $P(C_6H_5)_2$+-NCHCHN-+–CHPh), 4.59–4.70 (m, 2H, NCH_2), 5.28 (br, 1H, -CHOP), 3.77 (s, 3H, CH_3N); ^{13}C NMR (100.6 MHz, $CDCl_3$, ppm): δ 37.31 (CH_3N), 55.81 (NCH_2), 75.68 (-CHOP), 122.74, 123.13, (–NCHCHN–) 126.21, 128.49, 128.85 (*o*-, *m*-, *p*-carbons of –CHPh), 128.48 (d, $^3J_{31P-13C}$ = 8.0 Hz, *m*-$P(C_6H_5)_2$), 130.69 (*p*-$P(C_6H_5)_2$), 131.44 (d, $^2J_{31P-13C}$ = 11.1, *o*-$P(C_6H_5)_2$)), 136.45 (-$(CH_3)NCHN$–), 138.74 (*i*-carbon of CHPh), (not observed, *i*-$P(C_6H_5)_2$); assignment was based on the $^1H\text{-}^{13}C$ HETCOR, DEPT and $^1H\text{-}^1H$ COSY spectra; $^{31}P\text{-}\{^1H\}$ NMR (162.0 MHz, $CDCl_3$, ppm): δ 116.00 (s, O**P**Ph_2); IR: υ 3063

(aromatic C-H), 1438 (P-Ph), 1060 (O-P) cm^{-1}; Anal. for $C_{24}H_{24}N_2OPCl$ (422.66 g/mol): calcd. C 68.20, H 5.72, N 6.62; found C 68.07, H 5.56, N 6.46%.

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

$[Ru(\eta^6\text{-}p\text{-cymene})(\mu\text{-Cl})Cl]_2$ (0.072 g, 0.118 mmol) and $[(Ph_2P)\text{-}C_{12}H_{14}N_2O]Cl$, **2** (0.1 g, 0.235 mmol) were dissolved in dry CH_2Cl_2 (25 ml) under argon atmosphere and stirred for 24 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, 88%; M.p.: 177–79 °C $[\alpha]_D^{20}$= +34.6° (c 1, $CHCl_3$); ^{1}H NMR (400.1 MHz, $CDCl_3$, ppm): δ 9.38 (s, 1H, -(CH_3)NCHN-), 6.81–7.77 (m, 17H, P(C_6H_5)$_2$+-NCHCHN-+–CHPh), 5.47–5.50 (m, 1H, -CHOP), 5.45 (d, J = 6.0 Hz 2H, aromatic protons of *p*-cymene), 5.38 (s, 1H, aromatic protons of *p*-cymene), 5.01 (d, J = 5.2 Hz, 1H, aromatic protons of *p*-cymene), 4.70 (br, 2H, NCH_2), 3.88 (s, 3H, CH_3N), 2.52 (m, 1H, –CH- of *p*-cymene), 1.91 (s, 3H, C**H**$_3$Ph of *p*-cymene), 1.20 (d, J = 7.2 Hz, 3H, C**H**$_3$)$_2$CHPh of *p*-cymene), 1.03 (d, J = 6.8 Hz, 3H, C**H**$_3$)$_2$CHPh of *p*-cymene); ^{13}C NMR (100.6 MHz, $CDCl_3$, ppm): δ 17.49 (**C**H$_3$Ph of *p*-cymene), 21.00, 22.23 ((**C**H$_3$)$_2$CHPh of *p*-cymene), 30.12 (–**C**H- of *p*-cymene), 36.02 (**C**H$_3$N), 56.67 (N**C**H$_2$), 77.31 (br, CHOP), 86.56 (s, aromatic carbons of *p*-cymene), 88.88 (s, aromatic carbons of *p*-cymene), 89.43 (s, aromatic carbons of *p*-cymene), 93.29 (s, aromatic carbons of *p*-cymene), 96.54, 110.35 (quaternary carbons of *p*-cymene), 123.60, 124.33, 126.35,127.88, 128.52 (–NCHCHN– and *o*-, *m*-, *p*-carbons of –CHPh), 131.67 (*p*-P(C_6H_5)$_2$), 132.59 (d, $^3J_{31P-13C}$ = 11.1 Hz, *m*-P(C_6H_5)$_2$), 134.05 (d, $^2J_{31P-13C}$ = 11.1, *o*-P(C_6H_5)$_2$), 135.88 (-(CH_3)NCHN–), (not observed *i*-carbon of –CHPh), (not observed, *i*-P(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 123.69 (s, O**P**Ph$_2$); IR: υ 3056 (aromatic C-H), 2960 (aliphatic C–H), 1435 (P-Ph), 1016 (O-P) cm^{-1}; Anal. for $C_{34}H_{38}N_2OPRuCl_3$ (729.09 g/mol): calcd. C 56.01, H 5.25, N 3.84; found C 55.94, H 5.18, N 3.74%.

