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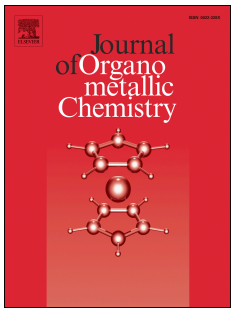

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Esin Ispir, Ertan Sahin, Mesut İkiz, Arif Aktas

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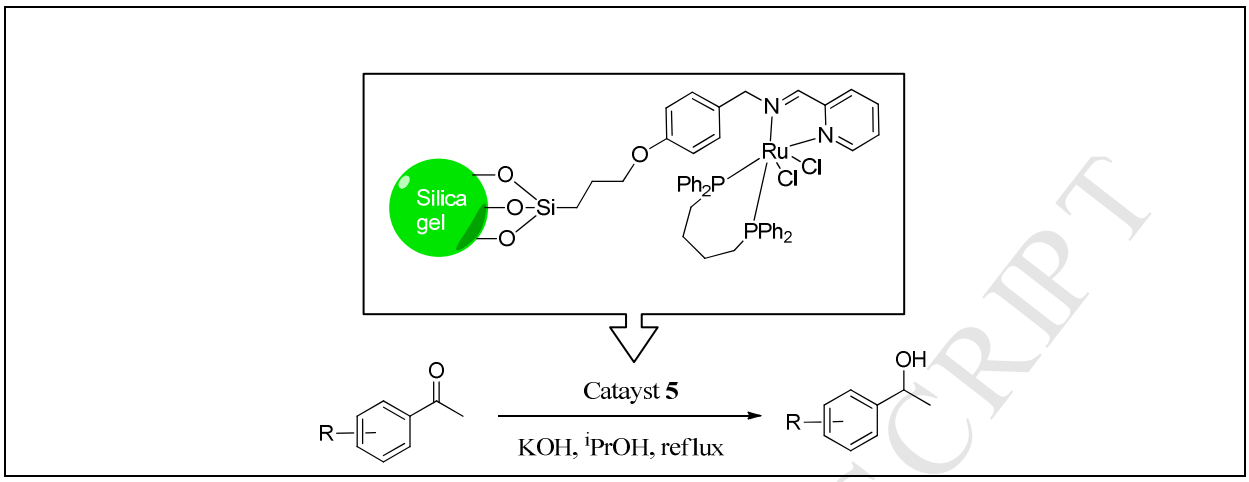


Comparative transfer hydrogenation performance of homogeneous and heterogeneous ruthenium (II) catalysts derived from a Schiff Base ligand

Esin Ispir*[a], Ertan Sahin[b], Mesut İkiz[a], Arif Aktas[a]

*E-mail: esinispir@ksu.edu.tr; Tel: 0090 3442801451

[a]*Department of Chemistry, Kahramanmaraş Sütçü Imam University, Kahramanmaraş, 46050–9, Turkey*

[b]*Department of Chemistry, Faculty of Science, Atatürk University, 25240, Erzurum, Turkey*

Abstract:

A new Schiff base ligand (E)-4-(((pyridin-2-ylmethylene)amino)methyl)phenol (L_1H) **1** was synthesized and grafted to solid support successfully. Mononuclear Ru(II) complex **2,** its solid supported analogue **4** and heterogeneous complex **5** were synthesized with $[RuCl_2(p\text{-cymene})]_2$ and $RuCl_2(PPh_3)$dppb.

According to the UV-visible, IR and NMR data, the Ru (II) complexes are formed by the coordination of both nitrogen atoms of the ligand. Molecular structures of the L_1H **1** was determined by single crystal X-ray diffraction study. The Ruthenium (II) complexes **2**, **4** and **5** were used as catalysts for the transfer hydrogenation of various ketones in 2-propanol. Following the comparison of complexes **2**, **4** and **5** between each other, it was observed that immobilized complexes have higher catalytic activity against the homogeneous structure. The results showed that the diphosphine incorporated complex **5** is more efficient than the other Ru (II) complexes.

Keywrds: Ru(II) complex, Schiff base, transfer hydrogenation, heterogeneous catalyst,

C*orresponding author*:

E-mail: esinispir@ksu.edu.tr. (E. İspir).

1. Introduction

The reduction of ketones and aldehydes to alcohols by a catalyst [1] and a stable hydrogen donor [2, 3] is called catalytic transfer hydrogenation and is an significant synthetic conversion both in academic and industrial applications [4]. The design the effective catalysts for transfer hydrogenation reactions have received considerable attention in the 1960s with Henbest, the first time, reported iridium catalyst gave moderate rates and turnovers for in transfer hydrogenation reactions [5]. Following that, $RuCl_2(PPh_3)_3$ was used as catalyst in the presence of trace amount of a base in hydrogen transfer reaction [6]. In the light of these studies, several various catalysts were designed with various metal ions such as Pd [7], Ru [1], Rh [8], Ir [9] and Os [10]. Among the transition metal ions, ruthenium is used in a wide range of applications such as transfer hydrogenation because of its characteristic features especially different oxidation states [11]. In addition to this, ligand design is another important factor and ligand structure has great electronic and steric and influence in the activity of catalyst. Within the pool of ligands, N containing molecules are drawing more attention in the area of organometallic catalysts due to its potential in the catalytic activity [12, 13].

Immobilization of a homogeneous catalyst to a solid material up ligand design has attracted much attention [14-16] due to their potential industrial applications. For this purpose, silica gel is the most used support material due to its excellent properties such as large pore size, low cost, high stability, thermal endurance and easy separation [17]. In addition to that, silica gel has an inert structure and does not solubilize in solvents; as a consequence, it can be used at harsh reaction medias such as high temperatures and pressures [18, 19]. Generally, organic ligand or metal complex is linked to silica *via* organosiloxane that was grafted on silica surface. Especially 3-cholorpropyl-triethoxysilane is used as linking agent for OH bearing ligands to graft them on the silica surface [20]. The pore size of the solid state support has been shown to affect the activity of some hydrogenation catalysts. On occasion heterogeneous catalysts have shown higher catalytic activity towards to the unimmobilized analogues [19].

In the literature, there are a great number of studies on ruthenium complexes as catalysts. Studies on ruthenium based catalysts have still taken considerable attention [3, 21].

