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Synthesis and catalytic applications of Ru and Ir complexes containing N,O-chelating ligand

Bilge Pakyapan[a], Serdar Batıkan Kavukcu[a], Zarife Sibel Şahin[b], Hayati Türkmen[a,*]

[a] University of Ege, Faculty of Science, Department of Chemistry, 35100 Izmir, Turkey
[b] University of Sinop, Scientific and Technological Research Application and Research Center, Sinop, Turkey

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ABSTRACT

A series of monometallic complexes (**Ru_{1-3}**, **Ir_{1-3}**) which have N,O-chelating ligand (pyrazine-2-carboxylate (**1**), pyridine-2-carboxylate (**2**), quinoline carboxylate(**3**) and bimetallic complexes (**$Ru_{4,5}$**, **$Ir_{4,5}$**) bridged by pyrazine-2,3- dicarboxylate (**4**) and imidazole-4,5-dicarboxylate(**5**) were synthesized and characterized by ^{1}H-, ^{13}C NMR, FT-IR, and elemental analysis. The crystal structure of **Ir_2** was determined by X-ray crystallography. The complexes (**Ru_{1-5}**, **Ir_{1-5}**) were applied to investigate the electronic and steric effect of ligand in their catalytic activities in transfer hydrogenation and alpha(α)-alkylation reaction of ketones with alcohols. The activities of iridium complexes (**Ir_{1-5}**) were much more efficient than ruthenium complexes (**Ru_{1-5}**). The highest activity for both reactions was observed for the complex (**Ir_2**) with pyridine-2-carboxylate. The Ir hydride species was monitored for both reactions.

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1. Introduction

Ruthenium and iridium complexes are one of the most productive areas among the transition metal chemistry as a catalyst [1]. The arene ligands such as *p*-cymene and pentamethylcyclopentadiene (Cp*) coordinate to the metal center very intense and their advantage is that the easy modification by adding or changing the substituents. Also, the other available coordination sites of these metals can be filled with donor atoms like N, O, S, P, C or as a chelating ligand with combinations of the two atoms [2]. Chelating ligands are commonly formed by linking donor groups via organic linkers. Thus, this property makes them highly versatile and very useful for the important catalytic transformations. The necessity of green processes in order to maintain a healthy nature is an impulse to the scientists. To achieve this aim, both iridium and ruthenium complexes have been successfully applied for catalytic hydrogen transfer and this success motived the researchers try these complexes on new catalytic transformations [3]. Especially, Ir(I) complexes have shown remarkable performance on the (α)-alkylation of ketones with alcohols yet the Ir(III) complexes are not very well-known [3]. Furthermore, high catalyst loading, expensive base usage and long reaction times still pose a problem for this transformation.

Alpha alkylated ketones are important concerns in organic synthesis as intermediates and also for their biological activity [4]. Because of the disadvantages of conventional methods such as low yields of product and toxic reagents usage leads the researchers to produce these products with greener methods. Alpha alkylation of ketones with alcohols is a very favorable process when it is compared to the common alkylation methods because of the fact that it has atom economy and water is formed as a only byproduct [5]. To solve the alkylation problems, hydrogen auto transfer or as known borrowing hydrogen process, which is the source of the atom efficiency, has been carried out. The mechanism commonly build upon three steps, (i) dehydrogenation, (ii) intermediate reaction, and (iii) hydrogenation [6]. These very well-known steps make this process more preferable when the synthesis, environment and economy parameters are considered.

Transfer hydrogenation (TH) is an essential alternative way to obtain a wide variety of pharmaceutically and industrially important chemicals because the usage of the pressurized hydrogen gas in direct hydrogenation puts this important transformation in a dangerous position. Thus, TH is a notably green method due to the properties which are high atom efficiency, simple mechanism, and low-cost hydrogen donors. Transition metal complexes, Ru [7], Ir [8] and Rh [9] in the first place, with ligand systems bearing donor atoms such as NN, NNN, CN, NO have successfully being applied in this transformation [10].

Many studies, such as characterization, catalytic or biological activity, have been made on nitrogen and the phenoxy oxygen

* Corresponding author.
E-mail address: hayati.turkmen@ege.edu.tr (H. Türkmen).

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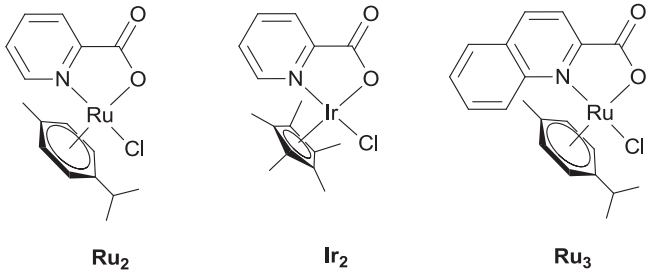


Fig. 1. Previously reported complexes [12–14].

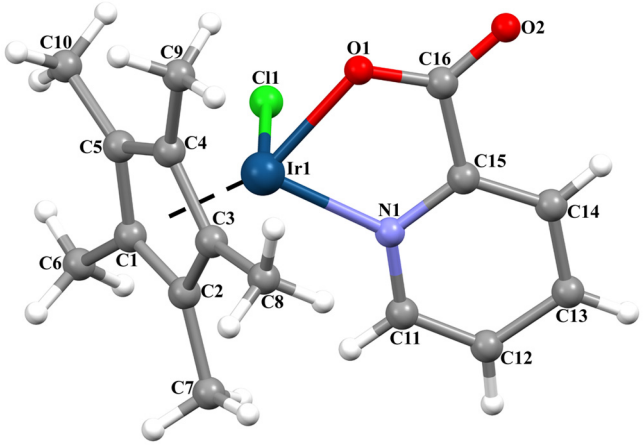
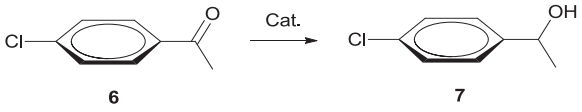


Fig. 2. Molecular structure of the complex **Ir$_2$**.

coordinated metal complexes [11] but nitrogen and carboxylate oxygen donor coordinated metal complexes are limited in the literature. Çetinkaya et al. have reported this type of Ru complexes (**Ru$_2$** and **Ru$_3$**) and investigated their catalytic activity on transfer hydrogenation reaction [12]. McGowan et al. examined cytotoxic activity of the **Ru$_2$** complex in various cancer cell lines [13]. Also, Schmidt et al. characterized **Ir$_2$** with the X-ray diffraction method (Fig. 1) [14]. We aimed to observe that the effect of the heterocyclic pyridine, pyrazine or imidazol carboxylate ligand on the catalytic reactions. For this purpose, we presented the synthesis and characterization of Ru(II) and Ir(III) arene complexes (arene = *p*-cymene, Cp*) bearing N,O-donor ligands. The activity of the complexes has been investigated in the transfer hydrogenation reaction and the alpha alkylation reactions of ketones with alcohols. The ketone product yield in the α-alkylation reaction was very promising with a low solvent volume and also low base – catalyst ratio in a short period of time in comparison with the literature [15]. The effect of the ligands such as additional benzene ring or nitrogen atom to these important transformations were also investigated.

