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A 2-(2’-pyridyl)quinoline ruthenium(II) complex as an active catalyst for the transfer hydrogenation of ketones

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Abstract: The ruthenium(II) complex *cis*-[RuCl$_2$(PPh$_3$)$_2$(L1)] (**1**) where L1 = 2-(2’-pyridyl)quinoline was obtained in high yield from the reaction of [RuCl$_2$(PPh$_3$)$_3$] with L1. The new compound was characterized by different spectroscopic methods including FT-IR, UV-Vis, NMR (^{1}H, ^{31}P) spectroscopy along with a mass spectrometric analysis (ESI-MS) and conductivity measurements. ^{31}P NMR spectroscopy provided evidence that the two PPh$_3$ ligands are orientated *trans* to each other in an octahedral environment. Complex (**1**) was tested in the transfer hydrogenation of various ketones in 2-propanol at 82°C. The catalytic activity of (**1**) displayed quantitative conversions for benzophenone and 4-chloroacetophenone.

Keywords: 2-(2′-pyridyl)quinoline, triphenylphosphine, Ruthenium(II) complexes, catalytic transfer hydrogenation

1 Introduction

The coordination and organometallic chemistry of ruthenium complexes has been studied extensively over the past several years [1,2]. In fact, well described synthetic protocols [3] are known owing to the unique properties of this versatile metal, such as a range of existing oxidation states (II, III and IV) [4], chemical stability, and redox and photophysical properties [5,6]. The plethora of applications in different scientific fields are generally divided in three broad categories: (a) drugs and medicinal applications [7], (b) third generation photovoltaic solar cells [8,9] and (c) catalysis [10].

In the field of catalysis, the transfer hydrogenation of ketones using 2-propanol as the hydrogen source is a synthetic method of particular importance in organic synthesis and in industry [11]. It constitutes an alternative to standard catalytic hydrogenation where the use of molecular hydrogen at high pressure is required [12]. A significant breakthrough includes the work of Noyori and co-workers with the development of new enatioselective transfer hydrogenation catalysts [13]. From the mechanistic point of view significant contribution has been made by Bäckvall et al.,[14] and Morris et al. [15], along with recent reports of Baratta et al. [16]. An excellent review paper by Wang and Astruc [11] describes the most recent advances in transfer hydrogenation using transition metal catalysts. In such reactions, Ru(II) complexes containing phosphine ligands are quite popular as they exhibit good catalytic activity [17,18].

As part of our ongoing research interest, in the present review emphasis is placed on the synthesis of new Ru(II) compounds, exploration of their coordination chemistry and examination of their applications in catalytic processes. With this in mind, we set out to examine the reaction of the typical ruthenium(II) triphenylphosphine precursor [RuCl$_2$(PPh$_3$)$_3$] with 2-(2’-pyridyl)quinoline (L1) (Scheme 1a), a common simple bidentate ligand, aiming to prepare a new efficient catalyst and to use it in the transfer hydrogenation of various ketones. The coordination chemistry of L1 with various metal ions is known [19,20] although triphenylphosphine transition metal complexes bearing this ligand have not been described in the literature. Previous work on the structurally related *cis*-[RuCl$_2$(PPh$_3$)$_2$(L)] (L = 2-(2′-pyridyl)quinoxaline) complex

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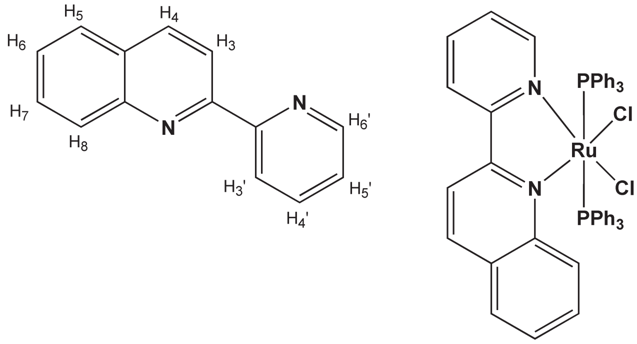


Scheme 1: (a) The molecular structure of L1 including a numbering scheme of the hydrogen atoms. (b) The structure of complex **1**.

[21] provided us with the required knowledge so as to extend our investigations. Herein we report on the synthesis and spectroscopic characterization of a new Ru(II) complex of the general structure *cis*-$[RuCl_2(PPh_3)_2(L1)]$ (Scheme 1b) and the catalytic behavior for the reduction of ketones (polarized unsaturated compounds). Complex **1** was evaluated in the transfer hydrogenation of benzophenone and acetophenone derivatives in 2-propanol at reflux in the presence of *i*PrOK.

