Middle East Journal of Science

https://dergipark.org.tr/mejs **MEJS**

e-ISSN:2618-6136

Research Article

NOVEL MONONUCLEAR METAL-PHOSPHINITE COMPOUNDS AND THEIR CATALYTIC PERFORMANCE IN TRANSFER HYDROGENATION OF KETONES

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Abstract: *Since the obtained chiral alcohols are rather useful as well as biologically active compounds, the reduction of ketones to their respective alcohols is a crucial topic in synthetic chemistry. Thus, a new phosphinite ligand was synthesized by the interaction of cationic species N-vinyl imidazolium (**1**) with PCy_2Cl. This phosphinite ligand in combination with $[Ru(\eta^6\text{-p-cymene})(\mu\text{-Cl})Cl]_2$ and $Ir(\eta^5\text{-}C_5Me_5)(\mu\text{-Cl})Cl]_2$ gave active catalytic systems for transfer hydrogenation reaction. Under optimum circumstances, ruthenium complex (**3**) showed rather a high conversion in the reduction reaction of acetophenone. Furthermore, reversibility of the transfer hydrogenation reaction was found to be low under these reaction circumstances.*

Keywords*: Transfer Hydrogenation; Ruthenium Complex; Iridium Complex; Phosphinite; Homogeneous Catalysis.*

Received: February 23, 2022 *Accepted: April 05, 2022*

1. Introduction

Phosphino-imidazolium salts were first designed by Chauvin and Canac to prepare transition metal complexes having ionic character [1,2], and when used in homogeneous catalytic reactions by Zhao et al., [3-6] these complexes exhibited a high activity [7,8]. Afterward, the synthesis and applications of phosphinite-imidazolium salts have also become an effective field of study. Phosphinite-imidazolium salts were used as catalysts in the preparation of phthalate and maleate diesters, 3,4-dihydropyrimidin-2(1H)-(thio)ones, E-cinnamates, and coumarin derivatives by Valizadeh et al. [9-12]. Iranpoor et al., using these compounds, investigated the catalytic efficiency of aryl halides in dehalogenation, silylation, and Heck reactions in the presence of $PdCl_2$ [13-15]. However, the application of complexes of phosphinite compounds based on the ionic liquid in asymmetric transfer hydrogenation reaction was first performed by our study group [16-18].

The reduction of carbonyl compounds using a catalyst, and dihydrogen (H_2), hydrides, or H_2-donors as a source of hydrogen is an important route to obtaining alcohols [19-21]. In molecular hydrogenation, dihydrogen is used as a hydrogenation source, while hydrides are used in metal hydride reduction, and a hydrogen donor is used in transfer hydrogenation. It has shown that transfer hydrogenation is more advantageous than the conventional use of hydrides or direct hydrogen. Among them are (a) equipment is simpler; (b) catalyst loading is lower; (c) handling is safer; (d) solvents are environmentally friendly; (e) by-products are facile removable and volatile; and (f) the process may be used in industrial processes [22,23]. In this reaction, hydrogen is transferred from an organic source (e.g. isopropanol or formic acid) to an unsaturated bond of a compound (e.g. ketone or alkene), a metal is

used as a catalyst, often a base is also required [24]. Metal catalysts such as transition metal complexes (Ru, Ir, or Rh) containing phosphinites displayed high catalytic activity and became the most common organometallic compound employed in the transfer hydrogenation reaction [25-32].

Continuing our previous research, the present study reports the synthesis of an imidazole containing ionic liquid (IL) via the regioselective epoxide ring-opening reaction. The ionic liquid (IL) was converted to the corresponding chiral functionalized ionic liquid-based phosphinite ligand (P-FIL) by adding phosphinite moiety to the ionic liquid through S_N2 reaction, and then the corresponding Ru(II) and Ir(III) transition metal complexes were prepared. Structures of all new compounds were elucidated by ^{31}P, ^{1}H, ^{13}C NMR, and FT-IR spectroscopies. Afterward, the application of Ru(II) and Ir(III) compounds as catalysts were investigated in the transfer hydrogenation (TH) of acetophenone derivatives to their respective 1-phenylethanol derivatives using isopropanol as a hydrogen source.

2. Materials and Methods

2.1. Materials

If it is not stated otherwise, materials and solvents were employed as received. The reactants 1-vinylimidazole (99%), chlorodicyclohexylphosphine (97%) (PCy_2Cl), n-butyllithium solution (1.6 M in hexane; n-BuLi), (±)-epichlorohydrin (99%), dichloro(*p*-cymene)ruthenium(II) dimer, $[Ru(\eta^6\text{-p-cymene})(\mu\text{-Cl})Cl]_2$ (99%) and pentamethylcyclopentadienyliridium(III) chloride, dimer, $Ir(\eta^5\text{-}C_5Me_5)(\mu\text{-Cl})Cl]_2$ were purchased from Sigma-Aldrich (Germany). The phosphinite ligand and their complexes were prepared under an inert atmosphere employing standard Schlenk techniques. CaH_2 was used to dry 2-propanol. A Bruker AV400 spectrometer was used to record ^{1}H, ^{13}C and, $^{31}P\text{-}\{^{1}H\}$ nuclear magnetic resonance (NMR) spectra. An Agilent Cary 630 Fourier Transform infrared spectrometer was used to obtain the infrared spectra. A Costech ECS 4010 instrument was used to conduct elemental analysis. Melting points of the products were obtained by means of a Stuart SMP40 apparatus with an open capillary. GC analysis was conducted with a Shimadzu GC 2010 Plus instrument equipped with cyclodex B (Agilent) capillary column (5% biphenyl, 95% dimethylsiloxane; 30 m × 0.32 mm × 0.25 μm).