2. Results and discussions

As shown in the Schemes 1 and 2, the complexes were synthesized by the reaction of the related ligand (**1**–**5**) and the $[RuCl_2(p\text{-cymene})]_2$ or $[IrCl_2Cp^*]_2$ in acetonitrile in the presence of a base (triethylamine or sodium bicarbonate) for 24 h at room temperature. The complexes were obtained in 81–94% yields and they were air- and moisture-stable yellow solids. The solubility of the monometallic complexes (**Ru$_{1-3}$** and **Ir$_{1-3}$**) was good in apolar and polar solvents. The bimetallic complexes (**Ru$_{4,5}$** and **Ir$_{4,5}$**) are poor soluble even in polar solvents because of this reason ^{1}H- and ^{13}C NMR studies could not be performed except the ^{1}H NMR of **Ru$_4$** and **Ir$_4$**. The characterization studies of the monometallic complexes (**Ru$_{1-3}$** and **Ir$_{1-3}$**) were made by ^{1}H- and ^{13}C NMR spectroscopy and elemental analysis. NMR chemical shifts were found to be in a good agreement with experimental values. In the ^{1}H NMR spectra, the *p*-cymene aromatic protons were detected as four doublets and the Cp* methyl protons were detected as



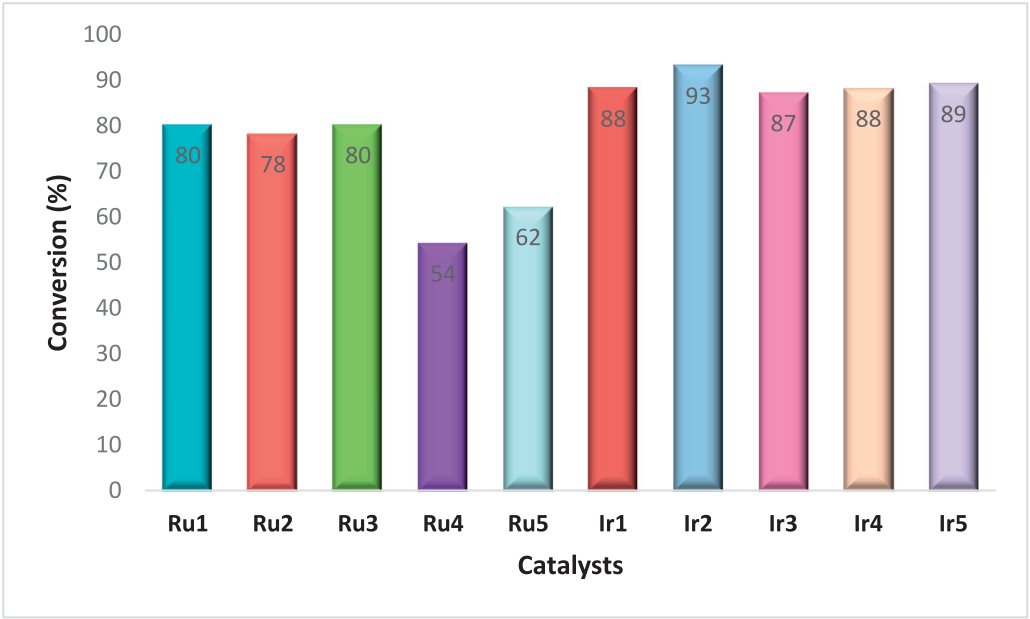


Fig. 3. The effects of different catalysts on the transfer hydrogenation of **6**.[a]
[a] Reaction conditions: **6** (1.00 mmol), KOH (1 mmol), Cat. (0.5%), IPA (1.00 mL), time (0.5 h), temperature (82 °C), under argon. Conversions were determined by using GC.

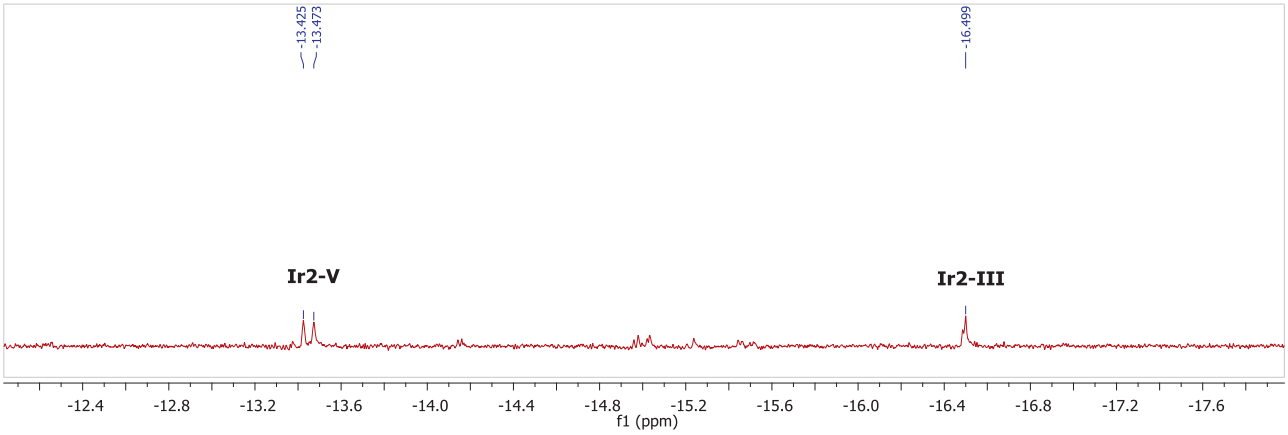
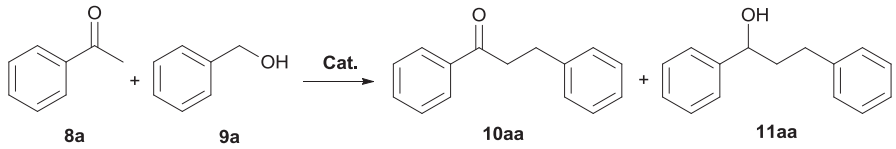


Fig. 4. The Ir-H species in the catalytic transfer hydrogenation reaction via ^{1}H NMR spectroscopy.