2 Experimental

2.1 Reagents and Materials

All manipulations were carried out under an argon atmosphere using standard Schlenk techniques (unless otherwise noted). Acetone was pre-dried over calcium chloride and distilled over K_2CO_3, while diethyl ether was pre-dried over $CaCl_2$ and then distilled over 4 Å molecular sieves under argon. All other materials and solvents were used as received. The starting material $[RuCl_2(PPh_3)_3]$ [22] and the ligand 2-(2′-pyridyl)quinoline (L1) [23] were prepared according to literature procedures with slight modifications. More precisely, the final step during the preparation of the $[RuCl_2(PPh_3)_3]$ precursor was performed under aerobic conditions (filtration and drying of the compound), while the synthesis of L1 was undertaken by the addition of 2-aminobenzyl alcohol to the relevant precursor 2-acetylpyridine instead of the 2-nitrobenzaldehyde derivative reported in the literature [23].

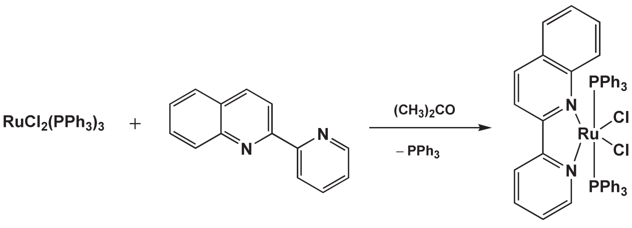
Infrared spectra were measured on a Shimadzu IR Affinity-1 spectrometer as potassium bromide pellets in the spectral range of 4000–400 cm^{-1}. The following abbreviations were used for the intensities of the IR absorption bands: vs = very strong, s = strong, m = medium, w = weak, br = broad. Elemental analyses were obtained from the Microanalysis Center of the Institut für Anorganische Chemie Universität Bonn. ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded at 298 K on a Varian 300 MHz spectrometer, using $CDCl_3$ as the solvent and TMS as an internal standard, at 25 °C. *J* values are given in Hz. The $^{31}P\{^1H\}$ NMR spectra were calibrated against an external 85% aqueous H_3PO_4 solution, which was dispensed into a capillary tube and measured in a 5 mm tube containing the deuterated solvent. The following abbreviations were used for the signal multiplicities: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad. Absorption spectra were recorded with a CARY 3E UV/Vis spectrometer in $CHCl_3$ and CH_2Cl_2. High resolution ESI mass spectra were recorded on a Bruker Daltonics FT-ICR-MS at the Institut für Organische Chemie, Universität Leipzig. Conductivity measurements were performed on an AQUALYTIC® AL20Con conductivity meter. Melting or decomposition points were determined using an Electrothermal 9100 (IA9000 series) Digital melting point apparatus and are uncorrected. The samples were sealed in capillary tubes and heated slowly until the compounds melted or decomposed. For the GC–MS experiments, all analyses were performed using an Agilent 6890N gas chromatograph equipped with a mass selective detector HP 5975 (Agilent Technologies, Waldbronn, Germany). The gas chromatograph was fitted with an HP5-MS capillary column, 30m × 0.25mm i.d., 0.25 µm film thickness Model 19091S-433 (Agilent Technologies). Helium (purity 99.999 %) was used as carrier gas at a flow of 1.7 $mL\cdot min^{-1}$ (constant flow). The GC oven temperature program was as follows: 35 °C (hold 2 min), rate 5 °C min^{-1} to 70 °C, rate 20 °C min^{-1} to 300 °C (hold 2 min). The total analysis time was 22.50 min. The injector was operated in a pulsed splitless mode and its temperature was 300 °C. The volume injected was 2.0 µL. The MSD (mass spectrometry detection) operated in full scan mode for ion selection and determination of background (40-450 m/z) and in single ion monitoring (SIM) for quantification and its temperature was 250 °C. The mass selective detector operated at 70 eV with electron impact ionization. The transfer line was set at a temperature of 280 °C, the quadrupole at 150 °C, and the ion source at 230 °C.