In this study, we report the synthesis and catalytic application of homogeneous and heterogeneous ruthenium (II) complexes in transfer hydrogenation of various ketones. In order to compare the catalytic activity of homogeneous and heterogeneous analogues, first of

all we synthesized mononuclear Ru(II) complex **2** and its solid supported analogue **4** with $[RuCl_2(p\text{-cymene})]_2$. Silica supported Ru(II)-p-cymene complex **4** was found to be more effective than its non-silica supported Ru(II)-p-cymene complex **2**. Furthermore, diphosphine ligand was incorporated into silica supported Ru(II) complex **4** to obtain complex **5**. Catalytic activity results show that diphosphine incorporated complex **5** is the most effective catalyst in transfer hydrogenation reactions.

2. Experimental

2.1. Materials and methods

All chemicals were purchased from chemical suppliers and purified to match the reported physical and spectroscopic data. The solvents were carefully dried using standard methods. Kiesegel gel 60 (Merck 0.2–0.5 mm) was used as solid supporting material for immobilization of the homogeneous catalysts.

Infrared spectra were obtained using KBr discs (4000-400 cm^{-1}) on a Shimadzu 8300 FTIR spectrophotometer. Elemental analyses (C, H, N) were performed using a Carlo Erba 1106 elemental analyzer. The electronic spectra in the 200–900 nm range were obtained using DMF on a Hithachi U-3900 spectrophotometer. Melting points were determined with an Electrothermal 9200 apparatus. ^{1}H and ^{13}C NMR spectra were recorded on a Varian AS-400 MHz instrument. Magnetic measurements were carried out by the Gouy method using $Hg[Co(SCN)_4]$ as calibrant. Metal contents in heterogeneous complexes **4** and **5** were determined by Perkin Elmer Optima 2100 DV ICP-OES. The thermal behavior characteristic of the immobilized compounds **2**, **4**, and **5** were collected on a SII thermal analysis system under nitrogen atmosphere at a heating rate of 10 °C/min in the range 30–900 °C. The surface morphology of the silica-supported ligand **3** and complexes **4, 5** were analyzed using Jeol Neoscope Benchtop Scanning Electron Microscope and Zeiss Evo LS10 SEM attached with Bruker Quantax EDS. The catalytic conversions were determined by GC analysis with YL6500 Instrument.

2.2. X-ray Structure Determination

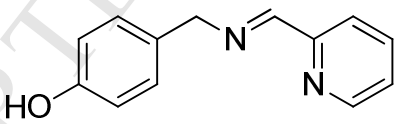
The data collections were performed on a Rigaku R-AXIS RAPID-S diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). Integration of the intensities,

correction for Lorentz and polarization effects and cell refinement was performed using Crystal Clear software [22].The structure was solved by direct methods and refined against F^2 by full-matrix least-squares calculations [23]. All non-H atoms have been refined anisotropically, whereas the H atoms have been treated with a riding model. *Crystal data for* **1**(L_1H): $C_{13}H_{12}N_2O$, crystal system, space group: monoclinic, $P2_1/c$; (no:14); unit cell dimensions: a = 8.620 (4), b = 14.637(7), c = 9.120(4) Å, α= 90, β = 94.058(3), γ = 90º; volume: 1147.80 (15) Å^3; Z = 4; calculated density: 1.23 g/cm^3; absorption coefficient: 0.080 mm^{-1}; F(000): 448; θ-range for data collection 3.4–29.6º; refinement method: full matrix least-square on F^2; data/parameters:2988/147; goodness-of-fit on F^2: 1.015; final R-indices [$I > 2\sigma(I)$]: R_1 = 0.043, wR_2 = 0.111; largest diff. peak and hole: 0.170 and -0.133 e Å^{-3}.

Crystallographic data were deposited in CSD with CCDC-1486601 registration number. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre (CCDC) via www.ccdc.cam.ac.uk/data_request/cif and are available free of charge upon request to CCDC, 12 Union Road, Cambridge, UK (fax: +441223 336033, e-mail: deposit@ccdc.cam.ac.uk).

2.3. General procedure for the synthesis of ligand and complexes

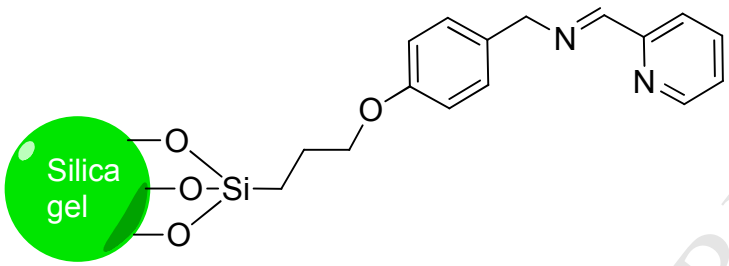
*2.3.1. Synthesis of (E)-4-(((pyridin-2-ylmethylene)amino)methyl)phenol **1** (L_1H)*



(E)-4-(((pyridin-2-ylmethylene)amino)methyl)phenol **1** (L_1H) (Fig. 1) was synthesized as follow; 10 mmol (1.23 g) 4-(aminomethyl)phenol and 10 mmol (1.07 g) of picolinaldehyde were condensed by refluxing in 70 ml of absolute ethanol for 3 h. The solution was left at room temperature. (E)-4-(((pyridin-2-ylmethylene)amino)methyl)phenol **1** was obtained as brown micro crystals; the micro crystals were filtered off, washed with 10 ml of absolute ethanol and then recrystallized from DMF. Mp: 130ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.02 (s, 1H), 8.64 (d, J = 64.7 Hz, 1H), 8.35 (s, 1H), 7.99 (s, 1H), 7.69 (s, 1H), 7.28 (s, 1H), 6.98 (s, 2H), 6.60 (s, 2H), 4.71 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.92, 155.84, 153.96, 148.89, 137.07, 129.84, 128.70, 125.00, 121.48, 115.58, 63.81. FT-IR (KBr, cm^{-1}): 3027,

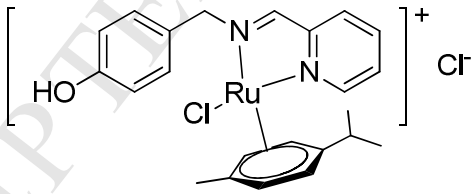
2876-2789, 1639. Anal. Cald. For: [$C_{13}H_{12}N_2O$], C: 73.56, H: 5.70, N: 13.20. Found: C: 73.29, H: 5.59, N: 13.01. UV-Vis. (λ_{max}, nm) in MetOH: 255, 273, 280, 391.