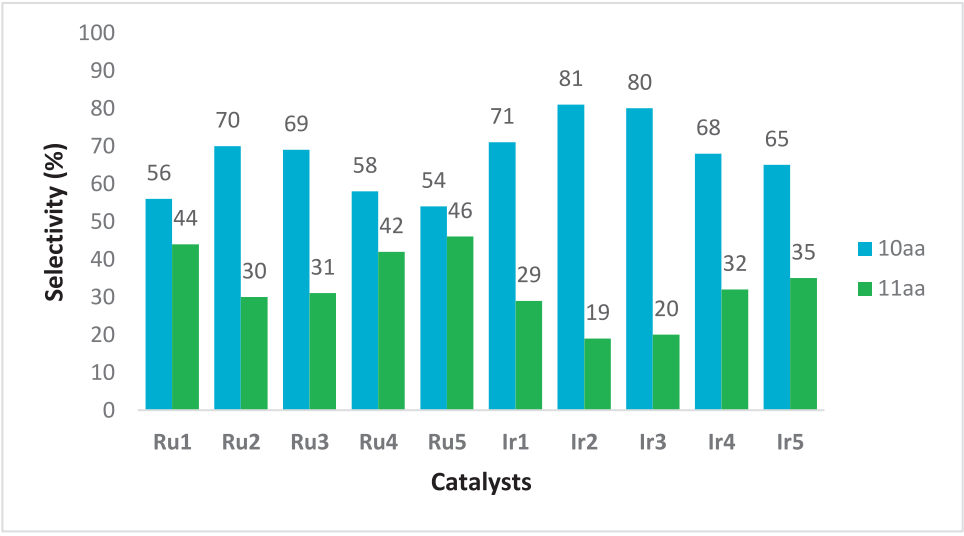


Fig. 5. The effects of different catalysts on the alpha alkylation of acetophenone with benzyl alcohol.
[a] Reaction conditions: Acetophenone (1.00 mmol), Benzyl Alcohol (1.00 mmol), KOH (0.20 mmol), Cat. (0.20 mol%), toluene (1.00 mL), time (2 h), temperature (120 °C), under air, analyzed by NMR.

Table 1
FTIR frequencies of the complexes.

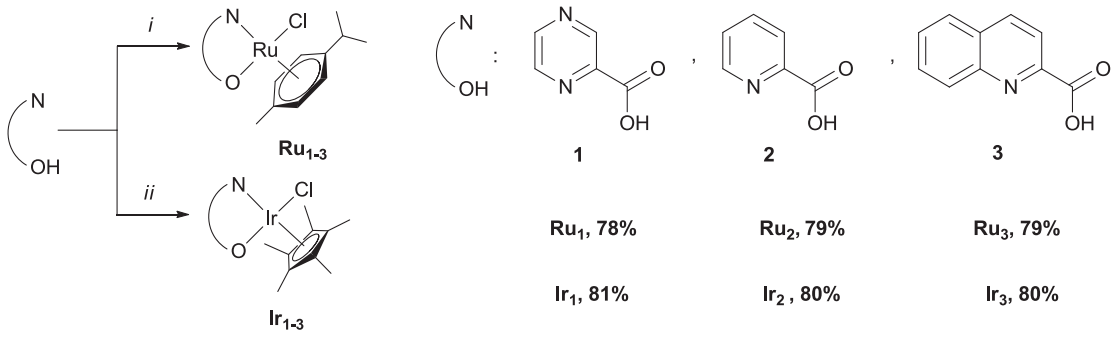
Complex	$\nu_{C=O}$	$\nu_{C\text{-}H(Aromatic,\ Aliphatic)}$	$\nu_{C=C(Aromatic)}$
Ru_1	1666	3037;2868,2931	1586
Ru_2	1652	3058;2876,2929	1567
Ru_3	1656	3037;2923	1597
Ru_4	1656	3037; 2971	1597
Ir_1	1662	3059;2983	1583
Ir_2	1653	3054;2910	1563
Ir_3	1661	3051;2922	1593
Ir_4	1661	3051;2988	1595

a singlet. The complexes exhibit piano-stool geometry. The IR spectrums of complexes (**Ru_{1-5}** and **Ir_{1-5}**) showed a band, approximately 2900–3100 cm^{-1} region, which was correspond to $\nu_{C\text{-}H}$ vibrations (Table 1). Successively, the peaks observed at region of 2800 cm^{-1} and 3100 cm^{-1} correspond to aromatic and aliphatic C-H stretching. Furthermore, the vibrations appearing in the range of 1650 and 1670 cm^{-1} were associated with the aromatic C=O peaks. Also, the vibrations appearing around 1600 cm^{-1} were link to the aromatic C=C peaks. Single crystals of **Ir_2** were obtained by the diffusion of pentane into saturated chloroform solution of the complex.

The molecular structure of complex **Ir_2** with the atom numbering is shown in Fig. 2. The asymmetric unit of complex **Ir_2** contains Ir(III) ion, pentamethylcyclopentadiene, pyridine-2-carboxylate, and coordinated chlorine anion. The bond distances of Ir-N, Ir-O and Ir-Cl are 2.104(12) Å, 2.108(10) Å, 2.398(4) Å, respectively.

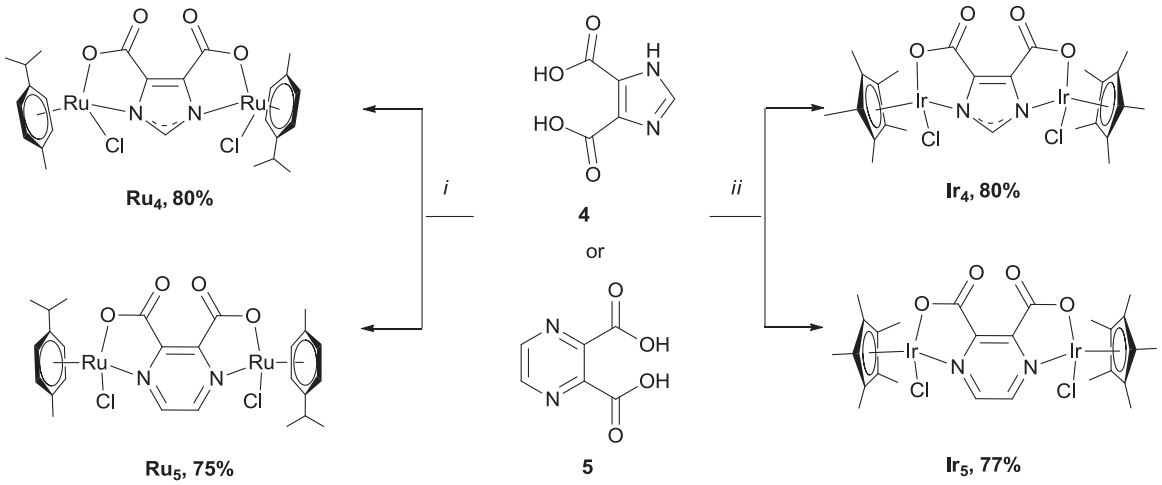
2.1. Transfer hydrogenation (TH)

To explore the effect of the catalysts (**Ru_{1-5}** and **Ir_{1-5}**) on the transfer hydrogenation of ketones, the 4′Cl-acetophenone (**6**) was chosen as a model substrate to evaluate the influence of mono-



Reaction conditions: **1, 2** or **3** (1 equiv.), triethylamine (1 equiv.), (*i*) $[RuCl_2(p\text{-cymene})]_2$ or (*ii*) $[IrCl_2(Cp^*)]_2$ (0.5 equiv.), MeCN, RT, overnight.

Scheme 1. Synthesis of the monometallic complexes.



Reaction conditions: **4** or **5** (1 equiv.), sodium bicarbonate (2 equiv.), (*i*) $[RuCl_2(p\text{-cymene})]_2$ or (*ii*) $[IrCl_2(Cp^*)]_2$ (1 equiv.), MeCN, RT, overnight.