2.2 Synthesis of cis-$[RuCl_2(PPh_3)_2(L1)]$ (1)

A mixture of $[RuCl_2(PPh_3)_3]$ (325 mg, 0.34 mmol) and L1 (70mg, 0.34 mmol) was added in a Schlenk tube and was degassed for about 0. 5 h. Dry acetone (15 mL) was then added via a double-ended needle to the mixture, giving instantly a deep blue solution which turned gradually to violet with the precipitation of a magenta colored solid. The suspension was stirred at ambient temperature for about 5 hours and then was filtered under argon. The resulting solid was then washed thoroughly with diethyl ether (3 × 10 mL) filtered off and subsequently dried under vacuum and then in an oven at 60 °C. Yield: 82% (250 mg). Mp: 207 °C (dec). Anal. Calcd. for (1)×1.5(H_2O), $C_{50}H_{43}Cl_2N_2O_{1.5}P_2Ru$: C, 64.59; H, 4.66; N, 3.01. Found: C, 64.77; H, 4.57; N, 2.97 %. IR (KBr, ν in cm^{-1}): 3055 (m, C–H arom), 1600 (w), 1481 (vs), 1433 (vs), 1370 (w), 1336 (w), 1314 (w), 1191 (w), 1156 (w), 1120 (w), 1089 (vs), 1029 (w), 998 (w), 840 (w, br), 792 (w), 773 (m), 746 (s), 696 (vs), 517 (vs), 494 (s), 458 (w). UV-Vis (ε, M^{-1} cm^{-1}): λ_{max} ($CHCl_3$) = 534 (1212), 352 (2738), 333 (6607); λ_{max} (CH_2Cl_2) 537 (957), 352 (1706), 334(5868). ^{1}H-NMR ($CDCl_3$, 300MHz, 298K) δ(ppm): 6.34 (m, H5’), 6.69 (m, H7), 6.84 (m, 12H, *m*-H), 6.97 (m, 6H, *p*-H), 7.14 (t, $^3J_{H,H}$ = 6 Hz, 2H, H6/4’), 7.23 (t, , $^3J_{H,H}$ = 6 Hz, H5), 7.37 (m, 12H, *o*-H), 7.60 (m, 2H, H3/4), 7.79 (d, $^3J_{H,H}$ = 6 Hz, H3’), 9.17 (br.s, H6’), 10.02 (d, $^3J_{H,H}$ = 9 Hz, H8). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.5 MHz, 298K): δ(ppm) = 20.09 (s, PPh_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121.5 MHz, 298K): δ(ppm) = 20.54 (s, PPh_3). ESI-MS (MeOH): (*m/z*, %) 867 ($[RuCl(PPh_3)_2L]^+$, 67), 605 ($[RuCl(PPh_3)L]^+$, 17).

2.3 General procedure for the transfer hydrogenation of ketones

Under inert atmosphere a two-necked round-bottomed flask was charged with a mixture of ketone (2.22 mmol), the ruthenium catalyst **1** (0.0055 mmol) and 10 mL of 2-propanol, and the mixture was stirred at 82 °C in a preheated oil bath. 14.9 mL of a 0.015 M solution of *i*PrOK in 2-propanol (0.22 mmol) was added to initiate the reaction. Approximately 0.1 mL of the reaction mixture was sampled and subsequently diluted with 3 mL of the solvent and analyzed by GC-MS. At the end of the reaction, the solution was cooled at ambient temperature and the solvent was evaporated to dryness. Hexane (15 mL) was added and the residue was filtered through a small pad of SiO_2 for purification. The desired alcohol product was identified and determined by comparison with the ^{1}H NMR data and the gas chromatography traces of authentic samples. The catalytic experiments were performed twice in order to ensure reproducibility of the results. Conversions obtained were related to the unreacted ketone. The percentage conversions were also determined by ^{1}H NMR spectroscopy (of the final product).



(1)

Scheme 2: Synthetic procedure for the ruthenium(II) complex **1**.

3 Results and Discussion

3.1 Synthesis and characterization of the ruthenium(II) complex

The reaction of the bidentate ligand L1 with an equimolar amount of $[RuCl_2(PPh_3)_3]$ in dry acetone affords the ruthenium(II) complex *cis*-$[RuCl_2(PPh_3)_2(L1)]$ (**1**) as a magenta colored solid in 85% yield (Scheme 2).

The new complex is air stable in the solid state, exhibiting remarkable thermal stability, and decomposes at 207 °C. It dissolves to some extent in chlorinated solvents (CH_2Cl_2 and $CHCl_3$) giving purple colored solutions. In solvents with coordinating ability, such as CH_3OH, CH_3CN and DMSO, dissociation takes place forming ionic species in solution. This was confirmed by performing conductivity measurements in these solvents. Representative plots of the specific conductance (*k*) versus time are presented in Fig. S1. It can be clearly seen that in acetonitrile and methanol, specific conductivity increases gradually with time. After 8h the molar conductance values (Λ_M) are higher than 160 S cm^2 mol^{-1} in CH_3CN and higher than 123 S cm^2 mol^{-1} in CH_3OH [24]. It can be concluded, therefore, that complex **1** in acetonitrile and methanol behaves as a 1:1 electrolyte [25]. On the other hand, in DMSO, the specific conductance value remains constant at 4.2 μs cm^{-1} after about 5 h of dissolution, reaching a plateau. The determined Λ_M value of 42 S cm^2 mol^{-1} is in the expected range for 1:1 electrolytes in DMSO [25-27]. In $CHCl_3$ and CH_2Cl_2, complex **1** does not dissociate significantly as the specific conductivity values are 0.2 μs cm^{-1} and 1.8 μs cm^{-1} respectively. The conductivity measurement findings are in accord with the previously reported results for the *cis*-$[RuCl_2(PPh_3)_2(L)]$ (L =2-(2′-pyridyl)quinoxaline) compound [28,29].

