Research Article

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

DOI 10.1515/chem-2016-0034
received November 15, 2016; accepted December 5, 2016.

Abstract: The ruthenium(II) complex cis-[RuCl₂(PPh₃)₂(L)] (1) where L₁ = 2-(2’-pyridyl)quinoline was obtained in high yield from the reaction of [RuCl₂(PPh₃)₃] with L₁. The new compound was characterized by different spectroscopic methods including FT-IR, UV-Vis, NMR (¹H, ³¹P) spectroscopy along with a mass spectrometric analysis (ESI-MS) and conductivity measurements. ³¹P NMR spectroscopy provided evidence that the two PPh₃ 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 [RuCl₂(PPh₃)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- [RuCl₂(PPh₃)₂(L)] (L = 2-(2’-pyridyl)quinoxaline) complex

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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. \(^{1}\)H and \(^{31}\)P[\(^{1}\)H] 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[\(^{1}\)H] NMR spectra were calibrated against an external 85% aqueous H\(_2\)PO\(_4\) 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\(_2\)Cl\(_2\). 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, 30 m × 0.25 mm 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·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\(_3\))] (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 x 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) x 1.5(H2O), C19H26Cl2N2O4P2Ru: 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), 1240 (w), 1191 (w), 1156 (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): λmax (CHCl₃) = 534 (1212), 352 (957), 325 (6607); λmax (CH₂Cl₂) = 537 (957), 352 (2738), 334 (5868). ν(C-Cl) (cm⁻¹): 534 (957), 352 (2738), 334 (5868).

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 [RuCl₂(PPh₃)₂] in dry acetone affords the ruthenium(II) complex cis-[RuCl₂(PPh₃)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 (CHCl₃ and CH₂Cl₂) giving purple colored solutions. In solvents with coordinating ability, such as CH₃OH, CH₂CN 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⁻¹ mol⁻¹ in CH₂CN and higher than 123 S cm⁻¹ mol⁻¹ in CH₃OH [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 5h of dissolution, reaching a plateau. The determined Λ_m value of 42 S cm⁻¹ mol⁻¹ is in the expected range for 1:1 electrolytes in DMSO [25-27]. In CHCl₃ and CH₂Cl₂, 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-[RuCl₂(PPh₃)L₁] (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 (¹H, ³¹P). The molecular composition was unequivocally confirmed by mass
spectrometric analysis (ESI-MS). Thus, upon dissolution in methanol, dissociation of one chloride ligand occurs immediately, generating the [RuCl(PPh3)3]1+ 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 PPh3 ligands is observed resulting in the formation of the [RuCl(PPh3)2]1+ 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 PPh3 group. The three characteristic strong bands at 746, 698 and 518 cm−1 could be attributed to the presence of the PPh3 ligand [30]. Absorption spectra of 1, recorded in CH3Cl and in CHCl3, are depicted in Fig. 1. In dichloromethane the high energy band at 334 nm is assigned to n→* 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 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 FT-IR spectrum of one of the PPh3 ligands resulting in the 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.

13P{1H} NMR spectroscopy provided strong evidence concerning the position of the PPh3 ligands around the metal core. The presence of a single resonance at δ = 20.54 ppm, strongly suggests that the two PPh3 ligands are in the trans configuration. This signal appears in the expected δ range, similar to that of the structurally related compounds cis-[RuCl2(PPh3)2(bipy)] (δ = 21.53 ppm; bipy = 2,2’-bipyridine) and cis-[RuCl2(PPh3)2(phen)] (δ = 23.26 ppm; phen = 1,10-phenanthroline) [18] respectively. The presence of other geometric isomers was not detected. 13P{1H} NMR spectroscopy also revealed that this compound is stable in CDCl3 over a period of 24 h. This stability is consistent with the conductivity measurements performed in the same solvent (vide supra). In DMSO-d6, however, the 13P{1H} 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 PPh3, 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(PPh3)L(DMSO)]Cl. In fact, integration of the signal at δ = 31.84 ppm is equal to that of free PPh3. Based on the results of a 13P{1H} 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(PPh3)L(DMSO)]Cl. PPh3 is then released,
giving the DMSO adduct \([\text{RuCl}(\text{PPh}_3)L(\text{DMSO})_2]\)Cl as is shown in equation 1.

\[
\text{[RuCl}_2(\text{PPh}_3)_2(L)_2] + 2 \text{DMSO} \rightarrow \text{[RuCl(PPh}_3)(L)(\text{DMSO})_2]Cl + \text{PPh}_3
\]

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 \([\text{RuCl}_2(\text{PPh}_3)_2L]\) (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).

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 (iPrOK) 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 acetoephone and its derivatives substituted with electron-donating (4-methoxy acetoephone) 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-chloroacetoephone (100%) and acetoephone (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.

It is clearly seen that an induction period is required for the transfer hydrogenation of acetoephone and 4-chloroacetoephone substrates. The TOF's achieved by complex 1 vary from 158 h$^{-1}$ for benzophenone to 79 h$^{-1}$ (4-chloroacetoephone) and 73 h$^{-1}$ (acetoephone). Notably the presence of a 4-chloro substituent in the \(para\) position of acetoephone enhances the catalytic activity of 1 in comparison to unsubstituted acetoephone (entry 5). On the other hand, a drop of the activity to 81% is observed for the 4-methoxy acetoephone derivative (entry 2). These findings are in accord with literature reports since electron donor-substituents on acetoephone accelerates the reaction [18,36] while a decrease in the catalytic activity is expected with electron withdrawing groups [37]. However, 4-fluoroacetoephone exhibited a conversion of 89%, slightly lower than that of acetoephone. For 4-bromoacetoephone 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 acetoephone (electrodonating or
Ruthenium(II) complex as catalyst for the transfer hydrogenation of ketones

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 triphenylphosphine 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-[RuCl₂(PPh₃)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 (iPrOK) was essential for an efficient conversion of the substrate to the corresponding alcohol. 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.

Acknowledgements: A.I. Philippopoulos would like to thank Prof. Dr. A.C. Filippou of the Chemistry Department of the University of Bonn for the elemental analyses measurements. Prof. Athanassios Giannis from the University of Leipzig is highly acknowledged for the Mass spectrometry measurements. N. Zacharopoulos would like to thank Ph.D candidate A. Peppas for recording the NMR spectra.

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 ¹H-NMR, and are average of two runs, time: h, TOF: h⁻¹
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