2.2. GC analyses

The GC parameters for TH of acetophenone derivatives are given below; init. temp., 50 ºC; init. time, 1.1 min; solv. del., 4.48 min; temp. ramp 15 ºC/min; ending temp., 270 ºC; hold time, 5 min; last time, 20.76 min; inj. port temp., 200 ºC; det. temp., 200 ºC; inj. vol., 2.0 μL.

2.3. A general protocol for the catalytic hydrogen transfer reaction

A representative protocol for TH of ketones is given below: a solution of pre-catalysts (**3-4**) (0.005 mmol), potassium hydroxide (0.025 mmol), and respective ketone (0.5 mmol) in isopropanol that was degassed (5 mL) was heated to reflux until the reactions finished. Then, a specimen was taken from this medium, followed by dilution with acetone and analyzing immediately by GC. The conversions are calculated depending on the remaining ketone. ^{1}H NMR spectra of the resulting products were as anticipated.

2.4. Preparation and structure elucidation of compounds

2.4.1 Preparation of 3-(3-chloro-2-hydroxypropyl)-1-vinyl-1H-imidazol-3-ium chloride, (1)

Concentrated HCl (10.50 mL, 128 mmol) was cautiously added into an ethanol (20 mL) solution of 1-vinylimidazole (11.30 mL, 11.764 g, 125 mmol), which was stirred at ambient temperature. ***Warning****: The neutralization of a base with a strong acid is rather exothermic.* Having added acid, it

was pended until the medium cooled to ambient temperature. Then, the addition of (±)-epichlorohydrin (10.16 mL, 12.027 g, 130 mmol) was carried out dropwise by stirring the solution, meanwhile, temperature of the solution was kept at 25 °C. Afterward, the reaction flask was closed and stirred at ambient temperature for 24 – 48 hours. Then, removal of the solvent of the solution in vacuo with warming at 70 °C, and keep warming under reduced pressure afforded a liquid that became more viscous when dried further, which was then recrystallized from ethyl acetate at 0 ºC. The precipitated solid part was filtered and dried under reduced pressure giving **1** as an off-white solid. Yield 27.22 g, 97.6 %, Melting Point = 99-101 °C. **^{1}H NMR (400.1 MHz, DMSO-*d*$_6$, ppm):** δ: 9.46 (s, 1H, –NC**H**N$^+$–), 8.19 and 7.85 (2xs, 2H, –NC**H**C**H**N–), 7.35-7.29 (m, 1H –C**H**=CH$_2$), 6.05 (br, 1H, –CHO**H**), 5.98-5.94 (m, 1H, –CH=C**H**$_2$ (**a**)), 5.44-5.40 (m, 1H, –CH=C**H**$_2$ (**b**)), 4.42-4.39 (m, 1H, –N$^+$C**H**$_2$ (**a**)), 4.20-4.15 (m, 1H, –N$^+$C**H**$_2$ (**b**)), 4.10 (br, 1H –C**H**OH), 3.45 (m, 2H,–C**H**$_2$Cl); **^{13}C NMR (100.6 MHz, DMSO-*d*$_6$, ppm): δ** 136.43 (–N**C**HN$^+$–), 129.22 (–N**C**H=CH$_2$), 124.46, 119.20 (–N**C**H**C**HN$^+$–), 109.21 (–NCH=**C**H$_2$), 68.86 (–**C**HOH), 52.99 (–N$^+$**C**H$_2$CH(OH)), 46.91 (–**C**H$_2$Cl); **IR (cm^{-1}):** υ 3369 (O-H), 3116, 3041 (aromatic C-H), 2989, 2888 (aliphatic C-H), 1575 (C=N), 1162 (C-N) cm^{-1}; Analysis results for **$C_8H_{12}Cl_2N_2O$** (223.10g/mol): calcd. C 43.07, H 5.42, N 12.56; found C 42.98, H 5.36, N 12.51.

