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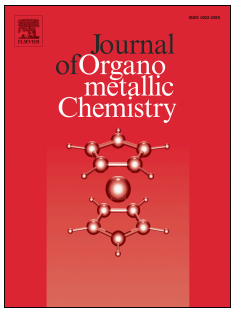

Transfer hydrogenation reaction using novel ionic liquid based Rh(I) and Ir(III)-phosphinite complexes as catalyst

Duygu Elma Karakaş, Feyyaz Durap, Akın Baysal, Yusuf Selim Ocak, Khadichakhan Rafikova, Eda Çavuş Kaya, Alexey Zazybin, Hamdi Temel, Cezmi Kayan, Nermin Meriç, Murat Aydemir

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Transfer Hydrogenation Reaction Using Novel Ionic Liquid Based Rh(I) and Ir(III)-Phosphinite Complexes as catalyst

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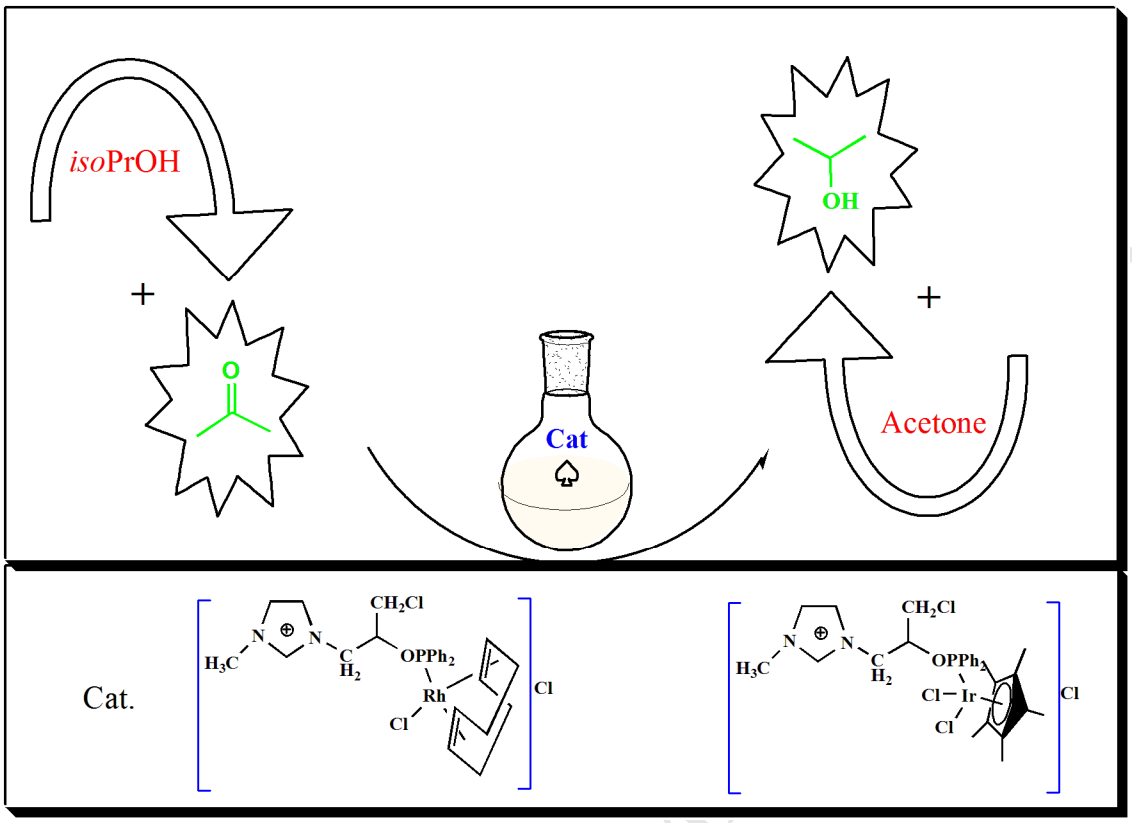
For the first time, (1-chloro-3-(3-methylimidazolidin-1-yl)propan-2-yl diphenylphosphinite chloride) (chloro η^4-1,5-cyclooctadiene rhodium(I))] and (1-chloro-3-(3-methylimidazolidin-1-yl)propan-2-yl diphenylphosphinite chloride) (dichloro η^5-pentamethylcyclopentadienyl iridium(III))] complexes have been synthesized with high yields. The novel catalysts were applied to transfer hydrogenation of various using 2-propanol as a hydrogen source. Notably, rhodium(I) complex is much more active in the transfer hydrogenation, giving the corresponding alcohols up to 99% conversions in 5 min (TOF $\leq$ 1176 h^{-1}).



Transfer Hydrogenation Reaction Using Novel Ionic Liquid Based Rh(I) and Ir(III)-Phosphinite Complexes as catalyst

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ABSTRACT

Hydrogen transfer reduction methods are attracting increasing interest from synthetic chemists in view of their operational simplicity. Thus, interaction of $[Rh(\mu\text{-}Cl)(cod)]_2$ and $Ir(\eta^5\text{-}C_5Me_5)(\mu\text{-}Cl)Cl]_2$ with phosphinite ligand $[(Ph_2PO)\text{-}C_7H_{11}N_2Cl]Cl$, **1** gave new monodendate (1-chloro-3-(3-methylimidazolidin-1-yl)propan-2-yl diphenylphosphinite chloride) (chloro η^4-1,5-cyclooctadiene rhodium(I))], **2** and (1-chloro-3-(3-methylimidazolidin-1-yl)propan-2-yl diphenylphosphinite chloride) (dichloro η^5-pentamethylcyclopentadienyl iridium(III))], **3** complexes, which were characterized by a combination of multinuclear NMR spectroscopy, IR spectroscopy, and elemental analysis. $^1H\text{-}\{^{31}P\}$ NMR, $^1H\text{-}^{13}C$ HETCOR or $^1H\text{-}^1H$ COSY correlation experiments were used to confirm the spectral assignments. The novel catalysts were applied to transfer hydrogenation of acetophenone derivatives using 2-propanol as a hydrogen source. The results showed that the corresponding alcohols could be obtained with high activity (up to 99 %) under mild conditions. Notably, (1-chloro-3-(3-methylimidazolidin-1-yl)propan-2-yl diphenylphosphinite chloride) (chloro η^4-1,5-cyclooctadiene rhodium(I))], **2** complex is much more active than the other analogous complex, **3** in the transfer hydrogenation. Furthermore, compound, **2** acts as excellent catalysts, giving the corresponding alcohols in 97-99% conversions in 5 min (TOF $\leq 1176\ h^{-1}$).