2.3.2. Synthesis of immobilized ligand L_2H ***3***



SiCPTMS (5 g) which was prepared according to the reported method [24] was immersed in 30 ml of dry toluene. *(E)-4-(((pyridin-2-ylmethylene)amino)methyl)phenol* **1** (L_1H) (5 mmol, 1.06 g) was solved in 5 ml toluene was added to slurry. The suspension was stirred for 24 h under reflux. The ligand grafted silica **3** was filtered and washed with ethanol thoroughly to remove unreacted L_1H. FT-IR (KBr, cm^{-1}): 3030, 2879-2779, 1639, 1092, 910. Solid UV-Vis. (λ_{max}, nm): 257, 273, 281, 394.

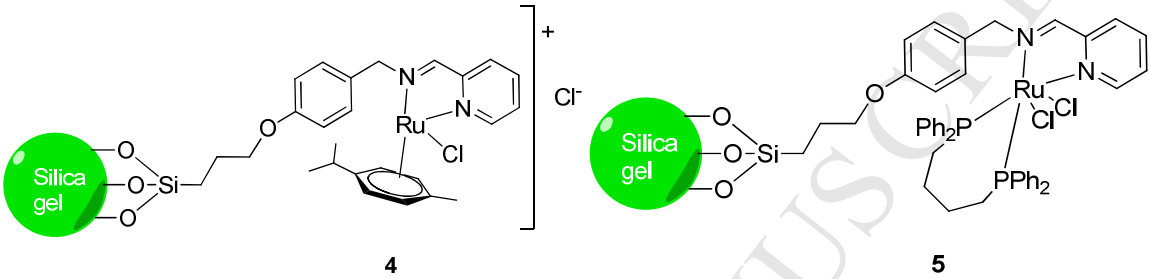
2.3.3. Synthesis of homogeneous Ru complex ***2***



Dichloro(*p*-cymene)ruthenium(II) dimer (0.28 g,0.47 mmol) was added to the solution of *(E)-4-(((pyridin-2-ylmethylene)amino)methyl)phenol* **1** (L_1H) (0.2 g, 0.94 mmol) in methanol (10 ml) for 6 h under nitrogen atmosphere in a schlenk tube. The precipitate was filtered and rinsed with petroleum ether (20 mL) and diethyl ether (20 mL). The complex **2** was obtained as brown solid. The Ru(II) complex is soluble in solvents such as EtOH and MetOH. Mp: 190^{o}C. ^{1}H NMR (300 MHz, DMSO) δ 9.95 (s, 1H), 9.65 (t, *J* = 23.4 Hz, 1H), 8.31 (d, *J* = 38.2 Hz, 1H), 8.23 (s, 2H), 7.78 (s, 1H), 7.28 (d, *J* = 7.7 Hz, 2H), 6.91 (d, *J* = 7.8 Hz, 2H), 6.31 (d, *J* = 5.7 Hz, 1H), 6.08 (d, *J* = 5.4 Hz, 1H), 5.92 (dd, *J* = 12.0, 5.8 Hz, 1H), 5.65 (d, *J* = 16.1 Hz, 1H), 5.30 (d, *J* = 16.1 Hz, 1H), 2.70 – 2.36 (m, 2H), 2.14 (s, 3H), 0.96 (dd, *J* = 28.6,

6.4 Hz, 6H). ^{13}C NMR (75 MHz, DMSO) δ 165.99, 157.96, 155.90, 154.53, 139.60, 131.31, 129.14, 128.08, 124.24, 115.83, 104.18, 103.58, 87.64, 84.50, 84.09, 83.81, 68.30, 30.40, 22.00, 21.48, 18.36.FT-IR (KBr, cm^{-1}): 3037, 2866-2785, 1630. Anal.Cald. For: [$C_{23}H_{26}Cl_2N_2ORu$], C: 53.28, H: 5.05, N: 5.40. Found: C: 53.16, H: 5.09, N: 5.31. UV-Vis. (λ_{max}, nm) in DMF: 274, 328, 363, 396, 404. μ_{eff}, BM: Diamagnetic.

2.3.4. Synthesis of heterogeneous Ru complexes ***4-5***



4 **5**

Complexes **4** and **5** were synthesized with same synthetic procedure. The complexes were prepared by stirring mixture of ligand-grafted silica **3** (1 g) and Ru(II) compounds [[$RuCl_2$(p-cymene)]$_2$, $RuCl_2(PPh_3)$dppb] (0.5 mmol) in toluene (20 mL) at 60 ^oC for 24 h. After stirring, complexes were filtered, washed with diethyl ether and hexane till washings were colorless. They were dried in air. The proposed structures of complexes are shown in Fig.1.

Complex **4**: FT-IR (KBr, cm^{-1}): 3446, 2925, 2853, 1636, 1092, 802,476. Solid UV-Vis. (λ_{max}, nm): 210, 286, 439.

ICP: Ru, 6788 mg/kg.

Complex **5**: FT-IR (KBr, cm^{-1}): 3444, 2925, 2857, 1632, 1090, 905, 486. Solid UV-Vis. (λ_{max}, nm): 222, 338, 443.

ICP: Ru, 32660 mg/kg.

2.3.5. General procedure for the transfer hydrogenation of ketones

Under nitrogen atmosphere, aromatic ketone (1 mmol), KOH (1 mL, 0.1 M) and complex **2** (1 mg, 0.003 mmol) were dissolved in degassed 2-propanol (9.75 mL) with nitrogen and the mixture was refluxed for 180 min. The same reaction conditions were used for complex **4** (10

mg) and complex **5** (10 mg). They were added in degassed 2-propanol as solid. The hydrogenation of the ketone was followed by GC using HP-5 column.

3. Result and Discussion

3.1. Synthesis, Characterization and Immobilization of L_1H

(E)-4-(((pyridin-2-ylmethylene)amino)methyl)phenol **1** (L_1H) (Fig. 1) was synthesized from the reaction of 4-(aminomethyl)phenol and picolinaldehyde. The ligand is soluble in common organic solvents such as EtOH, MeOH, DMF, CH_2Cl_2 and stable at room temperature. The structure of L_1H was further characterized by UV-visible spectra, FTIR, elemental analyses, NMR and X-Ray analyses.