2.4.2 Preparation of 3- (3-chloro-2-((dicyclohexylphosphaneyl)oxy)propyl)-1-vinyl-1H-imidazol-3-ium chloride, (2)

A CH_2Cl_2 (20 mL) solution of **1** (0.105 g, 0.47 mmol) under an inert atmosphere was cooled to −78 °C in an acetone and dry ice bath. A hexane solution of *n*-BuLi (0.293 mL, 0.47 mmol) was added dropwise into this cooled solution. Followed by the addition, the solution was stirred at −78 °C for 1 h and further 45 minutes at room temperature (RT). Afterward, the reaction solution was cooled to −78 °C again and a solution of dicyclohexylchlorophosphine (0.112 g, 0.47 mmol) in CH_2Cl_2 (10 mL) was added dropwise to this solution, which was stirred for a further 1 h at −78 °C. Having removed the cooling bath, the solution was further stirred for 3 hours at RT and ^{31}P NMR spectroscopy was used to follow the progress of the reaction. After ligand formation was observed, removal of the precipitated lithium chloride was performed by filtration under an inert atmosphere, followed by removal of the volatiles in vacuo, which gave a viscous oil phosphinite ligand, **2**. **^{31}P-{^{1}H} NMR** (162.0 MHz, $CDCl_3$, ppm): δ 148.99 (s, O**P**Cy$_2$).

2.5. General protocol for the synthesis of (IL-OPCy$_2$-Metal) complexes

Metal precursor (0.40 mmol) and [(Cy$_2$P)-$C_8H_{11}Cl_2N_2O$], **2** (0.40 mmol) were dissolved in dried CH_2Cl_2 (25 mL) under an inert atmosphere, and then this mixture was stirred for 1 h at RT. The volume of the solution was reduced to 1-2 mL in vacuo, and petroleum ether (15 mL) was added to afford the respective metal complexes as microcrystalline solid. This solid was separated by filtrating the mixture and dried under reduced pressure.

2.5.1 [3-(3-chloro-2-({[dichloro(η^6-*p*-cymene)ruthenium]dicyclohexylphosphanyl}oxy) propyl)-1-vinyl-1H-imidazol-3-ium chloride], (3)

Yield: 280 mg, 96.5%; Melting point:113-115 °C. **^{1}H NMR (400.1 MHz, DMSO-*d*$_6$, ppm):** *δ*: 9.59 (s, 1H, –NC**H**N$^+$–), 8.25, 7.91 (2xs, 2H, –NC**H**C**H**N$^+$–), 7.40-7.34 (m, 1H, –C**H**=CH$_2$), 5.99 (br, 1H, –CH=C**H**$_2$ (**a**)), 5.83-5.79 (m, 4H, aromatic protons of *p*-cymene), 5.43 (br, 1H, –CH=C**H**$_2$(**b**)), 5.41 (br, 1H, –C**H**OP), 4.43 (d, 1H, *J=13.23 Hz*, –N$^+$C**H**$_2$ (**a**)), 4.19 (d, 1H, *J=13.61 Hz*, –N$^+$C**H**$_2$ (**b**)), 3.69 (m, 2H, –C**H**$_2$Cl), 2.84-2.81 (m, 1H, –C**H**(CH$_3$)$_2$ of *p*-cymene), 2.46 (m, 2H, –C**H** of P(C$_6$H$_{11}$)$_2$), 2.08 (s, 3H, –C**H**$_3$Ph of *p*-cymene), 1.78 + 1.23-1.18 (m, 26H, (C**H**$_3$)$_2$CH Ph of *p*-cymene + CH$_2$ of P(C$_6$**H**$_{11}$)$_2$); **^{13}C NMR (100.6 MHz, DMSO-*d*$_6$, ppm):** δ: 136.63 (–N**C**HN$^+$–), 129.35 (–N**C**H=CH$_2$), 119.20, 124,54 (–N**C**H**C**HN$^+$–), 109.10 (–NCH=**C**H$_2$), 106.80, 100.53 (quaternary carbons of *p*-cymene), 86.83, 85.98 (s, aromatic carbons of *p*-cymene), 73.25 (d, $J_{P\text{-}C}$=*6.0 Hz* –**C**HOP), 53.01 (–

$N^+\underline{C}H_2CH(OP)$), 46.91 (–$\underline{C}H_2Cl$), many resonances at between 46.08-45.44 for –$\underline{C}H$ of $P(C_6H_{11})_2$), 30.43 (–$\underline{C}H(CH_3)_2$ of *p*-cymene), many signals at between 28.31-26.11 for –$\underline{C}H_2$ of $P(C_6H_{11})_2$), 21.96 (–$CH(\underline{C}H_3)_2$ Ph of *p*-cymene), 18.33 (–$\underline{C}H_3$Ph of *p*-cymene); **^{31}P-{^{1}H} NMR (162.0 MHz, $CDCl_3$, ppm) *δ*:** 156.01 (s, O$\underline{P}Cy_2$); **^{31}P-{^{1}H} NMR (162.0 MHz, DMSO-d_6, ppm) *δ*:** 158.20 (s, O$\underline{P}Cy_2$); **IR (cm^{-1});** υ 3041 (aromatic C-H), 2922, 2851 (aliphatic C–H), 1446 (P-Cy), 1054 (O-P), 533 (Ru-P); **Analytical results for $C_{30}H_{47}Cl_4N_2OPRu$ (725.56 g/mol):** calcd. C 49.66, H 6.53, N 3.86; found C 49.60; H 6.478; N 3.78 %.