Elemental analysis of the new substance is consistent with the calculated composition of the proposed structure, while its spectroscopic properties were examined by FT-IR, UV-Vis and NMR spectroscopy (^{1}H, ^{31}P). The molecular composition was unequivocally confirmed by mass spectrometric analysis (ESI-MS). Thus, upon dissolution in methanol, dissociation of one chlorine ligand occurs immediately, generating the $[RuCl(PPh_3)_2L]^+$ ion at *m/z* = 867 as the major species, according to an ESI-MS analysis (Fig. S2a). The isotope pattern of the parent peak ion is in agreement with the simulated ESI-MS spectrum (Fig. S2b and Fig. S2c in the supplementary data). Along with the replacement of the chlorine, a slow exchange of one of the PPh_3 ligands is observed resulting in the formation of the $[RuCl(PPh_3)L]^+$ ion at *m/z* = 605.

Our continuous efforts to obtain single crystals of complex (**1**) suitable for an X-ray diffraction study were not successful, giving in all cases only microcrystalline solids or films.

The FT-IR spectrum of **1** was recorded in the region of 4000–400 cm^{-1}. A comparison with the IR data of the free ligand and of previously reported metal complexes incorporating L1 [20] helped us to assign some of the typical bands of this organic molecule coordinated to the Ru(II) center. Thus, the medium intensity band at 3055 cm^{-1} is assigned to the C–H aromatic stretching vibrations of L1. Moreover, the two intense bands at 1481 cm^{-1} and 1433 cm^{-1} can be attributed to the ν(C=C) and ν(C=N) stretching vibrations, respectively. Upon coordination, the intensities of the γ(C–H) bands of the free ligand at 848 cm^{-1}, 800 cm^{-1}, 779 cm^{-1} and 743 cm^{-1} are reduced [20] and the spectrum in this region is dominated by the intense vibrations of the PPh_3 group. The three characteristic strong bands at 746, 698 and 518 cm^{-1} could be attributed to the presence of the PPh_3 ligand [30]. Absorption spectra of **1** , recorded in CH_2Cl_2 and in $CHCl_3$, are depicted in Fig. 1. In dichlomethane the high energy band at 334 nm is assigned to π–π* charge transfer transitions localized on bipyridine ligands [31]. The absorption spectrum displays a broad absorption band centered at 537 nm and a second one at about 352 nm that are assigned to metal-to-ligand charge transfer (MLCT) transition bands for Ru(II) complexes [32-34]. Observation of the second band at approximately 352 nm is hampered by the intense band at 334 nm. Notably, a positive solvatochromism has been observed for the lowest energy band of the spectrum of **1**, with the λ_{max} ranging from 534 nm (in $CHCl_3$) to 537 nm (in CH_2Cl_2).

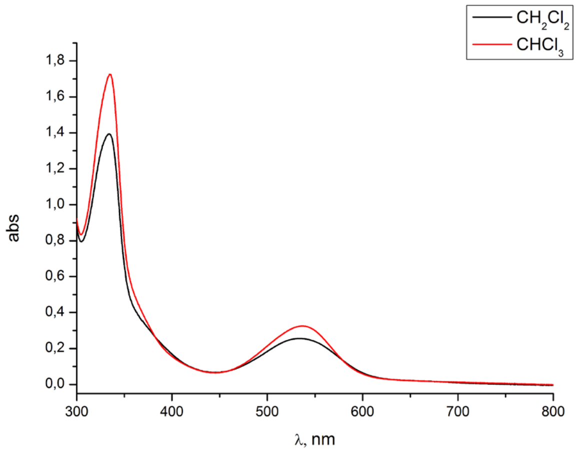


Figure 1: Absorption spectra of complex **1** in CH_2Cl_2 (3.4×10^{-4} M) and in $CHCl_3$ (2.1×10^{-4} M) at 298 K.

^{1}H and ^{31}P NMR spectroscopic techniques were used for the structural elucidation of compound **1**. The ^{1}H NMR spectrum of **1** was recorded in $CDCl_3$, and it displayed well resolved resonance signals for the protons of the ligand as expected for diamagnetic Ru(II) complexes. Assignment was based on integration and comparison with analogous ruthenium complexes reported in the literature [21]. For example, the two signals at 9.17 and 10.02 ppm are due to the presence of the H6' and H8 protons of the coordinated ligand respectively. The phenyl groups of the triphenylphosphine ligand appear as multiplets in the region of 6.84–7.37 ppm corresponding to *o*-H, *m*-H and *p*-H. ^{31}P{^{1}H} NMR spectroscopy provided strong evidence concerning the position of the PPh_3 ligands around the metal core. The presence of a single resonance at δ = 20.54 ppm, strongly suggests that the two PPh_3 ligands are in the *trans* configuration. This signal appears in the expected δ range, similar to that of the structurally related compounds *cis*-$[RuCl_2(PPh_3)_2(bipy)]$ (δ = 21.53 ppm; bipy = 2,2'-bipyridine) and *cis*-$[RuCl_2(PPh_3)_2(phen)]$ (δ = 23.26 ppm; phen = 1,10-phenanthroline) [18] respectively. The presence of other geometric isomers was not detected. ^{31}P{^{1}H} NMR spectroscopy also revealed that this compound is stable in $CDCl_3$ over a period of 24 h. This stability is consistent with the conductivity measurements performed in the same solvent (vide supra). In DMSO-d_6, however, the ^{31}P{^{1}H} NMR spectrum of a freshly prepared concentrated solution showed the presence of five resonance signals. The signal at δ = –5.7 ppm is typical of free PPh_3, and the other four singlets at δ = 21.40, 31.84, 40.09 and 47.95 ppm correspond to phosphorous containing species, in the integrated molar ratio of about 1/3/1/1, respectively. The resonance signals at δ = 21.40 and 31.84 ppm could be attributed to the initial complex **1** and the DMSO adduct $[RuCl(PPh_3)L(DMSO)_2]Cl$. In fact, integration of the signal at δ = 31.84 ppm is equal to that of free PPh_3. Based on the results of a ^{31}P{^{1}H} NMR investigation, the conductivity measurements performed and the data reported for similar compounds [20,28,29], we suggest that during the dissolution of **1** in DMSO one chloride ligand is replaced by DMSO affording the DMSO adduct $[RuCl(PPh_3)_2L(DMSO)]Cl$. PPh_3 is then released, giving the DMSO adduct $[RuCl(PPh_3)L(DMSO)_2]Cl$ as is shown in equation 1.