Keywords: Ionic Compound, Phosphinite, Rhodium, Iridium, Transfer Hydrogenation, Catalysis

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1. Introduction

Ketones are the most common unsaturated substrates used in organic synthesis. Extensive efforts have been devoted to their reduction into secondary alcohols especially via hydrogenation [**1**]. 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 [**2,3**]. In transfer hydrogenation, organic molecules such as primary and secondary alcohols [**4**] or formic acid and its salts [**5**,**6**] have been employed as the hydrogen source. The use of the hydrogen donor has some advantages over the use of molecular hydrogen since it avoids risks and constrains associated with hydrogen gas as well as the necessity for pressure vessels and other equipment.

Transition metal complexes are powerful 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 [**7**]. However, the appropriate choice of metal precursors and the reaction conditions are crucial for catalytic properties [**8**]. A number of transition metal complexes are known to be catalyzing hydrogen transfer from an alcohol to a ketone [**9,10,11**]. Over the last three decades, most effort on hydrogenation has been focused on the use of ruthenium [**12,13,14**], rhodium and iridium catalysts [**15,16,17]**. Rhodium and iridium complexes have been proven to lead to very efficient processes along with potential industrial applications [**18,19,20**].

In the past few years room temperature ionic liquids, consisting of 1,3-dialkylimidazolium cations and their counter ions, have attracted growing interest [**21,22,23,24**]. These ionic liquids are potential replacements for organic solvents both on laboratory and industrial scales due to their green characteristics such as thermal stability, lack of vapor pressure, non-flammability, wide liquid range, wide range of solubility and miscibility [**25**]. 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 viable

substitute for volatile organic solvents [**26**]. An unusual feature of ionic liquids is the tunability of their chemical and physical properties by selection of appropriate anion–cation combinations [**27**]. 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 [**28**].

The chemistry of *P*-based ligands has also been intensively explored in recent years [**29**]. 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 [**30**]. Many modified *P*-based ligands have important applications in organometallic chemistry and catalysis, giving selective catalysts for hydroformylation, hydrosilylation and transfer hydrogenation [**31,32,33,34**]. While much effort has been devoted to the synthesis of aminophosphines and their metal complexes, similar studies on the analogous phosphinites are less extensive [**35,36**], even though some of their complexes have proved to be efficient catalysts [**37,38**]. In addition, well-known phosphine ligands have also found widespread applications in transition metal catalyzed transformations [**39,40**]. 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 [**41**]. Although some phosphinite ligands and their derivatives have been employed successfully as ligands in the transfer hydrogenation of ketones [**42,43,44,** references therein), a screening of catalytic activities of ionic liquid based phosphinites in this reaction is not common in the literature. To the best of our knowledge, there is no report on the utility of these complexes including phosphinite ligands based on ionic liquid in Rh(II) and Ir(III) catalyzed transfer hydrogenation reaction. Extending our study to develop useful and very magnificent catalysts, in this paper, we report (*i*) the synthesis and full characterization of two rhodium and iridium

complexes, and (*ii*) for the first time their subsequent application in transfer hydrogenation of the ketones.

2. Experimental

2.1. Materials and methods

Unless otherwise stated, all reactions were carried out under an atmosphere of argon using conventional Schlenk glassware, solvents were dried using established procedures and distilled under argon immediately prior to use. Analytical grade and deuterated solvents were purchased from Merck. PPh_2Cl, epichlorohydrin, 1-methylimidazole, $[Rh(\mu\text{-}Cl)(cod)]_2$ and $Ir(\eta^5\text{-}C_5Me_5)(\mu\text{-}Cl)Cl]_2$ are purchased from Fluka and were used as received. In addition, 1-chloro-3-(3-methylimidazolidin-1-yl)propan-2-ol chloride and $[(Ph_2PO)\text{-}C_7H_{11}N_2Cl]Cl$ [45] were prepared according to the literature procedures [**46,47**].The infrared spectra was measured by a Perkin Elmer FT-IR Spectrum one and a Perkin Elmer Lambda 25, respectively. The FTIR spectra were recorded using a universal ATR sampling accessory (4000–550 cm^{-1}). ^1H (400.1 MHz), ^{13}C NMR (100.6 MHz) and $^{31}P\text{-}\{^1H\}$ NMR spectra (162.0 MHz) were recorded spectra on a Bruker AV400 spectrometer, with δ referenced to external TMS and 85% H_3PO_4 respectively. Elemental analysis was carried out on a Fisons EA 1108 CHNS-O instrument. Melting points were recorded by a Gallenkamp Model apparatus with open capillaries.

2.2. Transfer Hydrogenation of Ketones

Typical procedure for the catalytic hydrogen transfer reaction: a solution of catayst (1-chloro-3-(3-methylimidazolidin-1-yl)propan-2-yl diphenylphosphinite chloride) (chloro η^4-1,5-cyclooctadiene rhodium(I))], **2** or (1-chloro-3-(3-methylimidazolidin-1-yl)propan-2-yl diphenylphosphinite chloride) (dichloro η^5-pentamethylcyclopentadienyl iridium(III))], **3** (0.005 mmol), NaOH (0.025 mmol) and the corresponding ketone (0.5 mmol) in degassed 2-propanol (5 mL) were refluxed until the reactions were completed. Then, a sample of the reaction mixture was taken off, diluted with acetone and analyzed immediately by GC. The

conversions are related to the residual unreacted ketone. GC analyses were performed on a Shimadzu 2010 Plus Gas Chromatograph equipped with capillary column (5% biphenyl, 95% dimethylsiloxane) (30m x 0.32mm x 0.25μm). The GC parameters for transfer hydrogenation of ketones were as follows; initial temperature, 50 ºC; initial time, hold min 1 min; solvent delay, 4.48 min; temperature ramp 15 ºC/min; final temperature, 270 ºC, hold min 5 min; final time, 20.67 min; injector port temperature, 200 ºC; detector temperature, 200 ºC, injection volume, 2.0 μL.