2.5.2 [3-(3-chloro-2-({[dichloro(η^5-pentamethylcyclopentadienyl) iridium] dicyclohexyl phosphanyl}oxy)propyl)-1-vinyl-1H-imidazol-3-ium chloride], (4)

Yield: 310 mg, 94.7 %; m.p.: 124–126 °C; **^{1}H NMR (400.1 MHz, DMSO-d_6, ppm):** δ: 9.53 (s, 1H, –NC$\underline{H}N^+$–), 8.31, 7.76 (2xs, 2H, –NC$\underline{H}$C$\underline{H}N^+$–), 7.39 (br, 1H, –C$\underline{H}$=CH_2), 6.02 (br, 1H, –CH=C$\underline{H}_2$(a)), 5.58 (br, 1H, –C$\underline{H}$OP), 5.41 (br, 1H, –CH=C$\underline{H}_2$(b)), 3.87 (m, 1H, –N^+C$\underline{H}_2$(a)), 3.78 (m, 1H, –N^+C$\underline{H}_2$(b)), 4.49 (br, 2H, –C$\underline{H}_2$Cl), 1.53 (s, 15H $C_5\underline{Me}_5$), 1.98-1.23 (m, 22H, protons of $P(C_6H_{11})_2$) ; **^{13}C NMR (100.6 MHz, DMSO-d_6, ppm):** δ:136.6 (–N$\underline{C}HN^+$–), 129.35 (–N$\underline{C}H$=CH_2), 124.06, 119,63 (–N$\underline{C}H\underline{C}HN^+$–), 109.19 (–NCH=$\underline{C}H_2$), 93.92 (s, $\underline{C}_5Me_5$), 73.99 (d, $J_{P\text{-}C}$=*6.0 Hz*, –$\underline{C}$HOP), 50.02 (–$N^+\underline{C}H_2CH(OP)$), 45.70 (–$\underline{C}H_2Cl$), many resonances at between 44.28-43.73 for –$\underline{C}H$ of $P(C_6H_{11})_2$), many signals at between 28.76-25.54 for –$\underline{C}H_2$ of $P(C_6H_{11})_2$), 9.45 ($C_5\underline{Me}_5$); **^{31}P-{^{1}H} NMR (162.0 MHz, $CDCl_3$, ppm) *δ*:** 122.92 (s, O$\underline{P}Cy_2$); **^{31}P-{^{1}H} NMR (162.0 MHz, DMSO-d_6, ppm) *δ*:** 123.03 (s, O$\underline{P}Cy_2$); **IR (cm^{-1});** υ 3097 (aromatic C-H), 2922, 2847 (aliphatic C–H) 1446 (P-Cy), 1058 (O-P); **Analytical results for $C_{30}H_{48}Cl_4N_2OPIr$ (817.72 g/mol):** calcd.: C 44.07; H 5.92; N 3.43; found C 44.01; H 5.82; N 3.37 %

3. Results and Discussion

3.1. Synthesis and characterization of the ionic liquid, phosphinite ligand, and corresponding complexes

One of the most common techniques for the preparation of hydroxyl-functionalized ionic liquid is the ring-opening of epoxides. Based on this method [33-40], *N*-vinylimidazole was reacted with (±)-epichlorohydrin to afford the corresponding functionalized ionic liquid in 97.6 % isolated yield (Scheme 1). The initial formation of a new generation of desired ionic liquid 3-(3-chloro-2-hydroxypropyl)-1-vinyl-1H-imidazol-3-ium chloride, (**1**) was unambiguously confirmed by their spectroscopic analysis. In the ^{1}H NMR spectrum of compound **1**, the –NCHN$^+$– signal of the starting material *N*-vinylimidazole at δ 7.98 ppm shifted to 9.46 ppm due to the formation of the corresponding ionic liquid **1**, which was in agreement with the literature [41,19,42,18 and references therein]. The signal for extra OH proton was observed at around 6.05 (br) ppm, which is good evidence of the success of the alkylation of the imidazole ring with (±)-epichlorohydrin. The remaining protons were observed in their respective regions. The ^{13}C-{^{1}H} NMR spectrum of **(1)** also shows the presence of the *N*-vinylimidazolium carbons at δ 136.43, 129.22, 124.46, 119.20, and 109.21 ppm. In addition, the signal at 68.86 ppm belongs to –$\underline{C}$HOH, which is another evidence that the ring-opening reaction has occurred. In the IR spectrum, the signal of the hydroxyl group was observed as expected. Moreover, the elemental analysis result of **1** supports the formation of the compound.