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

$[Ru(\eta^6\text{-benzene})(\mu\text{-Cl})Cl]_2$ (0.059 g, 0.118 mmol) and $[(Ph_2P)\text{-}C_{13}H_{16}N_2O_2]Cl$, **2** (0.100 g, 0.235 mmol) were dissolved in dry CH_2Cl_2 (25 ml) under argon atmosphere and stirred for 24 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: 140 mg, 89%; M.p.: 125–127 °C $[\alpha]_D^{20}$= +29.3° (c 1, $CHCl_3$); ^{1}H NMR (400.1 MHz, $CDCl_3$, ppm): δ 9.14 (br, 1H, -(CH_3)NCHN-), 7.00–7.74 (m, 17H, P(C_6H_5)$_2$+-NCHCHN-+–CHPh), 5.67 (br, 1H, -CHPh), 5.39 (s, 6H, aromatic protons of benzene), 4.72 (br, 2H, NCH_2), 3.82 (br, 3H, -CH_3N); ^{13}C NMR (100.6 MHz, $CDCl_3$, ppm): δ 38.15 (**C**H$_3$N), 53.51 (N**C**H$_2$), 77.32 (br, -CHOP), 90.39 (s, aromatic carbons of benzene), 123.62, 124.38, 126.81, 128.51,129.30 (–NCHCHN– and *o*-, *m*-, *p*-carbons of –CHPh), 131.54 (d, $^3J_{31P-13C}$ = 11.1 Hz, *m*-P(C_6H_5)$_2$), 131.71 (*p*-P(C_6H_5)$_2$), 133.72 (d, $^2J_{31P-13C}$ = 13.1 *o*-P(C_6H_5)$_2$)), 137.37 (-(CH_3)NCHN–), (not observed, *i*-carbon of –CHPh), (not observed, *i*-P(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 121.18 (s, O**P**Ph$_2$); IR: υ 3058 (aromatic C-H), 1435 (P-Ph), 1016 (O-P) cm^{-1}; Anal. for $C_{30}H_{30}N_2OPRuCl_3$ (672.98 g/mol): calcd. C 53.54, H 4.49, N 4.16; found C 53.49, H 4.32, N 4.10%.

Synthesis of [3-[(2R)-2-{[(dichloro(η^5–pentamethylcyclopentadienyl)iridium)diphenyl phosphanyl]oxy}-2-phenylethyl]-1-methyl-1H-imidazol-3-ium chloride], (5)

$Ir(\eta^5\text{-}C_5Me_5)(\mu\text{-Cl})Cl]_2$ (0.094 g, 0.118 mmol) and $[(Ph_2P)\text{-}C_{12}H_{14}N_2O]Cl$, **2** (0.100 g, 0.235 mmol) were dissolved in dry CH_2Cl_2 (25 ml) under argon atmosphere and stirred for 24 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 Ir(III) complex as an orange microcrystalline solid. The product was collected by filtration and dried in vacuo. Yield: 180 mg, 93%; M.p.: 131–133 °C $[\alpha]_D^{20}$ = +46.9° (c 1, $CHCl_3$); ^{1}H NMR (400.1 MHz, $CDCl_3$, ppm): δ 9.08 (s, 1H, -(CH_3)NCHN-), 6.85–7.72 (m, 17H, P(C_6H_5)$_2$+-NCHCHN-+–CHPh), 5.67 (br, 1H, -CHOP), 4.72 (br, 2H, NCH_2), 3.83 (s, 3H, CH_3N), 1.35 (s, 15H, CH_3 of Cp*(C_5Me_5); ^{13}C NMR (100.6 MHz, $CDCl_3$, ppm): δ 8.21 (C_5Me_5), 36.93 (CH_3N), 54.80 (NCH_2), 76.93 (br, CHOP), 94.00 (d, J = 3.0 Hz, C_5Me_5), 122.77, 123.60 (–NCHCHN–), 126.30, 128.19, 128.41 (*o*-, *m*-, *p*-carbons of –CHPh), 128.05 (d, J = 8.0 Hz, *m*-P(C_6H_5)$_2$), 131.86 (s, *p*-P(C_6H_5)$_2$), 132.72 (d, J = 12.1 Hz *o*-P(C_6H_5)$_2$), 135.86, (-(CH_3)NCHN–) 138.36 (*i*-carbon of –CHPh) (not observed, *i*-P(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 93.17 (s, O**P**Ph$_2$); IR: υ 3056 (aromatic C-H), 2962, 2919 (aliphatic C–H), 1436 (P-Ph), 1015 (O-P) cm^{-1}; Anal. for $C_{34}H_{39}N_2OPIrCl_3$ (821.24 g/mol): calcd. C 49.72, H 4.78, N 3.41; found C 49.62, H 4.61, N 3.33%.

Conclusions

In conclusion, we have developed efficient Ruthenium (II) and Iridium (III) complexes of inexpensive and easy-to-prepare phosphinite ligand based on an ionic liquid. We have found that these complexes are efficient homogeneous catalytic systems that can be readily implemented and lead to secondary alcohols. High conversion and moderate to good enantioselectivity were obtained in the catalytic reaction. Furthermore, while originally developed as a potential alternative to modular-designed ligands in the literature, this

phosphinite based on ionic liquid ligand family is now considered a privileged class of ligands in its own right and searches for novel applications are continuing. Furthermore, the procedure is quite simple and efficient toward various ketones and does not require an induction period.

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Disclosure statement

The author states that there is no conflict of interest.

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