2.3. Synthesis of Compounds

2.3.1. Synthesis and Characterization of (1-chloro-3-(3-methylimidazolidin-1-yl)propan-2-yl diphenylphosphinite chloride) (chloro η^4-1,5-cyclooctadiene rhodium(I))], (2)

[Rh(μ-Cl)(cod)]$_2$ (0.062 g, 0.127 mmol) and [(Ph_2PO)-$C_7H_{11}N_2Cl$]Cl, **1** (0.100 g, 0.253 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**:140 mg, 86.3 %; m.p.:146-147^{o}C); **^{1}H NMR (400.1 MHz, $CDCl_3$, ppm)**: δ 10.37 (s, 1H, -(CH_3)NC**H**N-), 6.93-7.85 (m, 12H, P(C_6**H**$_5$)$_2$+-NC**H**C**H**N-), 6.05 (br, 1H, -C**H**OP), 5.73 (br, 2H, C**H** of cod), 4.90 (br, 1H, NC**H**$_2$, (a)), 4.70 (m, 1H, NC**H**$_2$, (b)), 4.37 (br, 1H, -C**H**$_2$Cl, (a)), 4.12-4.15 (m, 1H, -C**H**$_2$Cl, (b)), 3.95 (s, 3H, NC**H**$_3$), 3.30 (br, 1H, C**H** of cod), 2.98 (br, 1H, C**H** of cod), 2.44 (br, 4H, C**H**$_2$ of cod), 2.12 (br, 2H, C**H**$_2$ of cod), 1.90 (br, 2H, C**H**$_2$ of cod); **^{13}C NMR (100.6 MHz, $CDCl_3$, ppm)**: δ 28.07, 28.80, 32.46, 33.69 (**C**H$_2$ of cod), 36.73 (N**C**H$_3$), 46.10 (-**C**H$_2$Cl), 51.21 (N**C**H$_2$), 77.40 (d, ^2J = 22.1 Hz, (-**C**HOP), 71.70 (d, ^1J = 13.1 Hz, **C**H of cod), 111. 01 (d, ^1J = 7.0 Hz, **C**H of cod), 122.46, 122.77 (-N**C**H**C**HN-), 127.96 (d, $^3J_{31P–13C}$ = 11.1 Hz, *m*-P(**C**$_6$H$_5$)$_2$), 131.50 (*p*-P(**C**$_6$H$_5$)$_2$), 133.33 (d, $^2J_{31P–13C}$ = 15.1 Hz, *o*-P(**C**$_6$H$_5$)$_2$)), (not observed *i*-P(**C**$_6$H$_5$)$_2$), 138.86 (-(CH_3)N**C**HN-); *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 124.22 (d, $^{1}J_{(103Rh–31P)}$ =175.8 Hz, O**P**Ph_2); **IR**: υ 3055 (aromatic C-H), 2942, 2879, 2830 (aliphatic C–H), 1433 (P-Ph), 1047 (O-P) cm^{-1}; **$C_{27}H_{33}N_2OCl_3PRh$** (641.81 g/mol): calcd. C 50.53, H 5.18, N 4.37; found C 50.18, H 4.91, N 4.08 %.

2.3.2. Synthesis and Characterization of (1-chloro-3-(3-methylimidazolidin-1-yl)propan-2-yl diphenylphosphinite chloride) (dichloro η^5-pentamethylcyclopentadienyl iridium(III))], 3

[Ir(η^5-C_5Me_5)(μ-Cl)Cl]$_2$ (0.101 g, 0.127 mmol) and [(Ph_2PO)-$C_7H_{11}N_2Cl$]Cl, **1** (0.100 g, 0.253 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**:171mg, 85.2 %; m.p.:133-134^{o}C); **^{1}H NMR (400.1 MHz, $CDCl_3$, ppm)**: δ 9.96 (s, 1H, -(CH_3)NC**H**N-), 7.53-7.87 (m, 12H, P(C_6**H**$_5$)$_2$+-NC**H**C**H**N-), 5.34 (br, 1H, -C**H**OP), 4.67 (br, 1H, NC**H**$_2$, (a)), 4.54 (m, 1H, NC**H**$_2$, (b)), 4.09 (s, 3H, NC**H**$_3$), 3.29 (br, 2H, -C**H**$_2$Cl), 1.34 (s, 15H, C**H**$_3$ of Cp∗(C_5**Me**$_5$); **^{13}C NMR (100.6 MHz, $CDCl_3$, ppm)**: δ 8.19 (C_5**Me**$_5$), 36.78 (N**C**H_3), 43.46 (-**C**H_2Cl), 50.47 (N**C**H_2), 74.52 (-**C**HOP), 94.27 (d, ^{2}J = 12.0 Hz, **C**$_5Me_5$),, 123.28, 123.40 (-N**C**H**C**HN-), 128.54 (d, $^{3}J_{31P–13C}$ = 9.5 Hz, *m*-P(**C**$_6H_5$)$_2$), 131.99 (*p*-P(**C**$_6H_5$)$_2$), 134.73 (d, $^{2}J_{31P–13C}$ = 12.1 Hz, *o*-P(**C**$_6H_5$)$_2$)), (not observed *i*-P(**C**$_6H_5$)$_2$), 138.22 (-(CH_3)N**C**HN-); *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 96.36 (s, O**P**Ph_2); **IR**: υ 3055 (aromatic C-H), 2945, 2912 (aliphatic C–H), 1437 (P-Ph), 1042 (O-P) cm^{-1}; **$C_{29}H_{36}N_2OCl_4PIr$** (793.62 g/mol): calcd. C 43.89, H 4.57, N 3.53; found C 43.75, H 4.45, N 3.44 %.