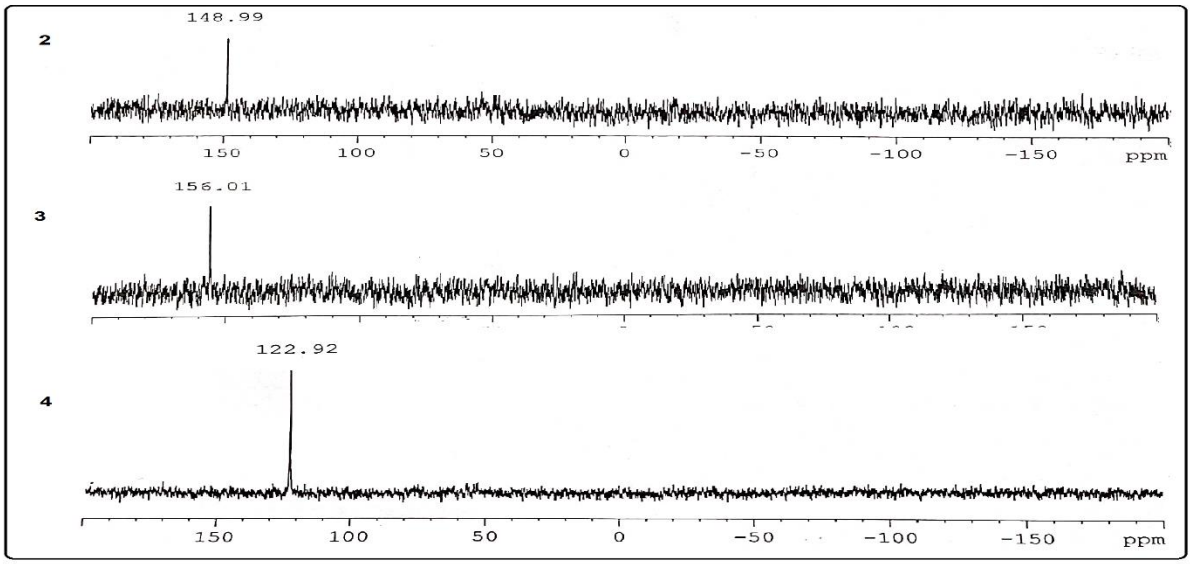
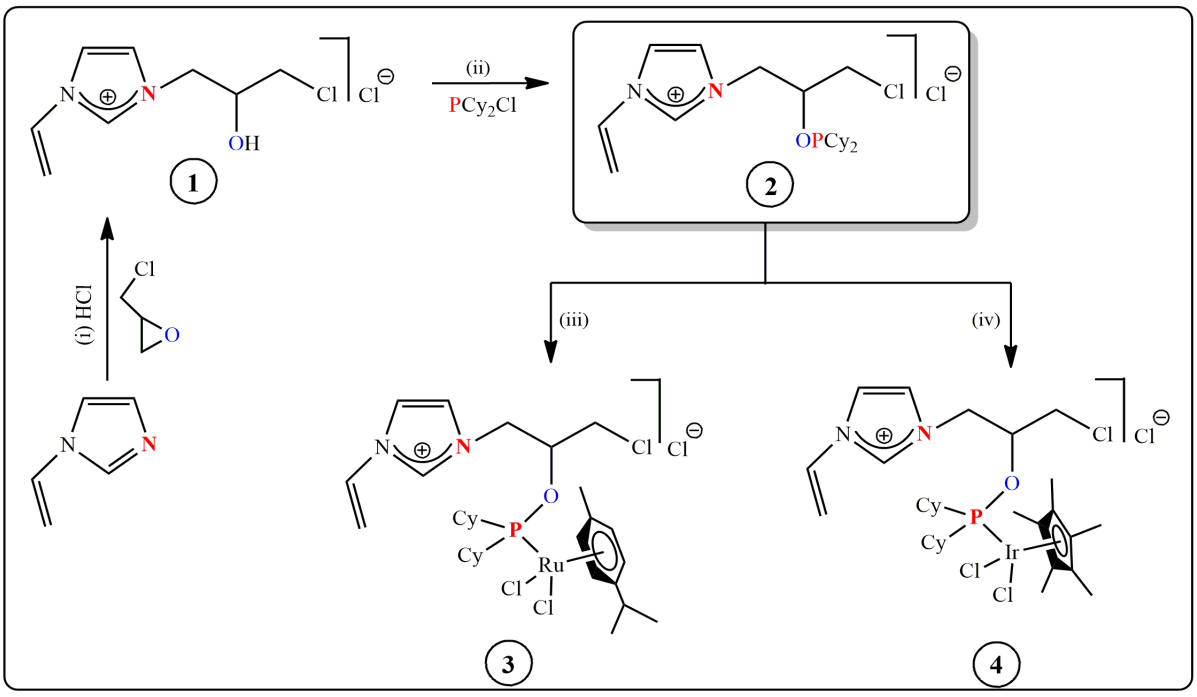


Figure 3. The ^{31}P-{^{1}H} NMR spectra of ligand (**2**) and its complexes (**3** and **4**),



Scheme 1. Synthesis of compounds **1-4**; (*i*) 1 equiv. (±)-Epicholorohydrin, 1 equiv. HCl, C_2H_5OH; (*ii*) 1 equiv. Cy_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. $[Ir(\eta^5\text{-}C_5Me_5)(\mu\text{-Cl})Cl]_2$, CH_2Cl_2.