Scheme 2. Synthesis of the bimetallic complexes.

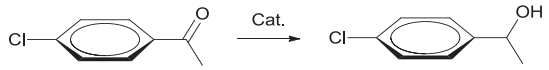
and bi-metallic complexes. The reaction was carried out in IPA at 82 °C (bath temp.) for 0.5 h using KOH as the base under argon atmosphere to find the most active catalyst. Monometallic complex $\mathbf{Ir_2}$ was determined as the most active catalyst among all complexes (Fig. 3). The amount of metal complexes was an important parameter to perform the catalytic reaction which carried out with 0.5 mol% monometallic complex, 0.25 mol% bimetallic complex. Also, in metal species, the catalytic activity of iridium complexes was better than those with ruthenium ones. The dehalogenation reaction did not take place under these conditions. The changes in the aromatic ring of chelating ligand did not have a significant effect on the catalytic yield.

The IPA was the best hydrogen donor among other alcohol derivatives (Table 2, entry 1) and the reaction was not achieved in H_2O. The KOH was the best base for the TH [16]. The reaction did not occur well in lower temperatures than 82 °C such as 60 °C and 25 °C (Table 2, entries 12,13). The conversion of 4′Cl-acetophenone to the desired product decreased on lowering the amount of base (Table 2, entry 10) In the absence of either $\mathbf{Ir_2}$ or base, no conversion was observed (Table 1, entry 14–15).

In addition, a mercury poisoning experiment was performed for the complex ($\mathbf{Ir_2}$) to determine whether the reaction was homogeneous or heterogeneous. The yield was significantly reduced as the activities for $\mathbf{Ir_2}$ dropped from 93% to 62% for TH (Table 2, 16). This experiment showed that the reaction was homogenously catalyzed.

The effect of different electron-withdrawing or -donating groups on acetophenone was analyzed, after the optimum conditions were decided and the most active catalyst was chosen. The results are summarized in Table 3. The presence of electron-withdrawing groups like chlorine (**7a**) and bromine (**7b**) on the aromatic ring of acetophenone gave the corresponding products with a yield of 93 and 87%, respectively. The electron-rich groups such as methoxy (**7c**) provided the desired products with a >99% yield. When ethyl (**7f**) was used for R_2 substituent the conversion was nearly the same. The yield for heptane-2-one (**7i**), an aliphatic ketone, was found to be 98%. Additional ring on the aromatic ring of acetophenone (**7d**) gave also a good result. The different ketone analogs like benzophenone (**7e**) and caprolactone (**7 g**) resulted in the corresponding products with the yields of 83 and 97%, respectively.

Table 2
The effects of solvent, base and catalyst on the transfer hydrogenation of **6**.[a].



6 **7**

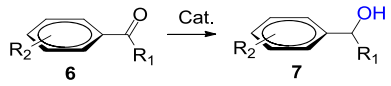
Entry	Solvent	Base	Cat.(% mol) /Base (mmol)	Conversion (%)
1	IPA	KOH	1.0/1.0	>99
2	H_2O	HCOOH/NaOOCH	1.0/1.0	Trace
3	MeOH	KOH	1.0/1.0	16
4	Ethane-1,2-diol	KOH	1.0/1.0	9
5	IPA	NaOH	1.0/1.0	72
6	IPA	K_2CO_3	1.0/1.0	52
7	IPA	Cs_2CO_3	1.0/1.0	37
8	IPA	KOH	0.5/1.0	93
9	IPA	KOH	0.5/0.5	62
10	IPA	KOH	1.0/0.5	97
11	IPA	KOH	0.1/1.0	77
12[b]	IPA	KOH	1.0/1.0	68
13[c]	IPA	KOH	1.0/1.0	24
14	IPA	-	1.0/-	-
15	IPA	KOH	-/1.0	12
16[d]	IPA	KOH	1.0/1.0	62

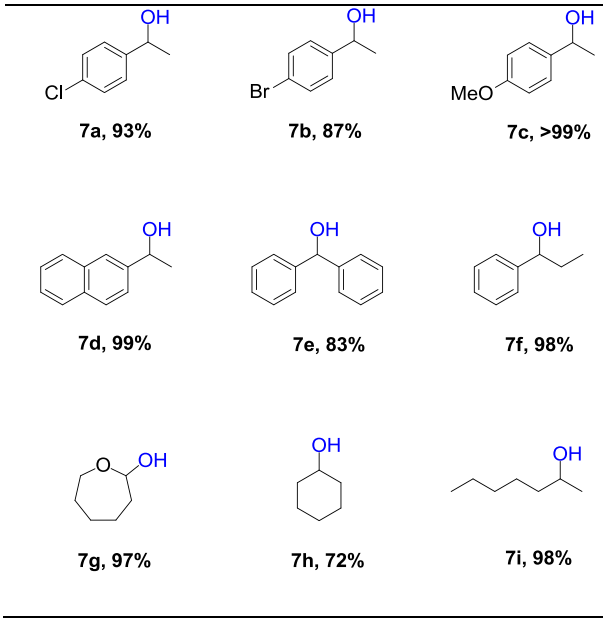
[a] **Reaction conditions: 6** (1.00 mmol), base, cat. **Ir_2**, IPA (1.00 mL), time (0.5 h), temperature (82 °C), under argon. Yield was determined by using GC. [b]T= 60 °C. [c]T= 25 °C.[d] Hg drop was added to the reaction medium.

The mechanism of catalytic transfer hydrogenation reaction of ketones to alcohols with catalyst **Ir_2** including N,O ligand system is summarized in Scheme 3. The mechanism begins with the removal of the halogen from the metal center with the aid of potassium hydroxide and a vacant coordination site is created (**Ir_2-I**). Isopropoxide coordinates to the iridium metal thanks to this vacant coordination site (**Ir_2-II**). At this step, there is a possibility that **IIa** and **IIb** types may occur in low concentrations. After removal of isopropoxide as acetone from **Ir_2-II**, the iridium monohydride species **Ir_2-III** is formed**.** The iridium dihydride species (**Ir_2-V**) is formed due to the second coordination of isopropoxide to **Ir_2-III** and subsequent separation of acetone (**Ir_2-IV**). The dihydride **Ir_2-V** is the active species. Iridium provides the transfer of hydrogen atoms to ketone to form **Ir_2-VI**. The cycle is followed by the release of alcohol and coordination of a new isopropoxide to form intermediate **Ir_2-II** [17,22].

Formation of the Ir-H species was monitored in the transfer hydrogenation reaction of acetophenone to 1-penyletanol via ^{1}H NMR

Table 3
Transfer hydrogenation of different substrates.





[a]**Reaction conditions: 6** (1.00 mmol), KOH (1.00 mmol), **Ir$_2$** (0.5 mol%), 2-propanol (1.00 mL), 0.5 h, 82 °C. Yields were determined by GC.