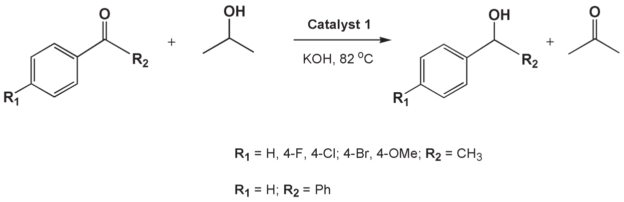
$$[RuCl_2(PPh_3)_2(L1)] + 2\,DMSO \longrightarrow$$
$$\longrightarrow [RuCl(PPh_3)(L1)(DMSO)_2]Cl + PPh_3 \qquad (1)$$

The occurrence of this reaction is in contrast to the results reported by Ojwach et al. [35] for the ruthenium(II) complexes of the type $[RuCl_2(PPh_3)_2L]$ (L = (pyridyl) benzoazole, (pyridyl)benzothiazole and (pyridyl) benzoxazole), where displacement of one PPh_3 by the DMSO-d_6 solvent has been proposed.

Further investigation is currently underway so as to have a better insight into the solution behaviour of complex **1** in this solvent.

3.2 Catalytic transfer hydrogenation studies

In this study, the catalytic activity of complex **1** for transfer hydrogenation of various ketones was examined using 2-propanol as a hydrogen donor in the presence of KOH at 82 °C (Scheme 3).



Scheme 3: Catalytic transfer hydrogenation of benzophenone and actophenone derivatives by catalyst **1**.

The percent conversion of all substrates to the corresponding alcohols was monitored over time by GC-MS. Initial attempts were conducted with benzophenone as the model substrate in the molar ratio of 400/1 (substrate/catalyst). We realized that upon increasing the amount of base (*i*PrOK) from 5 mol% to 7.5 mol%, a drastic increase in the catalytic conversion from 18 to 70% was observed over a period of 24 h, revealing the crucial role of the base in these transformation reactions [13,14].

Remarkably, the transfer hydrogenation of benzophenone was almost quantitative when the molar ratio of substrate/catalyst/base reached 400/1/40. In addition, at ambient temperature a 35% conversion was observed after 24 h. Intrigued by these results, we also examined the catalytic potency of **1** in acetophenone and its derivatives substituted with electron-donating (4-methoxy acetophenone) and electron-withdrawing groups (4-fluoro, 4-chloro, 4-bromo) in the *p*–position. All catalytic experiments then were carried out using 2 mmol of ketone, 0.25 mmol% of the ruthenium catalyst and 10 mmol% of KOH, with a substrate/catalyst/base molar ratio of approximately 400/1/40. The results are summarized in Table 1. From this Table it becomes evident that complex **1** is a potent catalyst that catalyzes successfully the reduction of benzophenone (100%), 4-chloroacetophenone (100%) and acetophenone (90%) to their corresponding alcohols (entries 1, 5 and 2) within a reaction time of 2.5–8h. The time-dependent conversion of the three substrates is shown in Fig. 2.

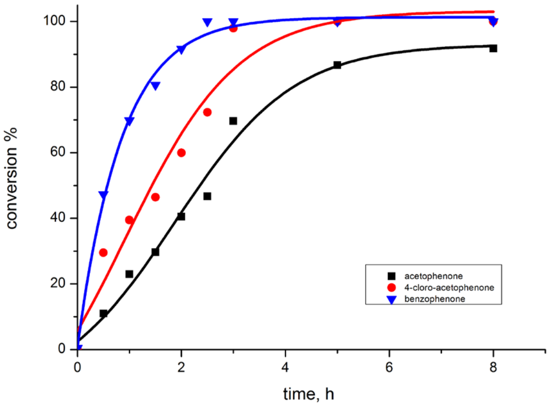
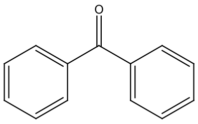
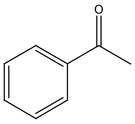
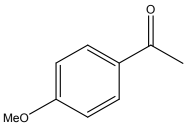
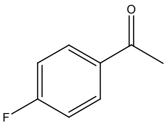
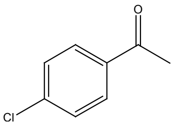
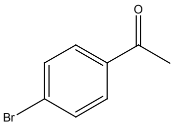


Figure 2: Time dependence of transfer hydrogenation of benzophenone, acetophenone and 4-chloroacetophenone by catalyst **1**.