The ^1H NMR spectra of the L_1H is shown in Fig. S6. L_1H has one phenolic OH group and its NMR signal was seen at 10.02 ppm as a singlet. Azomethine proton (CH=N) was observed at 8.64 ppm [25]. The singlet at 4.71 ppm was assigned to the $–CH_2-$ protons. The aromatic protons were observed in the region of 8.35–6.60 ppm. At the IR spectra of the L_1H, bands at 3037 cm^{-1} and 2866–2785 cm^{-1} that are assignable to ν(OH) and ν(Ar-CH) [26]. The sharp band at 1639 cm^{-1} is due to the vibration of the azomethine group (-CH=N-). The electronic absorption spectral data for L_1H was obtained in DMF solutions at room temperature.

Single crystals of L_1H **1** were grown from slow evaporation of DMF solution of ligand (Fig. 2.). Molecule crystallizes monoclinic $P2_1/c$ space group. The N1-C6 distance of 1.261 (3) Å shows a typical C=N double bon character. The molecules display intermolecular O-H…N (2.85 Å) and weak C-H…O (3.42 Å) hydrogen bonds, which stabilize the crystal structure.

Supporting material (SiCPTMS) was prepared according to literature from treating activated silica with 3-chloropropyltriethoxysilane. Then it was used to synthesize the immobilized ligand **3**. Immobilized ligand **3** was characterized with FTIR, Thermal and EDX analyses. As distinct from LıH's FTIR spectrum, immobilized ligand **3** shows characteristic bands at 1092 and 910 cm^{-1} corresponding to the stretching vibrations of Si-O-Si bands, respectively. In the thermal analyze spectrum the ~ 14% mass loss can be attributed to the grafted L_1H structure. In addition, N and C atoms seen at EDX analyze prove that L_1H was grafted to SiCPTMS successfully.

*3.2. Synthesis and Characterization of homogeneous **2** and heterogeneous catalysts **4, 5***

The homogeneous catalyst complex **2** has been prepared by the condensation between *(E)-4-(((pyridin-2-ylmethylene)amino)methyl)phenol* **1** (L_1H) and $[RuCl_2(p\text{-cymene})]_2$. The heterogeneous catalysts complexes **4** and **5** were obtained by the reaction of immobilized ligand **3** and ruthenium compounds $[RuCl_2(PPh_3)dppb$, $[RuCl_2(p\text{-cymene})]_2]$, respectively.

The homogeneous catalyst **2** was characterized by ^1H, ^{13}C NMR, IR and UV-Vis analyses. In order to better determine the structure of the complex **2** ^1H and ^{13}C NMR spectral studies was performed (Fig.S7). The ^1H NMR spectrum of complex **2** shows a singlet in the 9.95 ppm can be attributed to the proton of the –OH group [27]. The ^1H NMR resonance of azomethine proton (CH=N) was observed at 9.65 ppm. The singlet signal at 2.14 ppm was attributed to the $–CH_3$ protons. The IR spectra of the complexes were also studied and compared with ligand spectrum in order to determine the linkage of Schiff base ligands to the metal center in the complexes. Complex **2** and L_1H have similar bands but especially the azomethine ν(C=N) stretching shifted to lower frequency (1630), indicating the coordination of azomethine nitrogen to metal ion. The electronic spectrum of complex **2** was recorded in DMF in the range 800-200 nm. By comparing the spectra of the L_1H and the complexes **2**, the absorption band above 404 nm was assigned to ligand to metal charge transfer transitions [28].

The structures of complexes **4** and **5** were characterized with IR, solid UV-Vis, SEM, EDX and thermal analyses. The IR spectra of heterogeneous complexes **4** and **5** were similar to the homogeneous complex **2** spectrum. In addition to complex **2** spectrum, complexes **4** and **5** have characteristic vibrations at around 1092 and 802 cm^{-1} corresponding to the stretching vibrations of Si-O-Si bands, respectively. Also the lowering in frequencies of the C=N peaks at complexes **4** and **5** spectra is indicative of the formation of metal-ligand bonds. Complexes **4** and **5** exhibit absorption bands above 439 and 443 nm and these were assigned to L⟶M charge transition.

The EDX analyses (Fig. 3.) prove that ligand **3** was grafted on solid surface and heterogeneous complexes **4** and **5** were synthesized on the solid support with the expected atom peaks.

Thermal behaviors of immobilized ligand **3** and heterogeneous complexes **4** and **5** have been studied using thermo gravimetric analysis (TG) and differential thermal analysis (DTA) equipments. The thermal curves are given in Fig. 4. The main 14% weight loss in the temperature range of 400-700^oC for immobilized ligand **3** corresponds to the breakage of the

Schiff base molecule grafted to the activated silica. For heterogeneous complexes main mass loses are 22% and 68% respectively. Increased mass loses implying a higher amount of ruthenium compounds [$RuCl_2(PPh_3)$dppb, $[RuCl_2(p\text{-cymene})]_2$] are derived from the size of these compounds. The difference at % residues and % mass losses for the compounds suggested that heterogeneous Ru(II) complexes **4**, **5** were synthesized successfully on the solid support. For higher temperatures, the weight loss followed a slower rate, and the final peaks in the region of 700-1100^oC are due to partly thermal decompositions of the silica structure and formation of metal oxides for complexes **4** and **5**.

The SEM images if SiO_2, SiCPTMS, complex **4** and complex **5** are shown in Fig.5. Silica gel has a clean-cut surface. The morphological differences between activated silica gel and the ligand in SEM images are very important evidence of the grafting of ligand onto the silica gel granules. The grafting of the ligand onto the silica gel causes a roughening on the activated silica gel surface. Images of the metal complexes show further roughening on the surface, which may be due to interaction of the ruthenium metal atoms with the ligand to associate the fixed geometry of the complexes [22]

3.2. Catalytic Transfer Hydrogenation of Ketones

To examine and compare the catalytic capability of ruthenium (II) complexes of L_1H, a homogeneous **2** and two heterogeneous catalysts **4** and **5** were prepared and then employed in the transfer hydrogenation reactions using acetophenone as the model substrate with 2-propanol as the hydrogen donor and solvent (Table 1). Initially the reaction conditions were optimized and KOH was selected as a base due to the 67% conversion where the C:S ratio was 3/1000. When the homogeneous complex **2** was immobilized, the complex **4** was obtained and 10 mg amount of complex **4** was used in transfer hydrogenation reaction using acetophenone with the same ruthenium amount in complex. Interestingly enough, 54% conversion was screened in 10 minutes. This result showed that complex **2** gave much better result if it was immobilized on a solid state such as silica gel. In addition to this, complex **5** was synthesized with $RuCl_2(PPh_3)$dppb to see the influence of P atom on the activity and the conversion was found to be 96% in only 10 minutes.