The synthetic procedure to prepare the cyclohexyl-containing phosphinite ligand [17,42,43] is shown in Scheme 1. The reaction of the ionic liquid **1** with 1 equiv. of *n*-BuLi in CH_2Cl_2 at –78 °C for 1 h, and then the addition of 1 equiv. of $ClPCy_2$ produced phosphinite ligand 3-(3-chloro-2-((dicyclohexylphosphaneyl)oxy)propyl)-1-vinyl-1H-imidazol-3-ium chloride, **(2)**. The ^{31}P NMR characterization of the crude reaction presented a signal at δ 148.99 ppm (singlet) attributed to $–OPCy_2$.

Our result agrees with the values for previously reported phosphinites [44-47] (Fig. 1). Unfortunately, although ligand **2** was clearly present in the crude reaction mixture, it could not be isolated sufficiently pure for characterization studies. Because the phosphinite ligand decomposes gradually to give oxide ~ 44 ppm as singlet (-OP(O)Cy_2). Furthermore, doublet signals at about δ 57.7 ppm and at δ -20.1 ppm having $^1J_{(PP)}$: 285 Hz in the ^{31}P-{^{1}H} NMR spectrum support the occurrence of P(O)Cy_2PCy_2 [48] (Fig. 2).

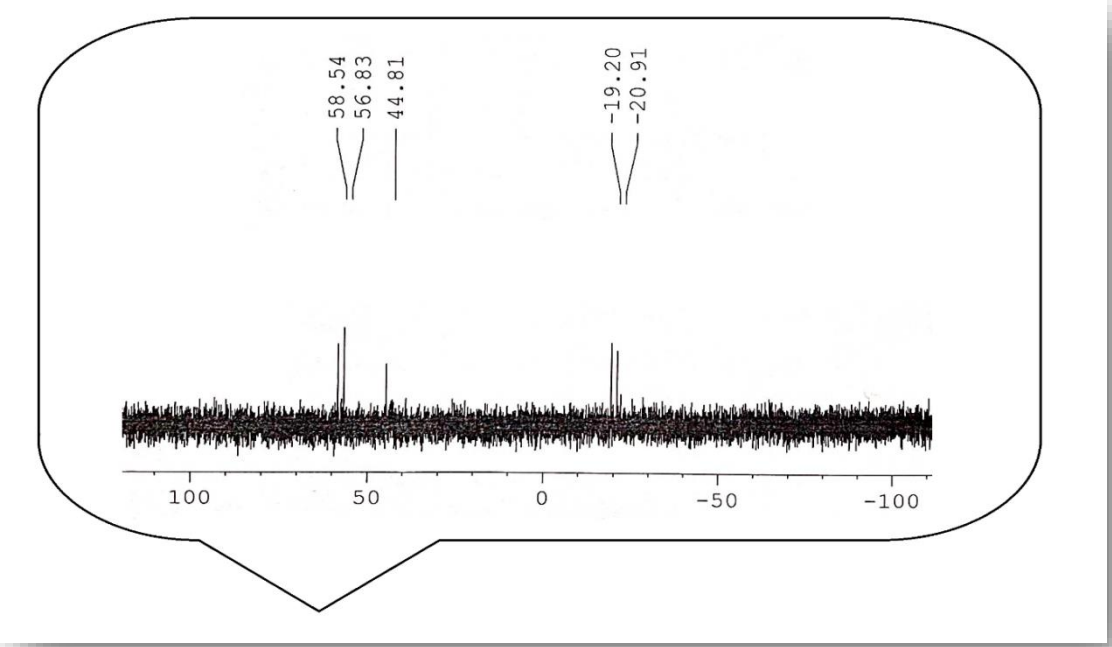


Figure 2. The ^{31}P-{^{1}H} NMR spectrum of decomposed products {(-OP(O)Cy_2) and P(O)Cy_2PCy_2}.