It is clearly seen that an induction period is required for the transfer hydrogenation of acetophenone and 4-chloroacetophenone substrates. The TOF's achieved by complex **1** vary from 158 h^{-1} for benzophenone to 79 h^{-1} (4-chloroacetophenone) and 73 h^{-1} (acetophenone). Notably the presence of a 4-chloro substituent in the *para* position of acetophenone enhances the catalytic activity of **1** in comparison to unsubstituted acetophenone (entry 5). On the other hand, a drop of the activity to 81% is observed for the 4-methoxy acetophenone derivative (entry 2). These findings are in accord with literature reports since electron donor-substituents on acetophenone accelerates the reaction [18,36] while a decrease in the catalytic activity is expected with electron withdrawing groups [37]. However, 4-fluoroacetophenone exhibited a conversion of 89%, slightly lower than that of acetophenone. For 4-bromoacetophenone the activity decreases dramatically (61%) with prolonged reaction time (24 h, entry 6) due to higher mesomeric effect of –Br, as has been described in the literature [18,38]. From the experimental data above we can conclude that *p*–substitution of the acetophenone (electrodonating or

Table 1: Transfer hydrogenation of different ketones using catalyst **1**.

Entry	Substrate	Conv. (%)	Time, h	TOF (h^{-1})
1		100	2.5	158
2		90	8	73
3		81	24	13
4		89	18	20
5		100	5	79
6		61	24	10

Reaction conditions: ketone (2 mmol), catalyst (0.25 mmol%), KOH (10 mmol%) Temperature: 83 °C, hydrogen donor: 2-propanol. Conversion was monitored by GC-MS analysis, as well ^{1}H-NMR, and are average of two runs, time: h, TOF: h^{-1}

withdrawing nature) significantly influences the catalytic behavior of **1** (entries 3, 4 and 6). Although the new pre-catalyst **1** does not feature an ancillary N–H functional group in its coordination sphere, such as the well known Ru(II) *N*-tosylethylenediamine complexes of Noyori et al. [13], it is quite active and successfully catalyzes the transfer hydrogenation of a number of substrates as shown above.

The *cis*-[RuCl$_2$(PPh$_3$)$_2$(bipy)] catalyst reported some years ago [18] that is structurally related to the one presented in this work, exhibits a 50% reduction of acetophenone to 1-phenhyethanol after 24 h at ambient temperature. In the presence of hydrogen. however, the catalytic activity increases significantly (90%) achieving a TOF of 280 h^{-1} (0.5 h) upon heating over 2.5 h. It is to be mentioned that the presence of molecular hydrogen was not necessary for the catalytic activity of **1**.

As far as the mechanism of transition metal catalyzed transfer hydrogenation of ketones used in this study is concerned, presumably a Ru(II)-hydride species is the catalytically active species [39]. Optimization of the reaction conditions is under way including adjusting reaction temperature, reaction time and molar ratios among the catalyst, the base and the substrate. Currently, we are working to further investigate the nature of the active catalyst along with the preparation of new pre-catalysts for transfer hydrogenation of C=O polar bonds.

4 Conclusions

In summary, a ruthenium triphenylphospine complex bearing the bidentate ligand 2-(2’-pyridyl)quinoline was prepared in a one pot high yield synthetic procedure and was characterized spectroscopically. The resulting complex *cis*-[RuCl$_2$(PPh$_3$)$_2$(L1)] (**1**) is an active pre-catalyst in the transfer hydrogenation of ketones. The catalytic experiment was performed in the substrate/catalyst/ base molar ratio of approximately 400/1/40 in the absence of molecular hydrogen. The catalytic activity of (**1**) displayed comparable quantitative conversions for benzophenone and 4-chloroacetophenone within a time period ranging from 2.5 to 5 h. The work described here also reveals that the presence of base (*i*PrOK) was essential for an efficient conversion of the substrate to the corresponding alcohol. The synthesis of other new Ru(II) complexes incorporating phosphine ligands and their application in transfer hydrogenation reactions is currently underway. Studies of the catalytic behavior of these substances to a number of different substrates and further improvement of the experimental conditions (reaction time, higher substrate to catalyst molar ratios, etc.) will enable us to collect valuable information about the rational design of more potent catalysts in the future.