3. Results and Discussion

3.1. Synthesis of the new complexes

First of all, the synthesis of 1-(3-chloro-2-(hydroxypropyl)-3-methyl-imidazolium chloride, **$[C_7H_{12}N_2OCl]Cl$,** was accomplished in one step from the reaction of 1-methylimidazole and

epichlorohydrin in ethanol at room temperature, according to a reported procedure [48]. Furthermore, as shown in Scheme 1, **[(Ph_2PO)-$C_7H_{11}N_2Cl$]Cl, 1** was prepared from the commercially available starting material PPh_2Cl and **[$C_7H_{12}N_2OCl$]Cl,** in the presence of triethylamine by hydrolysis [**49,50**]. In Scheme 1, phosphinite ligand **[(Ph_2PO)-$C_7H_{11}N_2Cl$]Cl, 1** was synthesized from the starting material PPh_2Cl, in CH_2Cl_2 solution by the hydrolysis method as in a previously described procedure [**51**]. The LiCl salt was separated by filtration and the ligand was obtained by extracting the solvent in vacuo in good yields. The progress of this reaction was conveniently followed by ^{31}P-{^1H} NMR spectroscopy. The signals of the starting material PPh_2Cl at δ 81.0 ppm disappeared and new singlet appeared downfield due to the corresponding phosphinite ligand. The ^{31}P-{^1H} NMR spectrum of **1** show no unexpected features. As expected, the ^{31}P-{^1H} NMR spectra of phosphinite, **[(Ph_2PO)-$C_7H_{11}N_2Cl$]Cl, 1** shows single resonances due to phosphinite at δ 118.46, (see Figure 1), [**52,53,54,55,56]** in line with the values previously observed for similar compounds [**57,58,59,60**]. The appropriate assignment of the ^1H 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 $J_{(31P\text{-}13C)}$ 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 [**61**]. The structures for these ionic based monodendate phosphinite ligands are consistent with the data obtained from IR spectra and elemental analyses (***for details see experimental section***).

Insert Scheme 1 Here

Firstly, we investigated simple coordination chemistry of $[Rh(\mu\text{-}Cl)(cod)]_2$ with [(Ph_2PO)-$C_7H_{11}N_2Cl$]Cl, **1** ligand**.** Reactions of $[Rh(\mu\text{-}Cl)(cod)]_2$ with [(Ph_2PO)-$C_7H_{11}N_2Cl$]Cl, **1** in

CH_2Cl_2 in a ratio of 1/2:1 at room temperature for 1 h gave micro-crystalline precipitate of complex (1-chloro-3-(3-methylimidazolidin-1-yl)propan-2-yl diphenylphosphinite chloride) (chloro η^4-1,5-cyclooctadiene rhodium(I))], **2**. Complexation reactions were straightforward, with coordination to rhodium being carried out at room temperature. This ligand was expected to cleave the $[Rh(\mu\text{-}Cl)(cod)]_2$ dimer to give the corresponding complex via monohapto coordination of the phosphinite. Bridge cleavage of the dimer $[Rh(\mu\text{-}Cl)(cod)]_2$ with phosphinite gave the mononuclear complexes in high yield. This complex is highly soluble in CH_2Cl_2 and slightly soluble in hexane and they can be crystallized from CH_2Cl_2/hexane solution. The coordination of the ligand through the P donor was confirmed by the $^{31}P\text{-}\{^1H\}$ NMR spectroscopy. The complex, **2** were isolated as indicated by doublets in the $^{31}P\text{-}\{^1H\}$ NMR spectra at (δ) 124.22 (d, $^1J_{RhP}$: 175.8 Hz), [**62,63**] (Figure 1), indicating that ionic based phosphinite ligand acting as monodendate ligand. ^1H and ^{13}C NMR spectra of compound **2** display all the signals of coordinated ligands. The ^1H NMR spectrum **2** displays the anticipated multiplets at δ 7.85-6.93 ppm for the protons of phenyls, broad singlets at δ 5.73, 3.30, 2.98, 2.44, 2.12 and 1.90 ppm for cod protons. In the $^{13}C\text{-}\{^1H\}$ NMR spectrum of compound **2**, $J(^{31}P\text{-}^{13}C)$ coupling constants of the carbons of the phenyl rings were observed, which are consistent with the literature values [**64**] (***for details see experimental section***). The structural compositions of the complex **2** were further confirmed by IR spectroscopy and microanalysis, and found to be in good agreement with the theoretical values.

Insert Figure 1 Here

Reactions of the ionic based monodendate phosphinite with metal $[Ir(\eta^5\text{-}C_5Me_5)(\mu\text{-}Cl)Cl]_2$ precursor is also depicted in Scheme 1. (1-chloro-3-(3-methylimidazolidin-1-yl)propan-2-yl diphenylphosphinite chloride) (dichloro η^5-pentamethylcyclopentadienyl iridium(III))], **3**

was obtained by the reaction of ligand with $[Ir(\eta^5\text{-}C_5Me_5)(\mu\text{-}Cl)Cl]_2$ in a molar ratio of 2/1 at room temperature for 1 h. In the $^{31}P\text{-}\{^1H\}$ NMR spectrum, resonance at δ 96.36 ppm may be attributed to complex of **3** (**Figure 1**). The ^1H NMR spectra are consistent with the anticipated structure. Analysis by ^1H NMR reveals this compound to be diamagnetic, exhibiting signals corresponding to the aromatic rings for **3** at 7.87-7.53 ppm. Another signal consisting of a singlet centered at 1.34 ppm are due to the presence of the methyl protons in the Cp* group, this information is complemented by the presence of signal at 9.96 ppm (s, 1H, -$(CH_3)NC\underline{\mathbf{H}}N$-). Furthermore, in the ^{13}C NMR spectrum of the complex **3** displays singlet at δ 8.19 ppm attributable to methyl carbons of Cp* and doublet at δ 94.27 due to carbons of Cp* ring. The structural composition of the complex **3** was further confirmed by IR spectroscopy and microanalysis, and found to be in good agreement with the theoretical values (for details see experimental section). Although, single crystals of both complexes were obtained by slow diffusion of diethyl ether into a solution of the compound in dichloromethane over several days, unfortunately we were not able to protect them from rapid decomposition in air.