With these results complex **5** was found to be best catalyst even with lower catalyst loading. Concurrently, a transfer hydrogenation reaction of a series of acetophenone derivatives with the 2-propanol in the presence of catalyst **5** and KOH was studied and the results are summarized in Table 2. The reduced products were defined by GC-MS.

Complex **5** display good catalytic activity in the transfer hydrogenation of all acetophenone derivatives. All ketones are efficiently reduced through transfer hydrogenation reaction except 2-bromo acetophenone. Complex **5** catalyzed the complete reduction of 3-bromo acetophenone with 96% conversion in 30 minute which is the shortest time among the other reductions. The same 99% conversion was occurred from the reduction of 2-methy acetophenone and 2-methoxy acetophenone both in 60 and 180 minutes, respectively. 4% conversion was obtained from the reduction of 2-bromo acetophenone although the reduction experiment was repeated for this ketone with several times. As seem probable, transfer hydrogenation of ketones to the corresponding alcohols, are affected by electron-withdrawing and electron-donating substituents [29]. The probable cause for this situation is methyl and methoxy groups on the aryl ring of ketones have a powerful tendency to donate electrons. In comparison, the average conversions of ketones having electron-donating substituents methyl and methoxy are higher than the average conversion of ketones having electron- withdrawing substituents. When the conversions of ketones including electron-donating substituents such as methyl and methoxy compared between each other, *ortho* substituated ketones gave the highest conversion (99%). In addition this, as seen from Table 2, substitute groups a *para* position gave lower conversions 97% and 91%, respectively, than *ortho* and *meta* positions. It is worth noting that the affect of electron-withdrawing substituent was analyzed, as expected, *para* position substituent on the aryl ring of ketone gave higher conversion 97% than *ortho* 4% and *meta* 96% substitute ketones.

Conclusions

In summary, we have presented a new Schiff base ligand L_1H **1** which was characterized by single crystal X-ray analysis and its immobilized form L_2H **3**. Afterwards one homogeneous complex **2** with ligand L_1H **1** and two heterogeneous complexes **4** and **5** with ligand L_2H **3** were prepared. $[RuCl_2(p\text{-cymene})]_2]$ was used in the preparation of ruthenium complexes **2** and **4**. Besides that $[RuCl_2(PPh_3)dppb]$ was used to obtain the complex **5** to show the impact of P atom on transfer hydrogenation reactions.

The homogeneous and heterogeneous complexes were tested as catalyst in transfer hydrogenation reactions of several ketones. From the comparison of homogeneous **2** and heterogeneous complexes **4**, it was seen that heterogeneous complex **4** was more active in transfer hydrogenation reactions. Same study was made with heterogeneous complex **5** and

the data have demonstrated that heterogeneous complex **5** shows higher catalytic activity than complexes **2** and **4**. Our experiences in these fields are ongoing and will be reported in the course of time.

Acknowledgements

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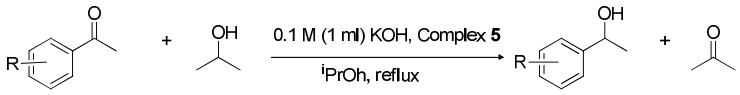
Table 1.

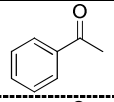
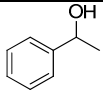
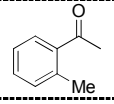
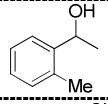
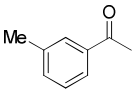
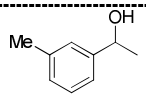
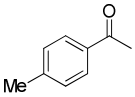
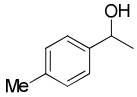
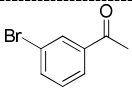
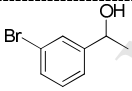
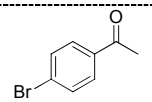
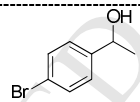
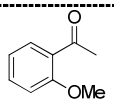
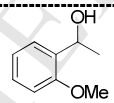
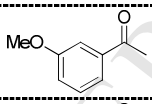
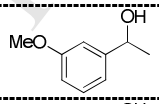
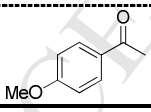
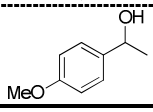
Optimization studies for complexes in TH reaction of acetophenone

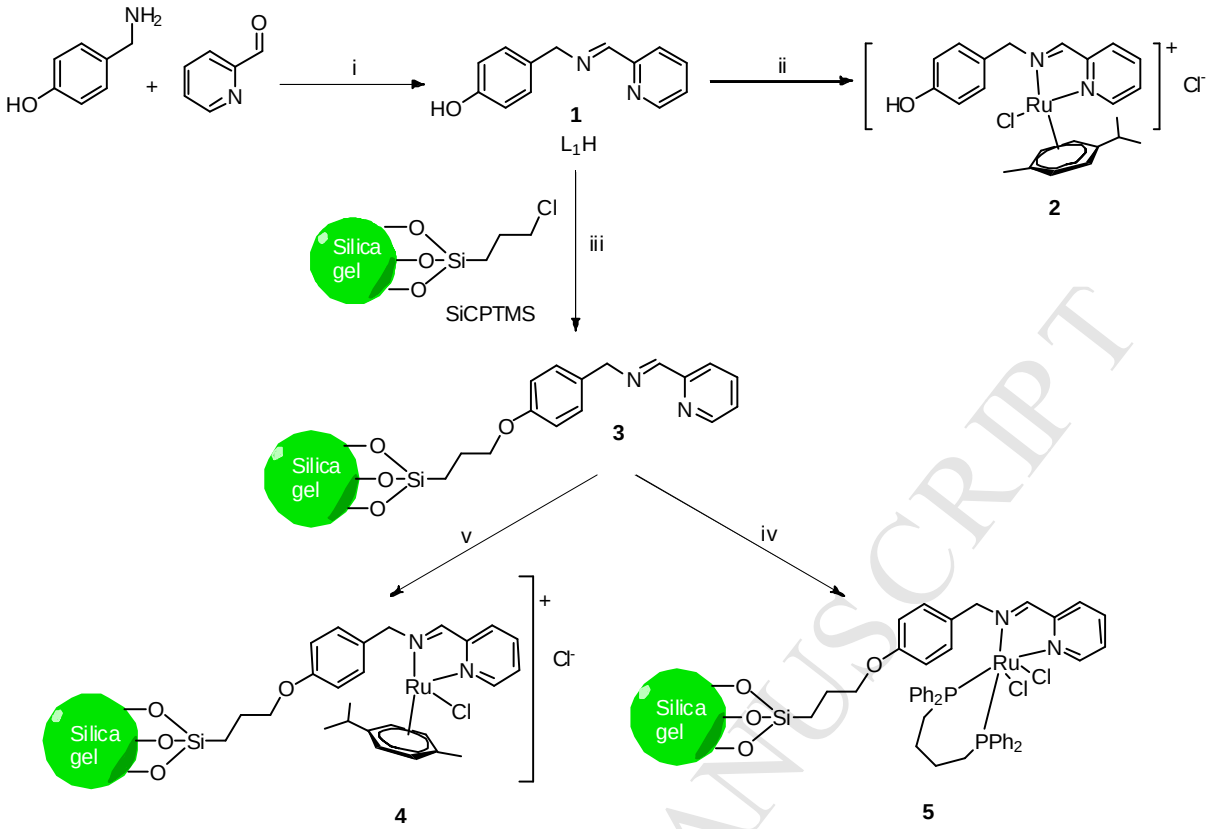
Entry	Catalyst	C/S	Base	Time (min)	Conversion (%[a])
1*	2	3/1000	NaOH	60	48
2*	2	3/1000	KOH	60	67
3	4	3/1000	KOH	10	54
4	5	3/1000	KOH	10	96