It is well-known that dimers {[Ru(arene)(μ-Cl)Cl]$_2$} are capable of forming mononuclear complexes possessing a general formula of [Ru(η^6-arene)Cl_2L] [49]. Therefore, Ru(II) and Ir(III) complexes were prepared through reactions of metal precursor ([Ru(η^6-*p*-cymene)(μ-Cl)Cl]$_2$ or Ir(η^5-C_5Me_5) (μ-Cl)Cl]$_2$) and phosphinite (**Scheme 1**). All the reactions proceeded very readily in CH_2Cl_2 at RT and were almost quantitative. In contrast to the free ligand, which is quite air-sensitive, the complexes are stable microcrystalline solids and can be kept in the open air for an extended amount of time. The complexes were fully characterized by several spectroscopic techniques such as ^{1}H NMR, ^{13}C NMR, IR, and elemental analysis. In the ^{31}P-{^{1}H} NMR spectrum, Ru(II) complex **(3)** exhibits a singlet downfield at δ 156.01 from the position of the free ligand (Fig. 1). Characteristic resonances of *p*-cymene protons for **3** were detected in the ^{1}H NMR spectrum at 5.82-5.79 ppm range as multiplets. For other characteristic signals of the *p*-cymene protons, the -CH, -CH_3, and -$CH(CH_3)_2$ resonances appeared at δ 2.84-2.81, 2.08, and 1.78 + 1.23-1.18 ppm, respectively. Furthermore, the -CH and CH_2 protons of Cy in the $OPCy_2$ group gave multiplets at 2.46 and 1.78 + 1.23-1.18 ppm, respectively. ^{13}C NMR spectrum of Ru (II) complex displays *p*-cymene signals, in addition to the resonances from the ligand. The IR spectrum of the Ru(II) complex **3** exhibits one new absorption peak at 553 cm^{-1} for Ru-P stretching vibration, indicating that phosphinite binds to the complex. So, we can conclude that our P-O donor ligand was bound to the Ru atom with a *p*-cymene group.

Simple coordination chemistry of (**2)** with $[Ir(\eta^5\text{-}C_5Me_5)(\mu\text{-}Cl)Cl]_2$ precursors was investigated as well. The ^{31}P NMR signal of the Ir(III) complex obtained from the interaction of the phosphinite and iridium precursor was observed at 122.92 ppm as a singlet. The existence of a single signal at 1.53 ppm in the ^{1}H NMR spectrum of the Ir(III) complex **(4)** indicates that Ir(III) complex is formed. In the ^{13}C NMR spectrum of the Ir(III) complex, the luminous signals at 44.28–43.73 and 28.76-25.54 ppm belong to the –CH and $-CH_2$ groups of the $-OP(C_6H_{11})$, respectively, and help illuminate the structure. In addition, the 9.45 and 93.92 ppm signals corresponded to the methyl and aromatic carbons of the Cp* coordinated complex **4**, respectively. Extra the aliphatic and *N*-vinylimidazole ring carbon signals of complex **4** appeared, as expected. The infrared spectrum of **(4)** exhibits the bands at 3097, 2922, 2847, 1446, and 1058 cm^{-1} are due to υ(aromatic C-H), υ(aliphatic C–H), υ(P-Cy), and υ(O-P), respectively. Additionally, elemental analysis results also support the proposed structures.

3.2. Transfer hydrogenation of ketones

The transition metal catalyzed-hydrogen transfer process is usually assumed to include metal hydrides as important intermediates. Both complexes **3** and **4** most probably follow a well-known mechanism that includes a metal-alkoxide intermediate and *β*-elimination [50,51]. It has been shown that the replacement of chlorides by a hydride is easy through an alkoxide displacement/*β*-hydride elimination sequence [52,53]. Ionic-liquid containing phosphinite ligands are indispensable compounds to obtain efficient catalysts that are homogeneous and organometallic [17-19]. The activity of the metal center is highly influenced by ligand choice. Ionic-liquid-based phosphinite complexes with coordination geometries of ruthenium or iridium show good activity in catalytic transfer hydrogenation [17-19,41].

The synthesized Ru(II) and Ir(III) complexes **(3)** and **(4)** were employed as catalysts in the TH of acetophenone and its derivatives. First, as mentioned above, we thought to explore the TH of acetophenone in the existence of iridium and ruthenium-based catalysts. Thus, acetophenone has been hydrogenated in the existence of a catalyst with KOH as a base in 2-propanol. The transfer hydrogenation results are given in Table 1. Isopropanol is used as a hydrogen source in the hydrogenation and in this circumstance, the process occurs under thermodynamic control: when isopropanol gives hydrogen, acetone forms, and this is able to behave as a hydrogen acceptor, so, equilibrium is generated. The boiling point of 2-propanol is 82 °C, which enables it a good option to carry out the process at reflux temperature too [54]. Table 1 (entry 2 and entry 6) obviously depicted that the process cannot happen when a base is not used. Thus, one can conclude that the use of a base is necessary for this reaction [54,30,32,44,55]. The amount of base is generally 5 equivalent with respect to the catalyst [56-58]. Thus, our complexes act as good catalysts in TH reaction of acetophenone when isopropanol is used as a hydrogen donor at 82 °C, in the existence of a base, and after a certain time (1/2 h and 2 h for **3-4,** respectively), (Table 1 entry 1, entry 5). It was found that Ru(II) complex, **3** exhibited better activity in the transfer hydrogen. Because, ruthenium has different oxidation states, and a variety of coordination geometries introduced by various ligands, which render it is a good candidate for the catalyst for transfer hydrogenation as well as for the asymmetric version of transfer hydrogenation [59]. Furthermore, an increase in the amount of substrate increases the reaction time and leads to a reduction in TOF (Table 1 entry 3-4, entry 7-8).

Table 1. Transfer hydrogenation of acetophenone with 2-propanol catalyzed by 3 and 4.