3.2. Catalytic transfer hydrogenation of ketones

Because of the good catalytic performance and the higher structural permutability of phosphinite based transition metal complexes in the reduction of ketones [**65,66**], recently, we have reported that the novel half-sandwich complexes, based on ligands with P-O backbone [**67,68**]. The observed activity of these complexes has encouraged us to investigate other analogous ligands and other transition metal complexes of these ligands. In this context, complexes (1-chloro-3-(3-methylimidazolidin-1-yl)propan-2-yl diphenylphosphinite chloride) (chloro η^4-1,5-cyclooctadiene rhodium(I))], **2** and (1-chloro-3-(3-methylimidazolidin-1-yl)propan-2-yl diphenylphosphinite chloride) (dichloro η^5-pentamethylcyclopentadienyl iridium(III))], **3** were selected as catalysts, 2-propanol/NaOH as the reducing system and acetophenone as a model substrate (**Scheme 2**), and the results are listed in Table 1. In a preliminary study, when the reaction temperature was increased to 82 °C, smooth reduction of

acetophenone into 1-phenylethanol occurred with conversion up to 99 % after 1/3 h for **2** and 1 h for **3** of reaction Table 1 (Entries 1 and 2). From the results, it is noteworthy that the complexes **2** and **3** display the differences in reactivity, with a complex/NaOH ratio of 1/5. Complex **2** is more active, quantitatively converting acetophenone with a high TOF of 297 h^{-1}. From these preliminary results, it can be concluded that (1-chloro-3-(3-methylimidazolidin-1-yl)propan-2-yl diphenylphosphinite chloride) (chloro η^4-1,5-cyclooctadiene rhodium(I))], **2** is more effective than (1-chloro-3-(3-methylimidazolidin-1-yl)propan-2-yl diphenylphosphinite chloride) (dichloro η^5-pentamethylcyclopentadienyl iridium(III))], **3** complex.

Insert Scheme 2 Here

At room temperature no appreciable formation of 1-phenylethanol was detected (Table 1, entries 3 and 4). As can be inferred from the Table 1 (Entries 5 and 6) the catalysts as well as the presence of NaOH are necessary to observe appreciable conversions. The base facilitates the formation of alkoxide by abstracting proton of the alcohol and subsequently alkoxide undergoes β-elimination to give metal hydride, which is an active species in this reaction. This is the mechanism proposed by several workers on the studies of transition metal catalyzed transfer hydrogenation reaction by metal hydride intermediates [**69,70**]. In addition, the replacement of the reaction atmosphere from an inert gas to an ambient atmosphere had no negative effect on the activity of the catalyst (Table 1, Entries 7 and 8). Therefore, the hydrogenation reactions were performed in air. Although, performing the reaction with the addition of water slowed the reaction, it had no influence on conversion of the product (Table 1, entries 9 and 10). As shown in Table 1 (Entries 11-14), increasing the substrate-to-catalyst ratio do not lower the conversions of the product in most cases except the time lengthened.

Remarkably, the transfer hydrogenation of acetophenone could be achieved up to 99 % conversion even when the substrate-to-catalyst ratio reached to 1000:1.

Insert Table 1 Here

The catalytic activity of complexes (1-chloro-3-(3-methylimidazolidin-1-yl)propan-2-yl diphenylphosphinite chloride) (chloro η^4-1,5-cyclooctadiene rhodium(I))], **2** and (1-chloro-3-(3-methylimidazolidin-1-yl)propan-2-yl diphenylphosphinite chloride) (dichloro η^5-pentamethylcyclopentadienyl iridium(III))], **3** were also extensively investigated with acetophehone derivatives. The catalytic reduction of acetophenone derivatives was all tested with the conditions optimized for acetophenone and the results are summarized in Table 2. The fourth column in Table **2** illustrates conversions of the reduction performed in a 0.1 M of 2-propanol solution containing **2** or **3** and NaOH (Ketone:Cat.:NaOH = 100:1:5). As expected, electronic properties (the nature and position) of the substituents on the phenyl ring of the ketone caused the changes in the reduction rate. An *ortho*- or *para*- substituted acetophenone with an electron-donor substituent, i.e., 2-methoxy or 4-methoxy is reduced more slowly than acetophenone (Table 2, entry 5, 6, 11 and 12) [**71**]. In addition, the introduction of electron withdrawing substituents, such as NO_2, F, Cl and Br to the *para*-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 (Entries 1-4 and 7-10) [**72,73**].

Insert Table 2 Here

We also carried out further experiments to study the effect of bulkiness of the alky groups on the catalytic activity and the results were given in Table 3 (entries 1-12). A variety of simple aryl alkyl ketones were transformed to the corresponding secondary alcohols. It was

found that the activity is highly dependent on the steric bulk of the alkyl group. The reactivity gradually decreased by increasing the bulkiness of the alkyl groups [**74**]. That's to say, when the size of alkyl group is increased, the activity was remarkable decreased [**75,76**].

Insert Table 3 Here

Encouraged by the high catalytic activities obtained in these preliminary studies, we next extended our investigations to include hydrogenation of various simple ketones (**Table 4**). Investigation of catalytic activity of these (1-chloro-3-(3-methylimidazolidin-1-yl)propan-2-yl diphenylphosphinite chloride) (chloro η^4-1,5-cyclooctadiene rhodium(I))], **2** and (1-chloro-3-(3-methylimidazolidin-1-yl)propan-2-yl diphenylphosphinite chloride) (dichloro η^5-pentamethylcyclopentadienyl iridium(III))], **3** has shown that they are efficient catalysts affording almost quantitative transformation of the ketones in short times and **2** is more active than **3** (**Table 3**). However, their efficiency was lower leading to longer conversion times. For instance, hydrogenations of cyclohexanone could be achieved in 30 min and 2 h by (1-chloro-3-(3-methylimidazolidin-1-yl)propan-2-yl diphenylphosphinite chloride) (chloro η^4-1,5-cyclooctadiene rhodium(I))], **2** and (1-chloro-3-(3-methylimidazolidin-1-yl)propan-2-yl diphenylphosphinite chloride) (dichloro η^5-pentamethylcyclopentadienyl iridium(III))], **3**, respectively. In addition, conversion of methyl isobutyl ketone occurred in 1 h and 3 h by **2** and **3**, respectively, while that of diethyl ketone occurred in 2 h and 4 h by **2** and **3**, respectively.

Insert Table 4 Here

4. Conclusions

In summary, for the first time (1-chloro-3-(3-methylimidazolidin-1-yl)propan-2-yl diphenylphosphinite chloride) (chloro η^4-1,5-cyclooctadiene rhodium(I))] and (1-chloro-3-(3-methylimidazolidin-1-yl)propan-2-yl diphenylphosphinite chloride) (dichloro η^5-pentamethylcyclopentadienyl iridium(III))] complexes have been synthesized with high yields. The complexes were characterized using multi nuclear NMR, IR and microanalysis. The use of the new complexes for the reduction of the ketonic C=O bond of ketones under hydrogen transfer conditions was also investigated. We found that these complexes are efficient homogeneous catalytic systems that can be readily implemented and lead to secondary alcohols from good to excellent conversions. Especially, (1-chloro-3-(3-methylimidazolidin-1-yl)propan-2-yl diphenylphosphinite chloride) (chloro η^4-1,5-cyclooctadiene rhodium(I))] was a more efficient catalyst in the transfer hydrogenation reaction. The modular construction of these catalysts and their flexibility toward transfer hydrogenation make these systems to pursue. Further studies of other transition metal complexes of this ligand are in progress and will be reported in due course.