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References

[1] Han Ang, W., Dyson P. J., Classical and Non-Classical Ruthenium-Based Anticancer Drugs: Towards Targeted Chemotherapy, Eur. J. Inorg. Chem., 2006, 20, 4003-4018.

[2] Dragutan I., Dragutan V., Demonceau A., Editorial of Special Issue Ruthenium Complex: The Expanding Chemistry of the Ruthenium Complexes, Molecules 2015, 20, 17244-17274.

[3] Spiccia L., Deacon G. B., Kepert C. M., Synthetic routes to homoleptic and heteroleptic ruthenium(II) complexes incorporating bidentate imine ligands, Coord. Chem. Rev., 2004, 248, 1329-1341.

[4] Crabtree, R. H., The Organometallic Chemistry of the Transition Metals, 6th ed.; John Wiley &Sons, 2014.

[5] Balzani V., Bergamini G., Marchioni F., Ceroni P., Ru(II)-bipyridine complexes in supramolecular systems, devices and machines. Coord. Chem. Rev., 2006, 250, 1254-1266.

[6] Balzani V., Juris A., Venturi M., Campagna S., Serroni S., Luminescent and Redox-Active Polynuclear Transition Metal Complexes, Chem. Rev., 1996, 96, 759-834.

[7] Clarke M. J., Ruthenium metallopharmaceuticals, Coord. Chem. Rev., 2003, 236, 209-233.

[8] Bozic-Weber B., Constable E. C., Housecroft C. E., Light harvesting with Earth abundant d-block metals: Development of sensitizers in dye-sensitized solar cells (DSCs), Coord. Chem. Rev., 2013, 257, 3089-3106.

[9] Vougioukalakis G. C., Philippopoulos A. I., Stergiopoulos T., Falaras P., Contributions in the development of ruthenium-based sensitizers for dye-sensitized solar cells, Coord. Chem. Rev., 2011, 255, 2602-262.

[10] Gade L.H., Hofmann P., Molecular Catalysts: Structure and Functional Design; Wiley-VCH: Weinheim, Germany, 2014.

[11] Wang D., Astruc D., The Golden Age of Transfer Hydrogenation, Chem. Rev., 2015, 115, 6621-6686.

[12] Zassinovich G., Mestroni G., Gladiali S., Asymmetric hydrogen transfer reactions promoted by homogeneous transition metal catalysts, Chem. Rev., 1992, 92 , 1051-1069.

[13] Noyori R., Ohkuma T., Asymmetric Catalysis by Architectural and Functional Molecular Engineering: Practical Chemo- and Stereoselective Hydrogenation of Ketones, Angew. Chem. Int. Ed., 2001, 40, 40-73.

[14] Chowdhury R. L., Backvall J.-E., Efficient ruthenium-catalysed transfer hydrogenation of ketones by propan-2-ol, J. Chem. Soc., Chem. Commun., 1991, 1063-1064.

[15] Clapham S. E., Hadzovic A., Morris R. H., Mechanisms of the H2-hydrogenation and transfer hydrogenation of polar bonds catalyzed by ruthenium hydride complexes, Coord. Chem. Rev., 2004, 248, 2201-2237.

[16] Baratta W., Baldino S., Calhorda M. J., Costa P. J., Esposito G., Herdtweck E., et al., CNN Pincer Ruthenium Catalysts for Hydrogenation and Transfer Hydrogenation of Ketones: Experimental and Computational Studies, Chemistry-A European Journal., 2014, 20, 13603-13617.

[17] Aydemir M., Baysal A., Ruthenium-catalyzed transfer hydrogenation of aromatic ketones with aminophosphine or bis(phosphino)amine ligands derived from isopropyl substituted anilines, Polyhedron 2010, 29, 1219-1224.

[18] de Araujo M. P., de Figueiredo A. T., Bogado A. L., Von Poelhsitz G., Ellena J., Castellano E. E., Donni., et al., Ruthenium Phosphine/Diimine Complexes: Syntheses, Characterization, Reactivity with Carbon Monoxide, and Catalytic Hydrogenation of Ketones, Organometallics 2005, 24, 6159-6168.

[19] Zucca A., Cordeschi D., Maidich L., Pilo M. I., Masolo, E., Stoccoro S., et al., Rollover cyclometalation with 2-(2'-pyridyl) quinoline, Inorg. Chem., 2013, *52*, 7717-7731.

[20] Qaseer H., Rhodium(III) Complexes with 2-(2'-Pyridyl)quinoline. Synthesis and Spectroscopic Characterization, Croat. Chem. Act., 2005, 78, 79-84.

[21] Philippopoulos A. I., Kolovou E., Tsierkezos N. G., Paulidou A., Mavridis I. M., Batistatou S., et al., Synthesis and characterization of the ruthenium(II) triphenylphosphine complex cis-[$RuCl_2(PPh_3)_2L$] (L = 2-(2′-pyridyl)quinoxaline ligand) for the catalytic hydrogenation of ketones, Glob. J. Inorg. Chem., 2011, 2, 92-101.