Table 4
Base/Catalyst Ratio.[a]

Entry	Base(mmol)/ Cat. (%)	Yield% (10aa/11aa)
1	0.2/1	98/2
2	0.2/0.5	91/9
3	0.2/0.2	81/19
4	0.2/0.1	69/31
5	0.1/0.1	74/16
6[b]	0.2/0.2	69/31

[a] Reaction conditions: Acetophenone (1.00 mmol), Benzyl Alcohol (1.00 mmol), KOH, **Ir$_2$**, toluene (1.00 mL), time (2 h), temperature (120 °C), under air, analyzed by NMR. [b]Under argon atmosphere.

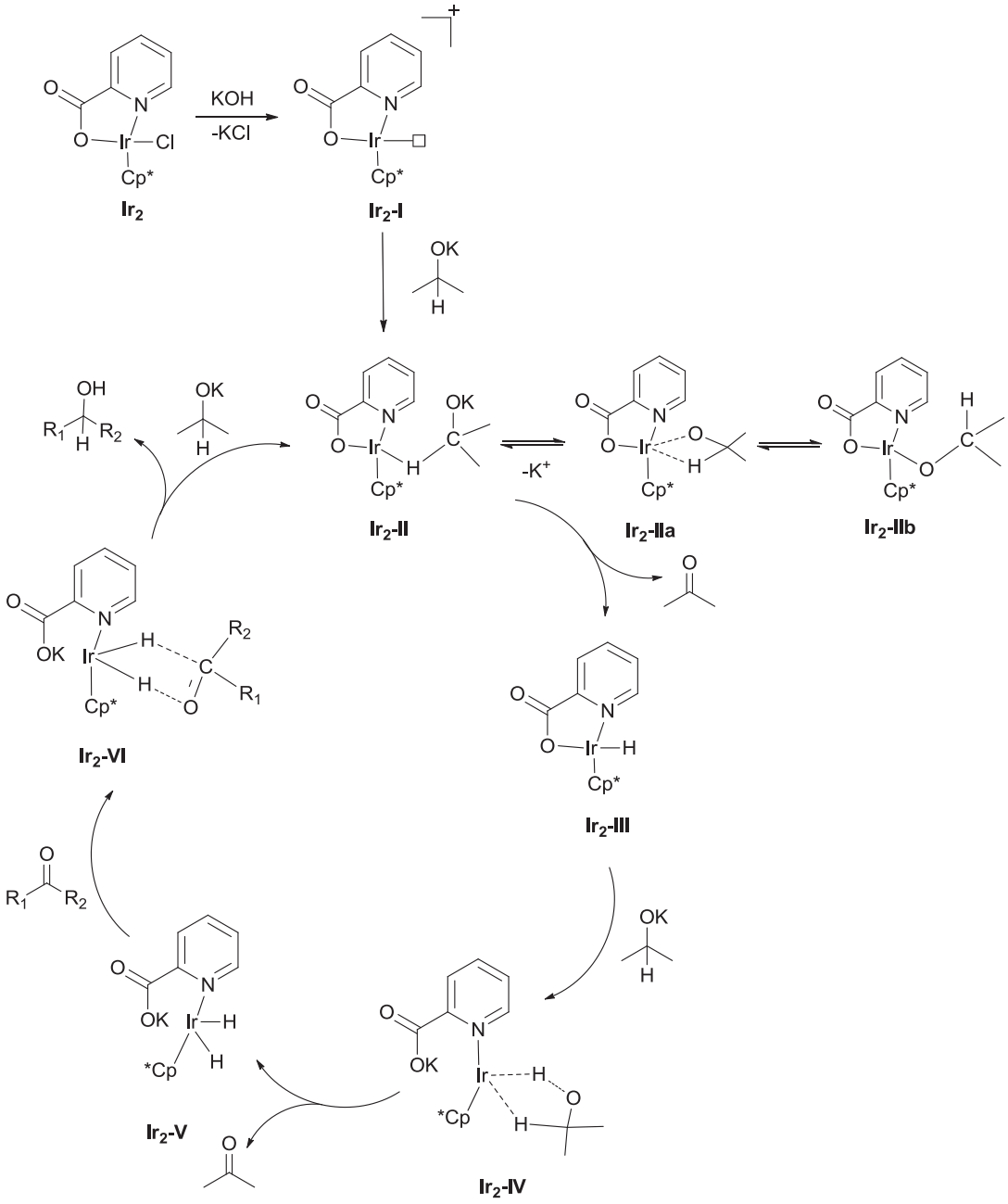
spectroscopy. The reaction was carried out in CD_3OD, 0.1 mmol 4′-chloroacetophenone, one drop IPA, 0.05 mol KOH and 2 mmol% **Ir$_2$**. The mixture was refluxed in 5 min and then analyzed with ^{1}H NMR spectroscopy. We observed one doublet at -13.4 ppm which is **Ir$_2$-V** dihyride species (J = 19.2 Hz) and one singlet at -16.5 ppm which is **Ir$_2$-III** hydride species (Fig. 4).

2.2. Alpha alkylation reaction of ketones with alcohols

The reaction between acetophenone (**8a**) and benzyl alcohol (**9a**) was used as a model reaction for investigation of alpha alkylation of ketones with alcohols (Fig. 5) [23]. Toluene was chosen as solvent according to the literature [15]. Base is also a very important factor on this reaction therefore, KOH was determined as base when we consider its strength, availability and price. In addition, different base and catalyst ratio trials were investigated. The best result was obtained with the 0.2 mmol base / 1% catalyst ratio (Table 4). However, the 0.2 mmol base / 0.2% catalyst also gave a satisfactory alpha alkylated ketone yield. For this reason, we decided to investigate different ketone substrates with this condition (Table 5). Moreover, when the amount of catalyst was reduced the conversion was also decreased. In consequence, we can say that the conversion in this reaction depends on the catalyst as well as the base amount. The product yields were good with both electron-withdrawing or electron-donating groups. When the reaction was carried out under argon atmosphere, the selectivity was changed (Table 4, entry 6). This is why the reaction was performed under air atmosphere because oxygen of the air makes easier the oxidation step of the **11aa** to **10aa**.

Li et al. reported that the Cp*Ir complex bearing a bipyridonate ligand as an active catalyst on the reaction of alpha alkylation of ketones with primary alcohols [18]. Their statement was the presence of the carbonyl group has a significant effect on the catalytic hydrogen transfer by making easier the formation of hydroxy iridium species. However, the procedure for the alpha alkylation reaction of ketones with alcohols has some disadvantages such as high catalyst loading (1 mol%), long reaction time (6 h) and usage of Cs_2CO_3 which is costly with reference to KOH. Our reaction conditions were milder when a comparison was made with the literature [18,23].