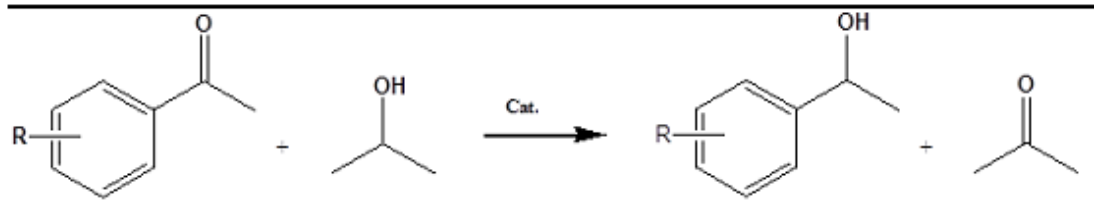
Entry	*Catalyst*	*S/C/KOH*	*Time*	*Conversion (%)[e]*	*TOF(h^{-1})[f]*
1	3 [a]	100:1:5	1/2 h	99	198
2	3 [b]	100:1	12 h	>5	>5
3	3 [c]	500:1:5	2 h	98	230
4	3 [d]	1000:1:5	9 h	97	108
5	4 [a]	100:1:5	2 h	98	49
6	4 [b]	100:1	12 h	>5	>5
7	4 [c]	500:1:5	8 h	99	62
8	4 [d]	1000:1:5	24 h	98	41

Reaction conditions:

[a] Refluxing in 2-propanol; acetophenone/Ru/KOH, (100:1:5); [b] Refluxing in 2-propanol; acetophenone/Ru, in the absence of base; [c] Refluxing in 2-propanol; acetophenone/Ru/KOH, (500:1:5); [d] Refluxing in 2-propanol; acetophenone/Ru/KOH, (1000:1:5); [e] Determined by GC (three independent catalytic experiments); [f] Referred at the reaction time indicated in column; TOF= (mol product/mol Ru(II)Cat.)x h^{-1}.

Under optimized conditions at hand, we investigated the extent of this TH reaction of acetophenone derivatives. It was observed that the corresponding alcohol is formed in a shorter time when using an acetophenone derivative that carries an electron-withdrawing moiety such as *p*-fluorine, *p*-chlorine, and *p*-bromine (Table 2, entry 1-3, entry 6-8). Because electron-withdrawing groups reduce the electron density of the C=O bond of the ketone, the ketone is more easily hydrogenated [60-62]. Secondly, TH of acetophenone derivatives containing *o*- and *p*-OCH_3 groups takes a longer reaction time and the TOF values are lower. Also, it was observed that when there is an electron-donating substituent on the *o*-position (-OCH_3), then, TOF value will be lower compared to the *p*-position. Indeed, the reaction time towards the transfer hydrogenation decreased from 9 h to 7 h when 4-MeO was used instead of 2-MeO catalyzed by **4** (Table 2, entry 9-10).

Table 2. Transfer hydrogenation results for substituted acetophenones with the catalyst systems, **3** and **4**[a].



Entry	R	Time	Conversion(%)[b]	TOF(h^{-1})[c]
***Catalyst*, 3**				
1	4-F	1/4 h	99	396
2	4-Cl	1/3 h	98	294
3	4-Br	1/2 h	99	198
4	2-MeO	3 h	94	31
5	4-MeO	2 h	98	49
***Catalyst*, 4**				
6	4-F	1 h	98	98
7	4-Cl	3/2 h	97	65
8	4-Br	2 h	99	50
9	2-MeO	9 h	93	10
10	4-MeO	7 h	95	14

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

4. Conclusions and Perspectives

In conclusion, a new series of phosphinite-based Ru(II) and Ir(III) complexes were synthesized using a precursor of ionic liquid. These complexes were found to be effective catalysts and they are able to be easily applied, resulting in secondary alcohols with good to high yields. Moreover, ruthenium complex (**3**) behaved as a better catalyst for the transfer hydrogenation than the analogous Ir(III) complex. These catalysts are attractive because of their modular design and versatility in terms of transfer hydrogenation and future reports will focus on the use of the complexes that we have synthesized in TH of other activated aryl/alkyl ketones.

Acknowledgment

The authors would like to thank Dicle University Research Fund (Project number: **FEN.20.001**) for its kind support.

The Declaration of Ethics Committee Approval

The author declares that this document does not require an ethics committee approval or any special permission. Our study does not cause any harm to the environment.

Declaration of Competing Interest

The authors declare no potential conflicts of interest related to the research, authorship, and publication of this article.

Authors' Contributions:

U. I: Conceptualization, Methodology, Writing - Original draft preparation (35 %)

N. M.: Conceptualization, Methodology, Resources, Investigation, Writing (30 %)

M. A: Conceptualization, Formal analysis, Writing - Original draft preparation (35 %)

All authors read and approved the final manuscript.

Compliance with research and publication ethics:

This study was performed by complying with research and ethics rules.

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