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Captions

Scheme 1 Synthesis of the [(Ph_2PO)-$C_7H_{11}N_2Cl$]Cl, **1**, (1-chloro-3-(3-methylimidazolidin-1-yl)propan-2-yl diphenylphosphinite chloride) (chloro η^4-1,5-cyclooctadiene rhodium(I))], **2** and (1-chloro-3-(3-methylimidazolidin-1-yl)propan-2-yl diphenylphosphinite chloride) (dichloro η^5-pentamethylcyclopentadienyl iridium(III))], **3** (**i**) 1 equiv. Ph_2PCl, 1 equiv. *n*-BuLi, CH_2Cl_2; (**ii**) 1/2 equiv. [Rh(μ-Cl)(cod)]$_2$, CH_2Cl_2; (**iii**) 1/2 equiv. [Ir(η^5-C_5Me_5)(μ-Cl)Cl]$_2$, CH_2Cl_2.

Figure 1 The ^{31}P-{^{1}H} NMR spectra of ligand and its complexes, [(Ph_2PO)-$C_7H_{11}N_2Cl$]Cl, **1,** (1-chloro-3-(3-methylimidazolidin-1-yl)propan-2-yl diphenylphosphinite chloride) (chloro η^4-1,5-cyclooctadiene rhodium(I))], **2** and (1-chloro-3-(3-methylimidazolidin-1-yl)propan-2-yl diphenylphosphinite chloride) (dichloro η^5-pentamethylcyclopentadienyl iridium(III))], **3.**

Scheme 2 Hydrogen transfer from 2-propanol to acetophenone.

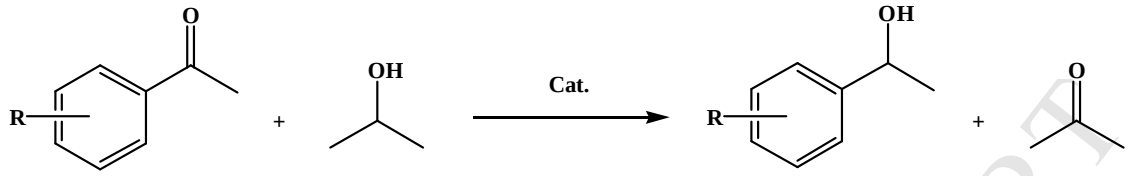
Table 1 Transfer hydrogenation of acetophenone with 2-propanol catalyzed by (1-chloro-3-(3-methylimidazolidin-1-yl)propan-2-yl diphenylphosphinite chloride) (chloro η^4-1,5-cyclooctadiene rhodium(I))], **2** or (1-chloro-3-(3-methylimidazolidin-1-yl)propan-2-yl diphenylphosphinite chloride) (dichloro η^5-pentamethylcyclopentadienyl iridium(III))], **3.**

Entry	*Catalyst*	*S/C/NaOH*	*Time*	*Conversion(%)*[i]	*TOF(h^{-1})*[k]
1	**2** [a]	**100:1:5**	1/3 h	99	297
2	**3** [a]	**100:1:5**	1 h	99	99
3	**2** [b]	**100:1:5**	1 h	trace	….
4	**3** [b]	**100:1:5**	1 h	trace	….
5	**2** [c]	**100:1**	1 h	<5	….
6	**3** [c]	**100:1**	1 h	<5	….
7	**2** [d]	**100:1:5**	1/3 h	99	297
8	**3** [d]	**100:1:5**	1 h	98	98
9	**2** [e]	**100:1:5**	3/2 h	98	65
10	**3** [e]	**100:1:5**	4 h	98	25
11	**2** [f]	**500:1:5**	1 h	98	490
12	**3** [f]	**500:1:5**	3 h	99	165
13	**2** [g]	**1000:1:5**	3 h	99	330
14	**3** [g]	**1000:1:5**	5 h	99	200

Reaction conditions:

[a] Refluxing in 2-propanol; acetophenone/Cat./NaOH, 100:1:5; [b] At room temperature; acetophenone/Cat./NaOH, 100:1:5; [c] Refluxing in 2-propanol; acetophenone/Cat., 100:1, in the absence of base; [d] Refluxing the reaction in air; [e] Added 0.1 mL of H_2O; [f] Refluxing in 2-propanol; acetophenone/Cat./NaOH, 500:1:5; [g] Refluxing in 2-propanol; acetophenone/Cat/NaOH, 1000:1:5; [i] Determined by GC (three independent catalytic experiments); [k] Referred at the reaction time indicated in column; TOF= (mol product/mol)Cat.)x h^{-1}.

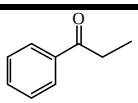
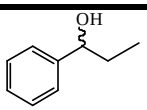
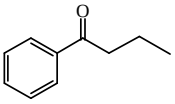
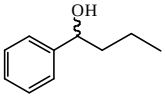
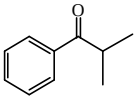
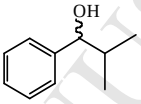
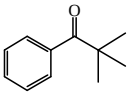
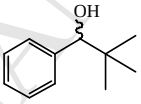
Table 2 Transfer hydrogenation results for substituted acetophenones with the catalyst systems prepared from $[(Ph_2PO)\text{-}C_7H_{11}N_2Cl]Cl$, **1** and $[Rh(\mu\text{-}Cl)(cod)]_2$ or $[Ir(\eta^5\text{-}C_5Me_5)(\mu\text{-}Cl)Cl]_2$.[a]