The encouraging results lead us to try different ketone and alcohol substrates as summarized in Tables 5 and 6 in determined conditions according to the optimization examinations. The effect of electron-donating or electron-withdrawing groups had been studied. The general yields for both substrate group were in between 72–95%. It was found that the different substitution patterns do not have a significant effect on the formation of desired products. The electron-withdrawing groups on the ketone substrate's para position caused relatively less yield (Table 5, 10ba) in comparison to its ortho position analogue (Table 5, 10ca). Substrates bearing electron-donating group such as methyl gave higher yields

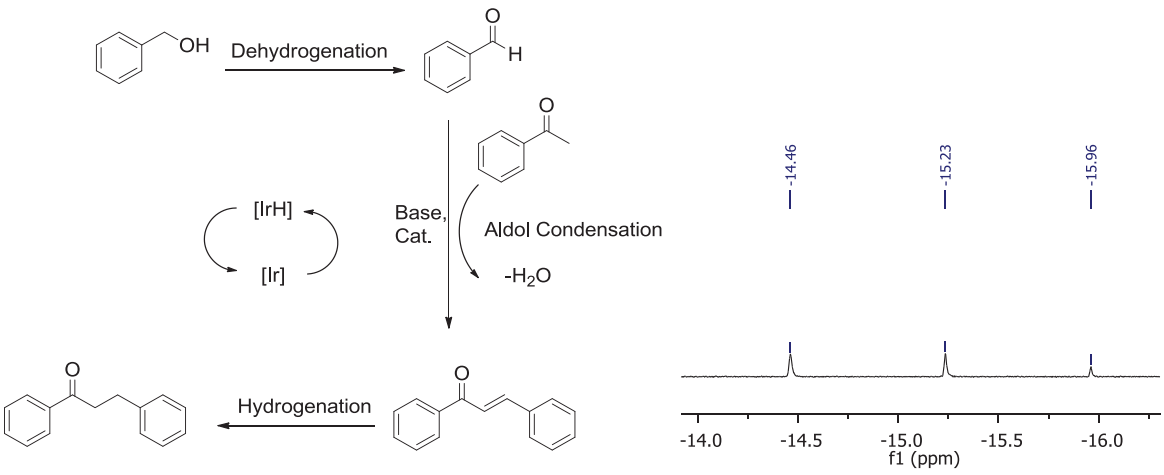


Scheme 3. Proposed mechanism for the catalytic transfer hydrogenation reaction.

(Table 5, 10fa). Cyclic and aliphatic ketone derivatives such as cyclohexanone and isobutyl methyl ketone also gave good results. In addition to the ketone substrate assay, selected alcohols were also allowed to react with acetophenone. Moderate to good yields were obtained for different substrates with electron-withdrawing or electron-donating groups. The substrates which bears electron-donating group such as methoxy gave good results (Table 6, 10ac) while aliphatic group such as heptanol gave the desired product in moderate yield (Table 6, 10ai).

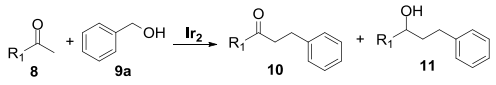
In our work Ru(II) and Ir(III) complexes were used for both transfer hydrogenation and alpha alkylation reactions. In the literature Çetinkaya et al. reported the highly active Ir(I) catalyst for the alpha alkylation of ketones with primary alcohols. The results of our study were also satisfying with relatively similar conditions in comparison with the mentioned study. Although the amount of catalyst is high in our work, the synthesis of the catalysts need less effort as we used cheap commercially available ligands and mild reaction conditions [21,23].

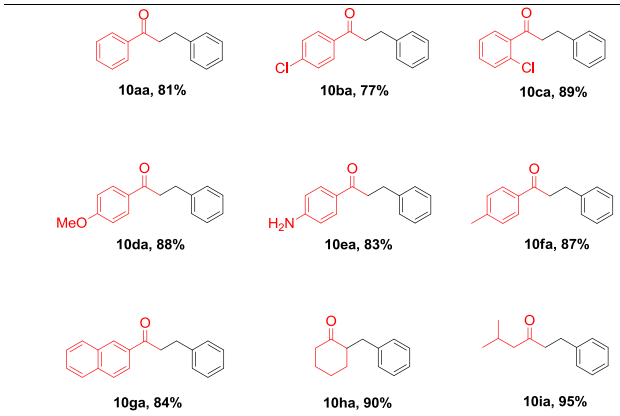
As known, the borrowing hydrogen mechanism constitute the basis of the alpha alkylation of ketones. The plausible mechanism starts with the decoordination of Cl with the help of basic media provided by KOH as a result $[IrCp^*_2]^+$ is produced. Dehydrogenation of benzyl alcohol produce the active hydrogen which is the foundation of the formation of Ir-H intermediate. Then, the aldol condensation between the benzaldehyde, which is given by the dehydrogenation of benzyl alcohol, and acetophenone is occured. Thereupon, rehydrogenation, using the hydrogen from the Ir-H species, generates the final alkylated ketone product. The reaction monitored by ^{1}H NMR and three singlets at -14.46, -15.23 and -15.96 ppm were observed in the hydridic region which reveals the occurrence of the iridium hydride species (Scheme 4) (The full spectrums are in SI).



Scheme 4. The reaction mechanism of the alpha alkylation of ketones (left) and Ir-H formation in ^{1}H NMR (right).

Table 5
Alpha alkylation of different ketones with benzyl alcohol.





[a] Reaction conditions: Ketones (**8**) (1.00 mmol), **9a** (1.00 mmol), KOH (0.20 mmol), Cat. **Ir$_2$** (0.2 mol%), toluene (1.00 mL), time (2 h), temperature (120 °C), under air, analyzed by NMR.

3. Conclusions

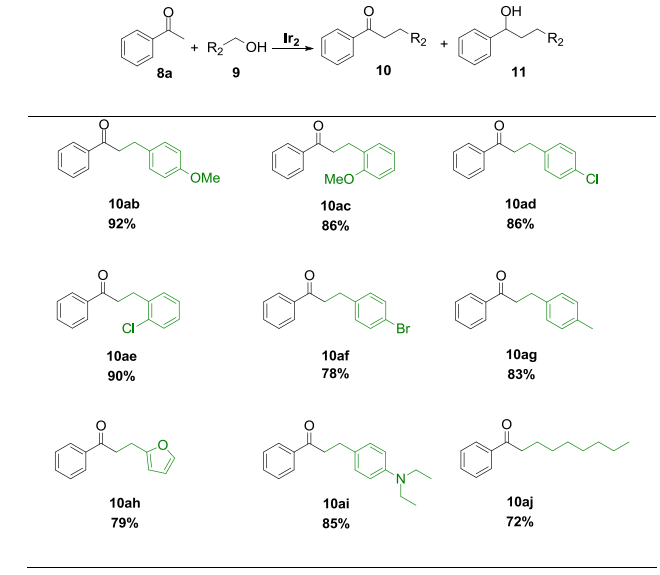
Ru(II) and Ir(III) complexes (**M$_{1-5}$**) bearing N,O - donor ligands were synthesized. The catalytic properties of the complexes were investigated in the TH of ketones and α-alkylation reaction of ketones with alcohols. The activity of synthesized bimetallic complexes was lower than the monometallic complexes in the transfer hydrogenation and α-alkylation of ketones with alcohols. Complex **Ir$_2$** has been found that the most active complex among the synthesized complexes for both transfer hydrogenation and α-alkylation reaction. The Ir(III) complexes gave higher yields in a shorter time than the Ru(II) complexes in the transfer hydrogenation and α-alkylation reaction. The ketone product yield was affected by the catalyst amount in the α-alkylation reaction. Also, the ketone product yield decreased when the amount of catalyst was reduced. The differences in the ligands such as additional benzene ring or nitrogen atom did not affect the catalytic activity prominently.