[22] Hallman P. S., Stephenson T. A., Wilkinson G., Tetrakis(triphenylphosphine)dichlororuthenium(II) and Tris(triphenylphosphine)dichlororuthenium(II), Inorg. Synth., John Wiley & Sons, 2007.

[23] Zacharopoulos N.; Synthesis and characterization of Ru(II) complexes and their Application as catalysts in transfer hydrogenation reactions, Master thesis, National and Kapodistrian University of Athens, Athens, Greece, 2016.

[24] The molar conductivities (Λ_M / S cm^2 mol^{-1}) were calculated from the experimental conductivities (k / S cm^{-1}) and the concentrations (C/mol L^{-1}) of the solutions using the equation $\Lambda_M = 10^3 k/C$.

[25] Geary W. J., The use of conductivity measurements in organic solvents for the characterisation of coordination compounds, Coord. Chem. Rev., 1971, 7, 81-122.

[26] Archer M. D., Gasser R. P. H., Electrolyte solutions in dimethyl sulphoxide. Part 2.-Caesium iodide, J. Chem. Soc., Faraday Trans., 1966, 62, 3451-3458.

[27] Arrington D. E., Griswold E.; Conductance study of quaternary ammonium halides in dimethyl sulfoxide at 25 deg, J. Phys. Chem. A 1970, 74, 123-128.

[28] Tsierkezos N. G., Philippopoulos A. I., Conductometric and voltammetric studies on the bis(triphenyl phosphine) ruthenium(II) complex, cis-[$RuCl_2(L)(PPh_3)_2$], where L: 2-(2′-pyridyl)quinoxaline, Inorg. Chim. Acta 2009, 362, 3079-3087.

[29] Tsierkezos N. G., Ritter U., Philippopoulos A. I., Schröder D., Electrochemical studies of the bis (triphenyl phosphine) ruthenium(II) complex, cis-[$RuCl_2(L)(PPh_3)_2$], with L = 2-(2′-pyridyl)quinoxaline, J. Coord. Chem., 2010, 63, 3517-3530.

[30] Basuli F., Kumar Das A., Mostafa G., Peng S.-M., Bhattacharya S., Chemistry of ruthenium with some phenolic ligands: synthesis, structure and redox properties, Polyhedron 2000, 19, 1663-1672.

[31] Meyer T. J., Photochemistry of metal coordination complexes: metal to ligand charge transfer excited states, Pure Appl. Chem., 1986, 58, 1193–1206.

[32] Klassen D. M., Excited states of mixed ligand complexes of ruthenium (II) with 2-(2-Pyridyl) quinoline and 2,2-biquinoline, Chem. Phys. Letters 1982, 93, 383-386.

[33] Faiz J., Philippopoulos A. I., Kontos A. G., Falaras P., Pikramenou Z., Functional Supramolecular Ruthenium Cyclodextrin Dyes for Nanocrystalline Solar Cells, Adv. Funct. Mater., 2007, 17 , 54-58.

[34] Batista A. A., Santiago M. O., Donnici C. L., Moreira I. S., Healy P. C., Berners-Price S. J., et al., Electrochemical

and spectroscopic studies on $RuCl_2(PPh_3)_2(N)_2$ and $RuCl_2(PPh_3)_2(N–N)$ complexes (N = pyridine derivatives and N–N = phenanthroline or bipyridine derivatives). X-ray structure of $RuCl_2(PPh_3)_2$(phen), Polyhedron 2001, 20, 2123-2128.
[35] Ogweno A. O., Ojwach S. O., Akerman M. P., (Pyridyl) benzoazole ruthenium(II) and ruthenium(III) complexes: role of heteroatom and ancillary phosphine ligand in the transfer hydrogenation of ketones, Dalton Trans., 2014, 43, 1228-1237.
[36] Aydemir M., Baysal, A., Özkar S., Yıldırım L. T., Ruthenium complexes of aminophosphine ligands and their use as pre-catalysts in the transfer hydrogenation of aromatic ketones: X-ray crystal structure of thiophene-2-(N-diphenylthiophosphino)methylamine, Polyhedron 2011, 30, 796-804.
[37] Gao J.-X., Ikariya T., Noyori R., A Ruthenium(II) Complex with a C2-Symmetric Diphosphine/Diamine Tetradentate Ligand for Asymmetric Transfer Hydrogenation of Aromatic Ketones, Organometallics 1996, 15, 1087-1089.
[38] Standfest-Hauser, C., Slugovc, C., Mereiter, K., Schmid, R., Kirchner K., Xiao, L., Weissensteiner W., Hydrogen-transfer catalyzed by half-sandwich Ru(ii) aminophosphine complexes, J. Chem. Soc., Dalton Trans., 2001, 2989-2995.
[39] Clapham S. E., Hadzovic, A., Morris R. H., Mechanisms of the H2-hydrogenation and transfer hydrogenation of polar bonds catalyzed by ruthenium hydride complexes, Coord. Chem. Rev., 2004, 248, 2201-2237.