Entry	*R*	*Time*	*Conversion(%)[b]*	*TOF(h^{-1})[c]*
***Cat: Rh(I) complex,* 2**				
1	**4-F**	**5 min**	**98**	**1176**
2	**4-Cl**	**10 min**	**99**	**594**
3	**4-Br**	**15 min**	**96**	**384**
4	**4-NO_2**	**5 min**	**97**	**1164**
5	**2-MeO**	**1 h**	**95**	**95**
6	**4-MeO**	**2 h**	**92**	**46**
***Cat: Ir(III) complex,* 3**				
7	**4-F**	**10 min**	**98**	**588**
8	**4-Cl**	**25 min**	**97**	**333**
9	**4-Br**	**45 min**	**96**	**128**
10	**4-NO_2**	**10 min**	**98**	**588**
11	**2-MeO**	**2 h**	**93**	**47**
12	**4-MeO**	**7/2 h**	**90**	**26**

[a] Catalyst (0.005 mmol), substrate (0.5 mmol), 2-Propanol (5 mL), NaOH (0.025 mmol %), 82 °C, respectively, the concentration of acetophenone derivatives is 0.1 M; [b] Purity of compounds is checked by NMR and GC (three independent catalytic experiments), yields are based on methyl aryl ketone; [c] TOF = (mol product/mol Cat.) x h^{-1}.

Table 3 Transfer hydrogenation results for substituted alkyl phenyl ketones with the catalyst systems prepared from [(Ph_2PO)-$C_7H_{11}N_2Cl$]Cl, **1** and [Rh(μ-Cl)(cod)]$_2$ and [Ir(η^5-C_5Me_5)(μ-Cl)Cl]$_2$.[a]

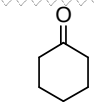
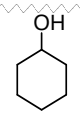
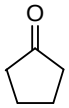
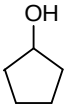
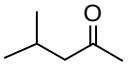
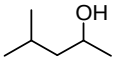
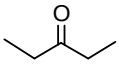
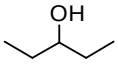
Entry	*Cat.*	*Time*	*Substrate*	*Product*	*Conv. (%)[b]*	*TOF(h^{-1})[c]*
1	**2**	**30 min**			**99**	**198**
2	**3**	**2 h**			**98**	**49**
3	**2**	**1 h**			**98**	**98**
4	**3**	**3 h**			**98**	**33**
5	**2**	**2 h**			**97**	**49**
6	**3**	**5 h**			**99**	**20**
7	**2**	**4 h**			**98**	**25**
8	**3**	**9 h**			**99**	**11**

[a] Catalyst (0.005 mmol), substrate (0.5 mmol), 2-propanol (5 mL), NaOH (0.025 mmol %), 82 °C, respectively, the concentration of alkyl phenyl ketones is 0.1 M;

[b] Purity of compounds is checked by NMR and GC (three independent catalytic experiments), yields are based on methyl aryl ketone;

[c] TOF = (mol product/mol Cat.) x h^{-1}.

Table 4 Transfer hydrogenation of various simple ketones with 2-propanol catalyzed by (1-chloro-3-(3-methylimidazolidin-1-yl)propan-2-yl diphenylphosphinite chloride) (chloro η^4-1,5-cyclooctadiene rhodium(I))], **2** and (1-chloro-3-(3-methylimidazolidin-1-yl)propan-2-yl diphenylphosphinite chloride) (dichloro η^5-pentamethylcyclopentadienyl iridium(III))], **3.**[a]

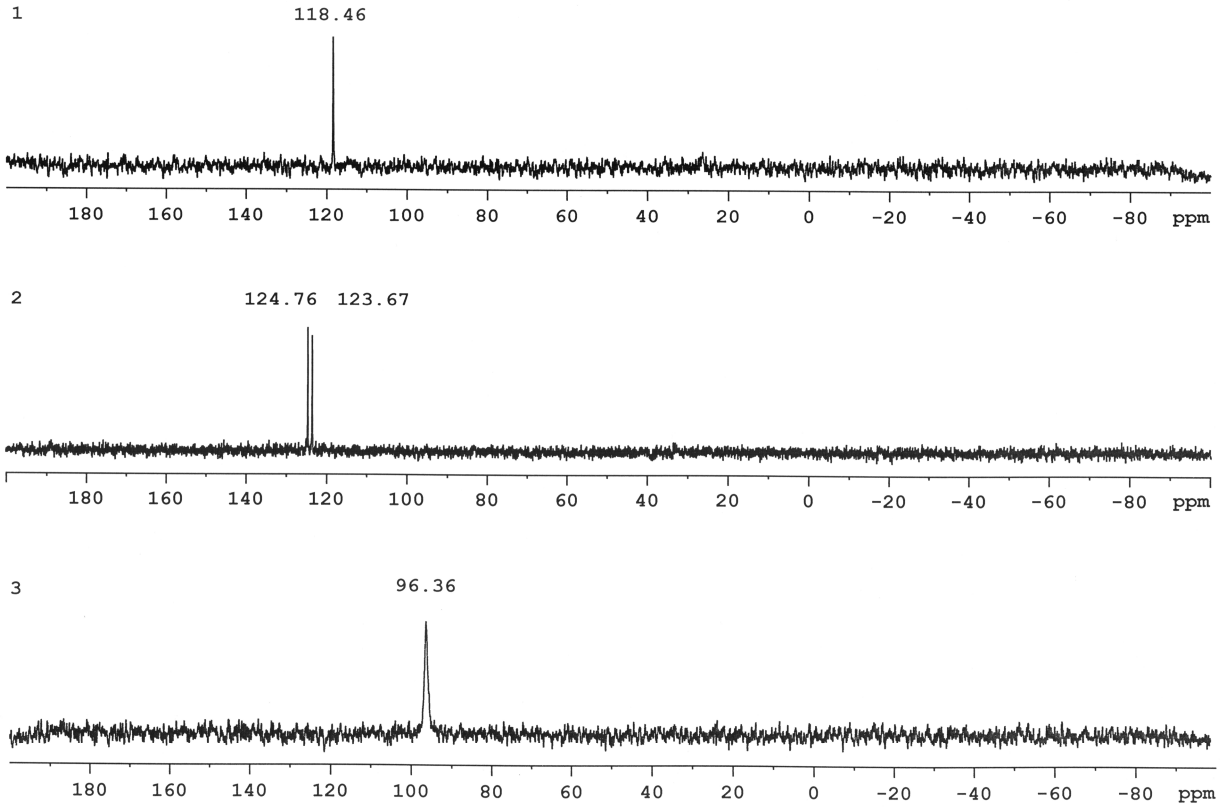
Entry	*Cat.*	*Substrate*	*Product*	*Time*	*Conv. (%)[b]*	*TOF(h^{-1})[c]*
1	**2**			**30 min**	**98**	**196**
2	**3**			**2 h**	**99**	**50**
3	**2**			**30 min**	**99**	**198**
4	**3**			**2 h**	**98**	**49**
5	**2**			**1 h**	**98**	**98**
6	**3**			**3 h**	**99**	**33**
7	**2**			**2 h**	**99**	**50**
8	**3**			**4 h**	**98**	**25**