4. Experimental section

4.1. General information

All experimental manipulations of complexes were carried out under inert atmosphere using standard Schlenk line techniques unless otherwise stated. The glass equipment was heated under vacuum in order to remove oxygen and moisture and then they were filled with argon. The other reagents were used as received from suppliers without further purification. $[RuCl_2(p\text{-cymene})]_2$ was prepared according to the method reported by Bennett and Smith through the reaction of ruthenium (III) chloride with α–terpinene [19]. Catalytic reactions for α-alkylation were carried out under air and catalytic reactions for transfer hydrogention were carried out under argon gas on Carousel 12 Plus Reaction Station system. ^{1}H and ^{13}C NMR spectra of compounds were recorded by Varian 400 and 600 MHz spectrometers and chemical shifts were recorded in ppm. J values were given in Hz. NMR chemical shifts were referenced to the solvent signal in $CDCl_3$. The reactions

Table 6
Alpha alkylation of different alcohols with acetophenone.



[a] Reaction conditions: **8a** (1.00 mmol), alcohols (**9**) (1.00 mmol), KOH (0.20 mmol), Cat. **Ir$_2$** (0.20 mol%), toluene (1.00 mL), time (2 h), temperature (120 °C), under air, analyzed by NMR.

of alpha alkylation of ketones with alcohols were also monitored by Nuclear Magnetic Resonance (NMR). Reagents were purchased from Aldrich or Merck. Melting points measured on Gallenkamp electrothermal melting point apparatus without correction. FT-IR spectra were recorded on Perkin Elmer Spectrum 100 series.

4.2. Synthesis and characterization of compounds

Monometallic complexes **M$_{1-3}$** were prepared from [Ru(*p*-cymene)Cl$_2$]$_2$ or [IrCl$_2$Cp*]$_2$ with pyrazine-2-carboxylic acid(**1**), pyridine-2-carboxylic acid (**2**), quinoline carboxylic acid(**3**). Acetonitrile (10 mL) was used as solvent and reactions were performed in the presence of NEt$_3$ for 24 h at room temperature. The yellow solid was filtrated and washed with diethyl ether (20 mL). The product was dried under vacuum. The reaction of [RuCl$_2$(*p*-cymene)]$_2$ and [IrCl$_2$Cp*]$_2$ with imidazole-4,5-dicarboxylic acid gave the bimetallic complexes (**Ru$_4$** and **Ir$_4$**) respectively. The complexes (**Ru$_5$, Ir$_5$**) were synthesized according to literature [20].

Complex **Ru$_1$**: This compound has been synthesized from [RuCl$_2$(*p*-cymene)]$_2$ (0.153 g, 0.25 mmol) and **1** (0.50 mmol) ligand in acetonitrile in the presence of triethylamine for 24 h at room temperature. The yellow solid has been obtained, washed with diethylether and dried under vacuum. Yield = 78%, 159 mg. m.p = 208 °C. IR (KBr pellet), υ_{max}/cm^{-1}: 1652 (C=O). ^{1}H NMR (400 MHz, CDCl$_3$): δ 9.03 (d, J = 4.4 Hz, 1 H, py-H), 7.96 (m, 1 H, py-H), 7.89 (t, J = 7.6 Hz, 1 H, py-H) 7.57 (m, 1 H, py-H), 5.62 (d, J = 6.4 Hz, 2 H, cym-Ar-H), 5.45 (dd, J = 5.6 Hz, 2 H, cym-Ar-H), 2.83 (m, 1 H, cym-CH), 2.25 (s, 3 H, cym-CH$_3$), 1.19 (d, J = 6.4 Hz, 6 H, cym-(CH$_3$)$_2$). ^{13}C NMR (100 MHz, CDCl$_3$): δ 170.9, 154.2, 150.9, 140.1, 128.5, 125.8, 101.4, 98.6, 82,9, 81.5, 80.5, 40.3, 39.6, 30.9, 22.3, 18.0. Anal. Calcd for C$_{17}$H$_{21}$ClNO$_2$Ru (M: 408,03): C, 49.92; H, 5.09; N, 3.34%; Found: C, 50.06; H, 5.19; N, 3.43%.

Complex **Ru$_2$**: The compound **Ru$_2$** was prepared in the same manner as **Ru$_1$** using **2** as ligand. Yield = 79%, 160 mg. m.p = 195 °C . IR (KBr pellet), υ_{max}/cm^{-1}: 1666 (C=O). ^{1}H NMR (400 MHz, CDCl$_3$): δ 9.04 (s, 1 H, pz-H), 8.96 (d, J = 1.6 Hz, 1 H, pz-H), 8.75 (d, J = 2.4 Hz, 1 H, pz-H), 5.61 (d, J = 5.6 Hz, 2 H, cym-Ar-H), 5.44 (dd, J = 5.6 Hz, 1 H, cym-Ar-H), 2.79 (m, 1 H cym-CH), 2.20 (s, 3 H, cym-CH$_3$), 1.17 (d, J = 6.4 Hz, 6 H, cym-(CH$_3$)$_2$). ^{13}C NMR (100 MHz, DMSO – d$_6$) δ 170.9, 154.2, 150.9, 140.0, 128.5, 125.8, 101.4, 98.6, 83.0, 82.8, 81.5, 80.5, 45.9, 40.4, 40.2, 40.0, 39.8, 39.6, 39.4, 30.9, 22.3, 22.2, 18.6, 8.9. Anal. Calcd for C$_{16}$H$_{20}$ClN$_2$O$_2$Ru (M: 408,87): C, 46.91; H, 4.84; N, 6.75%; Found: C, 47.00; H, 4.93; N, 6.85%.

Complex **Ru$_3$**: The compound **Ru$_3$** was prepared in the same manner as **Ru$_1$** using **3** as ligand. Yield = 79%, 187 mg. IR (KBr pellet), υ_{max}/cm^{-1}: 1656 (C=O). ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.69 (d, J = 8.8 Hz, 1 H, Ar-H), 8.37 (d, J = 8.8 Hz, 1 H, Ar-H), 8.16 (d, J = 8.4 Hz, 1 H, Ar-H), 7.94 (m, 1 H, Ar-H), 7.76 (t, J = 6.8 Hz, 1 H, Ar-H), 5.74 (d, J = 6 Hz, 1 H, cym-Ar-H), 5.56 (dd, J = 6, 2 H, cym-Ar-H), 5.43 (d, J = 6 Hz, 1 H, cym-Ar-H), 2.63 (m, 1 H, cym-CH), 2.27 (s, 3 H, cym-CH$_3$), 1.12 (d, J = 7.2 Hz, 3 H, cym-CH$_3$) 1.02 (d, J = 6.8 Hz, 3 H, cym-CH$_3$). ^{13}C NMR (100 MHz, CDCl$_3$): δ 178.1, 171.1, 147.5, 139.8, 131.5, 130.7, 129.1, 128.9, 128.9, 122.6, 103.3, 100.1, 86.1, 86.1, 84.9, 81.1, 80.8, 80.7, 51.2, 46.2, 46.2, 45.8, 30.9, 22.5, 21.8, 21.7, 18.7, 13.1, 8.6, 7.0, 6.9. Anal. Calcd for C$_{22}$H$_{27}$ClNO$_2$Ru (M: 474,08): C, 55.65; H, 5.64; N, 2.88%; Found: C, 55.75; H, 5.74; N, 2.96%.