Conditions:* 0.003 mmol **2**, 1 mmol acetophenone, 1 mL 0.1 M base, reflux, C/S: catalyst (Ru)/substrate, [a]determined by GC,

Table 2.
Catalytic transfer hydrogenation of ketones with ruthenium complex **5**



Entry	Ketone (1 mmol)	Alcohol	C/S	Time (min.)	Conversion (%)
1			3/1000	10	96
2			3/1000	60	99
3			3/1000	120	98
4			3/1000	180	97
5			3/1000	60	4
6			3/1000	30	96
7			3/1000	120	97
8			3/1000	180	99
9			3/1000	120	98
10			3/1000	180	91



(i) Ethanol, rt, 3 h; (ii) $[RuCl_2(p\text{-cymene})]_2$, MetOH, reflux, 6 h; (iii) SG-Cl, Toluene, reflux, 24 h; (v, iv) $[RuCl_2(p\text{-cymene})]_2$, $RuCl_2(PPh_3)$dppb, Toluene, 60°C, 24 h

Fig.1. General synthesis of L_1H ligand and its homogeneous and heterogeneous Ru(II) complexes.

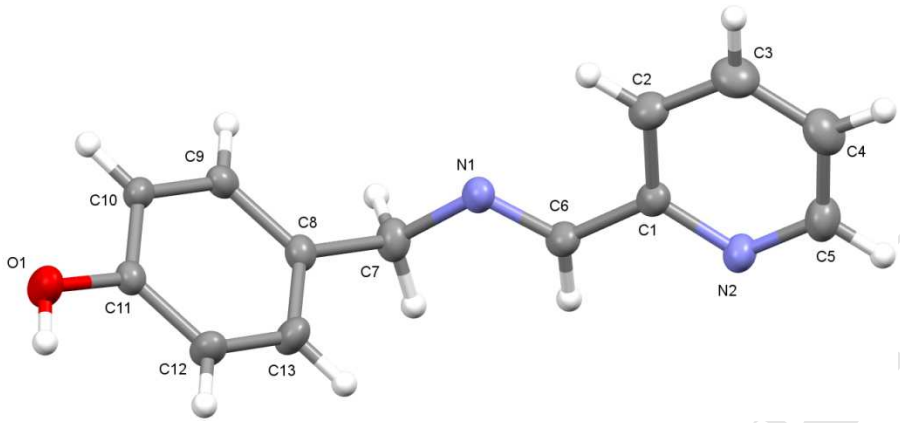
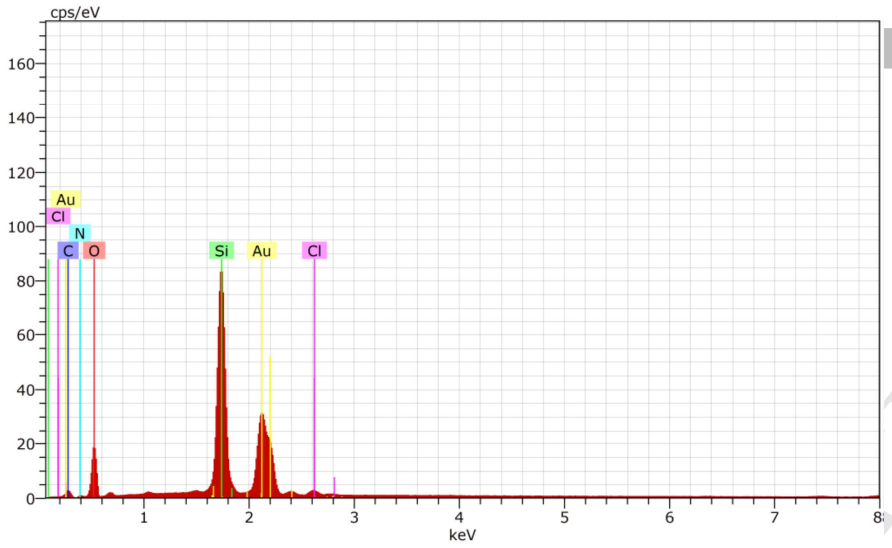
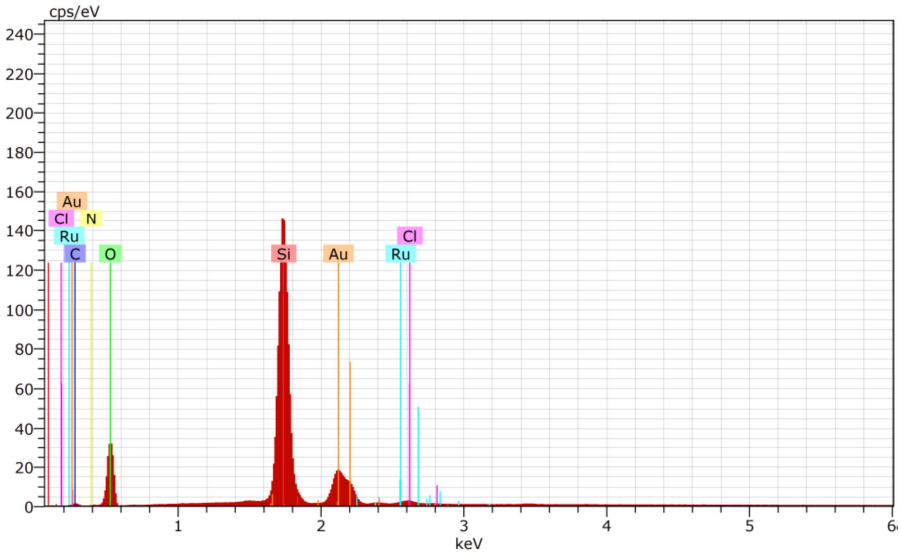