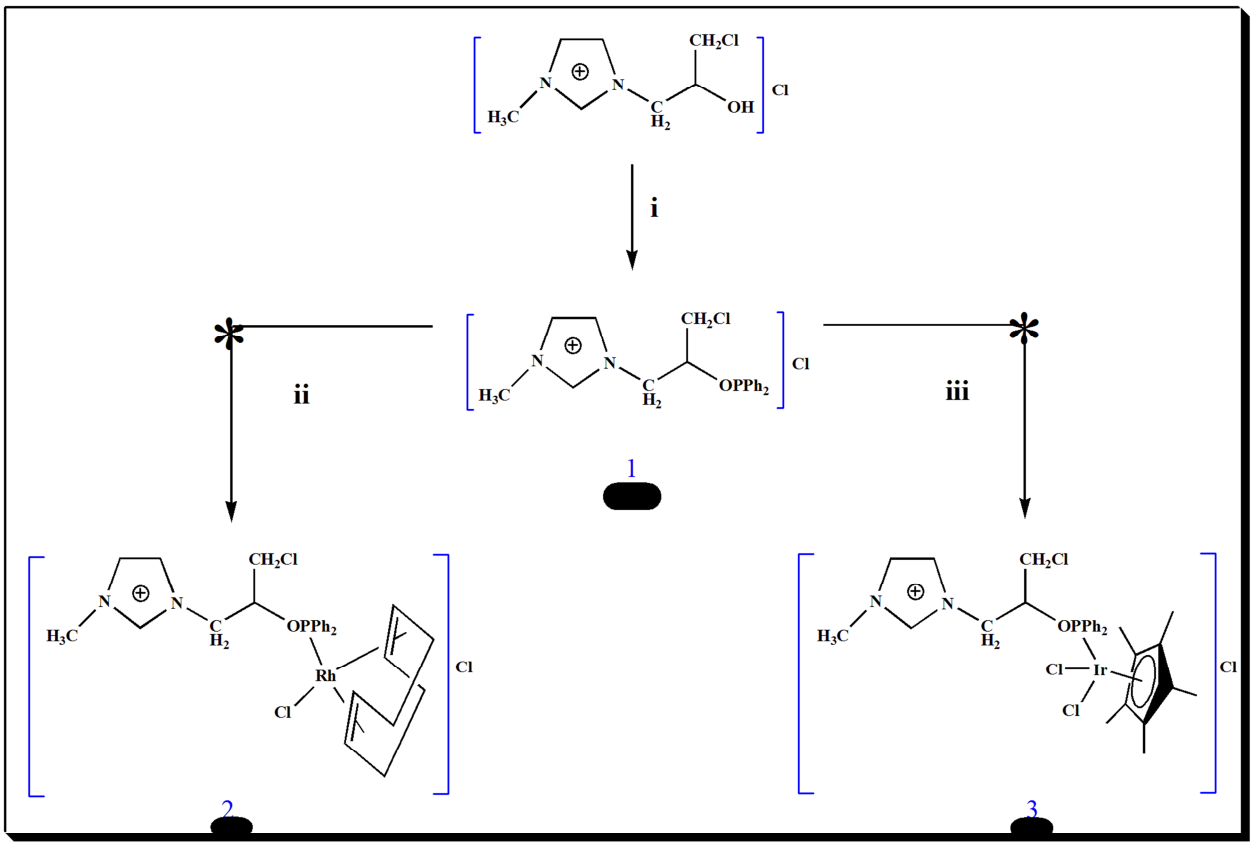
Reaction conditions:

[a] Refluxing in 2-propanol; acetophenone/Cat./NaOH, 100:1:5;

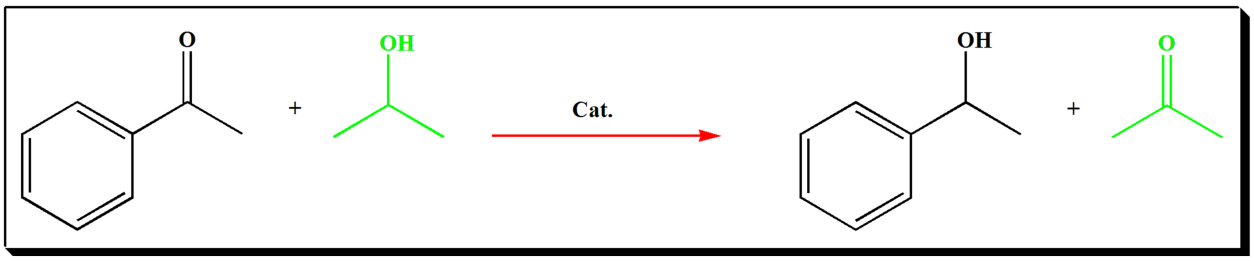
[b] Determined by GC (three independent catalytic experiments), purity of compounds is checked by NMR and GC (three independent catalytic experiments), yields are based on methyl aryl ketone;

[c] TOF = (mol product/mol Cat.) x h^{-1}.





Scheme 1



Scheme 2

RESEARCH HIGHLIGHTS

- ✓ **We have shown, for the first time synthesizing of a new kind of two Rh(I)-, Ir(III)-phosphinite catalysts based on ionic liquid.**

- ✓ **Both of them are efficient catalyst for the transfer hydrogenation of various ketones and and lead to secondary alcohols from good to excellent conversions.**

- ✓ **Especially, 1-chloro-3-(3-methylimidazolidin-1-yl)propan-2-yl diphenylphosphinite chloride) (chloro η^4-1,5-cyclooctadiene rhodium(I))] acts as excellent catalysts, giving the corresponding alcohols in 97-99% conversions in 5 min (TOF ≤ 1176 h^{-1}).**