Complex **Ru$_4$**: This compound has been synthesized by the reaction of [RuCl$_2$(*p*-cymene)]$_2$ and ligand (**4**) in acetonitrile in the presence of NaHCO$_3$ for 24 h at room temperature. The yellow solid has been obtained, washed with diethylether (20 mL) and dried under vacuum. Yield = 80%, 145 mg. ^{1}H NMR (400 MHz, DMSO–d_6): δ 8.42 (s, 1 H, Im-H), 5.65 (m, 2 H, cym-Ar-H), 5.50 (dd, J = 17.6, 5.9 Hz, 1 H, cym-Ar-H), 5.38 (dd, J = 16.4, 5.9 Hz, 1 H, cym-Ar-H), 2.66 (m, 1 H, cym-CH), 2.10 (dd, J = 14.0, 1.1 Hz, 3 H, cym-CH$_3$), 1.13 (m, 6 H, cym-(CH$_3$)$_2$). Anal. Calcd for C$_{27}$H$_{36}$Cl$_2$N$_2$O$_4$Ru$_2$ (M: 726,01): C, 44.56; H, 4.92; N, 3.76%; Found: C, 44.69; H, 5.00; N, 3.86%.

Complex **Ru$_5$**: This compound was synthesized according to the literature [20].

Complex **Ir$_1$**: This compound has been synthesized by the reaction of [IrCl$_2$Cp*]$_2$ and ligand (**1**) in acetonitrile in the presence of triethylamine for 24 h at room temperature. The yellow solid has

been obtained, washed with diethylether (20 mL) and dried under vacuum. Yield = 81%, 202 mg. IR (KBr pellet), υ_{max}/cm^{-1}: 1653 (C=O). ^1H NMR (400 MHz, $CDCl_3$): δ 8.56 (d, J = 4 Hz, 1 H, py-H), 8.15 (d, J = 8 Hz, 1 H, py-H), 7.95 (t, J = 8 Hz, 1 H, py-H), 7.56 (t, J = 8 Hz, 1 H, py-H), 1.72 (s, 15 H, Cp*-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.1, 149.1, 139.1, 128.4, 127.7, 85.4, 8.9. Anal. Calcd for $C_{17}H_{22}ClIrNO_2$ (M: 500,10): C, 40.73; H, 4.32; N, 2.71%; Found: C, 40.83; H, 4.43; N, 2.80%. Crystals were obtained by solvent diffusion method by diffusing pentane into a saturated chloroform solution of the complex.

Complex **Ir$_2$**: The compound **Ir$_2$** was prepared in the same manner as **Ir$_1$** using **2** as ligand. Yield = 80%, 200 mg. IR (KBr pellet), υ_{max}/cm^{-1}: 1662 (C=O). ^1H NMR (400 MHz, $CDCl_3$): δ 9.29 (s, 1 H, pz-H), 8.84 (d, J = 4 Hz, 1 H, pz-H), 8.53 (dd, J = 4 Hz, 1 H, pz-H), 1.72 (s, 15 H, Cp*-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.1, 149.1, 139.1, 128.4, 127.7, 85.4, 77.3, 77.2, 76.9, 76.7, 8.9. Anal. Calcd for $C_{16}H_{21}ClIrN_2O_2$ (M: 501,09): C, 38.26; H, 4.11; N, 5.48%; Found: C, 38.36; H, 4.22; N, 5.59%.

Complex **Ir$_3$**: The compound **Ir$_3$** was prepared in the same manner as **Ir$_1$** using **3** as ligand. Yield = 80%, 220 mg. IR (KBr pellet), υ_{max}/cm^{-1}: 1661 (C=O). ^1H NMR (400 MHz, $CDCl_3$): δ 8.47 (d, J = 8.0 Hz, 1 H, Ar-H), 8.38 (d, J = 8.0 Hz, 1 H, Ar-H), 8.22 (d, J = 8.0 Hz, 1 H, Ar-H), 7.96 (d, J = 8.0 Hz, 1 H, Ar-H), 7.88 (t, 1 H, Ar-H), 7.76 (m, 1 H, Ar-H), 1.65 (s, 15 H, Cp*-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.8, 157.1, 145.2, 142.5,139.1, 136.6, 134.7, 132.8, 125.5, 123.9, 121.0, 85.4, 77.3, 77.2, 77.0, 76.6, 8.9. Anal. Calcd for $C_{21}H_{24}ClIrNO_2$ (M: 550,11): C, 45.75; H, 4.31; N, 2.44%; Found: C, 45.85; H, 4.40; N, 2.55%.

Complex **Ir$_4$**: This compound has been synthesized by the reaction of $[IrCl_2Cp^*]_2$ and **4** ligand in acetonitrile in the presence of $NaHCO_3$ for 24 h at room temperature. The yellow solid has been obtained, washed with diethylether (20 mL) and dried under vacuum. Yield = 80%, 180 mg. ^1H NMR (400 MHz, DMSO-d_6): δ 7.72 (s, 1 H, Im-H), 1.61 (s, 30 H, Cp*-H). Anal. Calcd for $C_{27}H_{38}Cl_2Ir_2N_2O_4$ (M: 910,15): C, 35.55; H, 4.11; N, 2.92%; Found: C, 35.64; H, 4.21; N, 3.08%.

Complex **Ir$_5$**: This compound synthesized according to the literature [20].

4.3. General procedure for the transfer hydrogenation of ketones

The reaction was carried out in Radleys Carousel 12 Plus Reaction Station. Ketone (1 mmol), catalyst (0.005 mmol), KOH (1 mmol) and *i*PrOH (1 ml) were weighed into an oven-dried Radleys tube and stirred at 82 °C for 0.5 h under argon atmosphere. The reaction was cooled and diluted with EtOAc, and an aliquot was filtered through a pad of Celite and analyzed by both ^1H NMR and GC.

4.4. General procedure for the alpha alkylation of ketones with alcohols

The reaction was carried out in Radleys Carousel 12 Plus Reaction Station. The substrates (ketone (1.0 mmol)/alcohol (1.0 mmol)), catalyst (0.002 mmol), KOH (0.2 mmol), and 1,3,5-trimethoxybenzene (used as an internal standard) were combined in an oven-dried Radleys tube. Toluene (1.0 ml) was added to the tube, and the mixture was refluxed under air for 2 h at 120 °C. The reaction was cooled and diluted with EtOAc, and the reaction mixture was filtered through a pad of Celite. The filtrate was concentrated under reduced pressure, and the resulting residue was analyzed by ^1H NMR.

Supplementary Material: Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 1853459. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Declaration of Competing Interest

The authors declare no conflict of interest.

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Supplementary materials

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