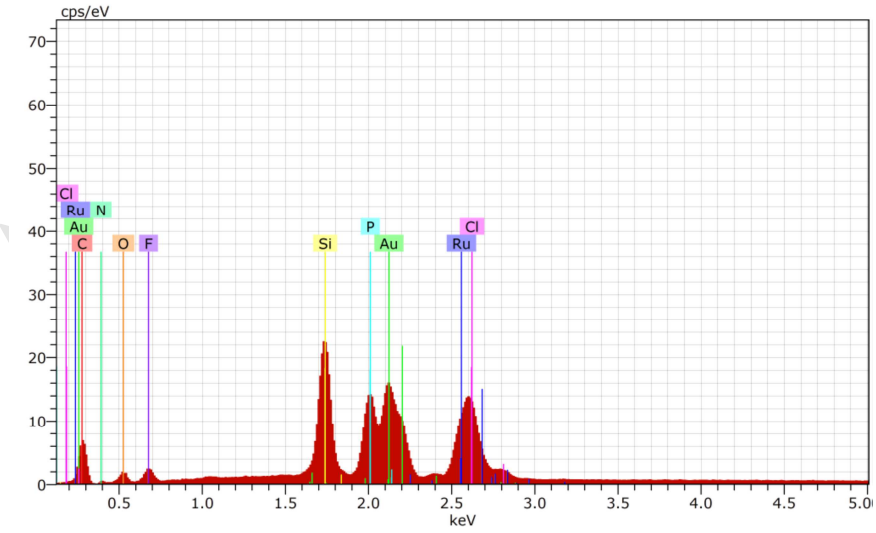
Fig.2. Molecular structure of(E)-4-(((pyridin-2-ylmethylene)amino)methyl)phenol **1**(L_1H). Thermal ellipsoids are drawn at the 40% probability level.



SiCPTMS

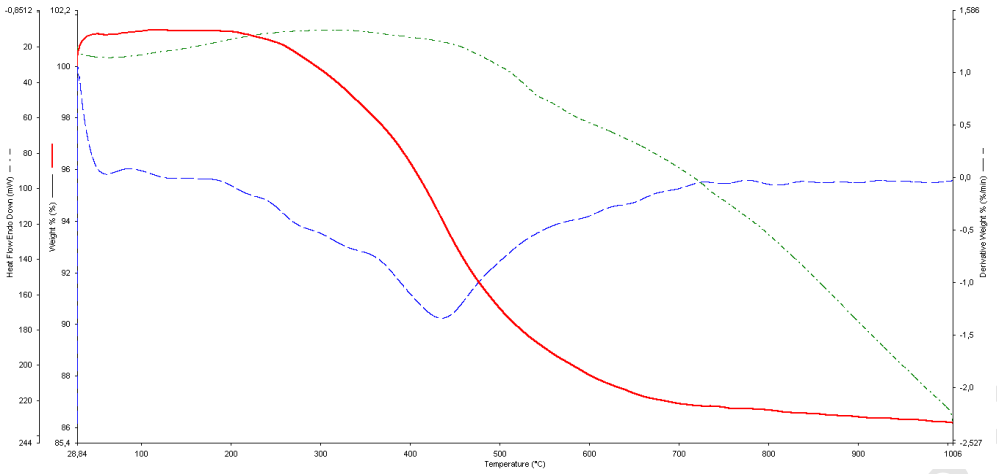


Complex **4**

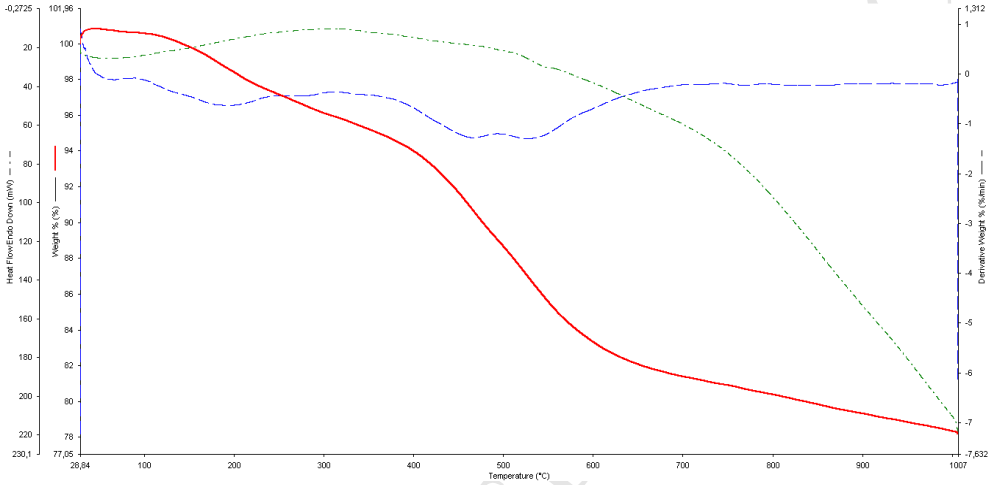


Complex **5**

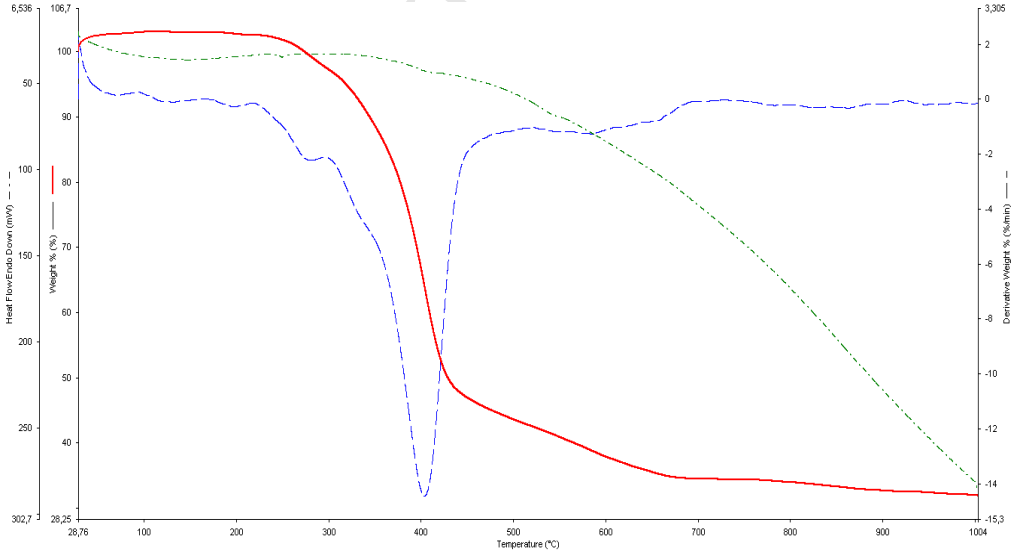
Fig.3. EDX images of complex **4** and complex **5**



(a)

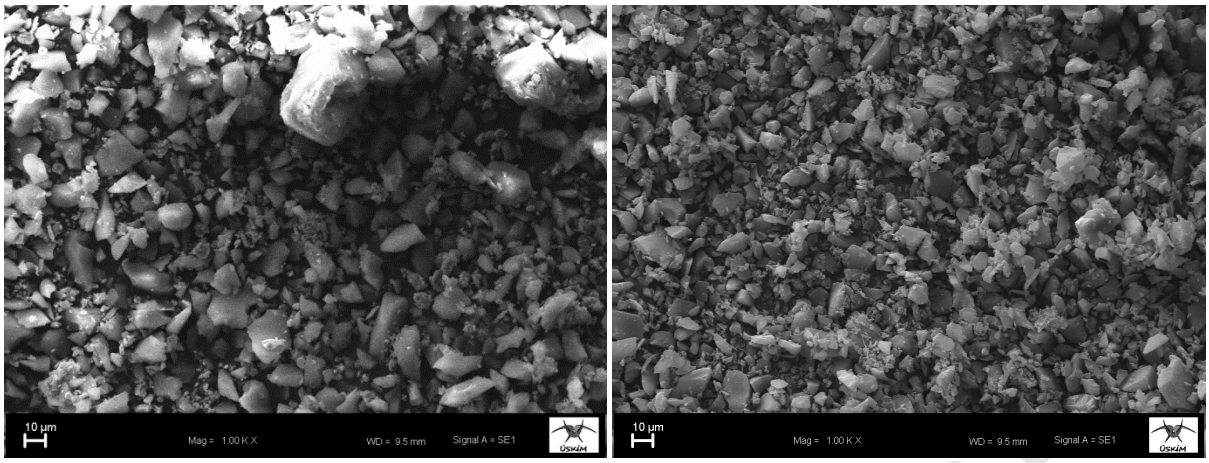


(b)

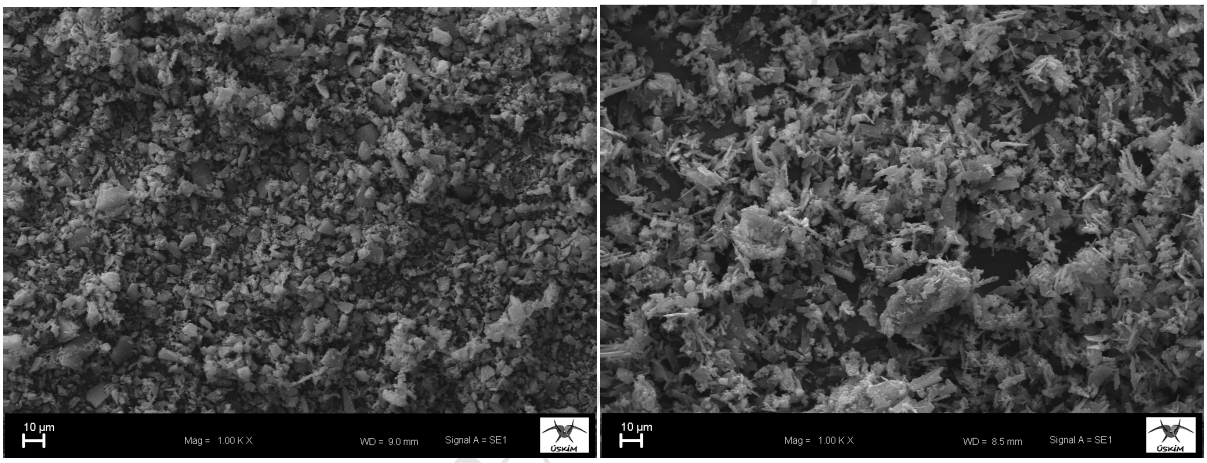


(c)

Fig.4. T.G. and D.T.A. of immobilized ligand **3** (a), Complex **4** (b) and Complex **5** (c)



(a) (b)



(c) (d)

Fig.5. SEM images of support material (a), SiCPTMS (b), Complex **4** (c), Complex **5** (d)

► A new Schiff base ligand L_1H **1** was synthesized and grafted to solid support successfully. And single-crystal X-ray analyse was performed for L_1H **1**.

► Mononuclear Ru(II) complex **2,** its solid supported analogue **4** and heterogeneous complex **5** were synthesized with $[RuCl_2(p\text{-cymene})]_2$ and $RuCl_2(PPh_3)$dppb.

►The synthesized metal complexes were performed as catalysts for the transfer hydrogenation of various ketones in 2-propanol.

► Following the comparison of complexes, it was observed that immobilized complexes have higher catalytic activity against the homogeneous structure.

► Catalytic activity results show that diphosphine incorporated complex **5** is the most effective catalyst in transfer hydrogenation reactions.