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Pyridyl based ruthenium(II) catalyst precursors and their dihydride analogues as the catalytically active species for the transfer hydrogenation of ketones

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Dedicated to Professor S. Perlepes on the occasion of his 65th birthday.

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ABSTRACT

In this study we describe the one-pot and high yield synthesis of the ruthenium(II) complex *cis*-dichloride $[RuCl_2(PPh_3)_2(L1)]$ (L1 = 4-methyl-2-(2′-pyridyl)quinoline) (1). The solid state structure of L1 is described. The catalytic activity of 1 in the transfer hydrogenation of various ketones by 2-propanol at 82 °C, has been studied and compared with the activity of the known catalyst precursors *cis*-$[RuCl_2(PPh_3)_2(L2)]$ (L2 = 2-(2'-pyridyl)quinoline) (2), *cis*-$[RuCl_2(PPh_3)_2(L3)]$ (L3 = 2-(2′-pyridyl)quinoxaline) (3) and *cis*-$[RuCl_2(PPh_3)_2(bipy)]$ (bipy = 2,2′-bipyridine) (4). The ruthenium monohydride complex $[RuHCl(PPh_3)_2(L3)]$ 3-H (Cl *cis* to H) was prepared from the reaction of 3 with 2.5 equivalents of a KO*i*Pr solution. Reaction of 3 with 10 equivalents of KO*i*Pr yields the cis-$[RuH_2(PPh_3)_2(L3)]$ (3-H_2). Treatment of 1, 2 and 4 with KO*i*Pr (in excess) affords the ruthenium cis-dihydride complexes $[RuH_2(PPh_3)_2(L1)]$ (1-H_2), $[RuH_2(PPh_3)_2(L2)]$ (2-H_2) and $[RuH_2(PPh_3)_2(bipy)]$ (4-H_2). The formation of 1-H_2, 2-H_2, 3-H_2 and 4-H_2 is supported by NMR spectroscopic data. The *cis*-dihydrides 1-H_2 to 4-H_2 catalyze successfully the transfer hydrogenation of benzophenone to benzhydrol in the absence of a base, suggesting that presumably the active catalyst is a ruthenium dihydride complex (RuH_2). Catalyst 1 has been potentially recovered and reused at least four times.

1. Introduction

Undoubtedly hydrogenation is a fundamental chemical process that holds scientific interest continuous over the last decades [1,2]. Generally it is divided into classical hydrogenation and to transfer hydrogenation (TY).

The latter is an alternative to standard hydrogenation where 2-propanol or formic acid are used as hydrogen donors different to molecular hydrogen. This is a benign and eco-friendly method where the use of high pressurized molecular H_2 is not required and in general the hydrogen donors are readily available [3].

A breakthrough in the field includes the work of Noyori and coworkers with the development of new enantioselective transfer hydrogenation ruthenium(II) catalysts $[(\eta^6\text{-arene})Ru(Tsdpen)Cl]$; (H)Tsdpen = N-*p*-tosyl-1,2-diphenylethylenediamine [4]. The so-called Noyori type catalysts are mainly constituted of organic molecules modified by appropriate N—H functional groups. In this respect, the term "metal–ligand bifunctional catalysis" has been proposed, opening a new field in the area of homogenous catalysis.

The tremendous impact of this chemical process, not only in academia, is outlined by the increased number of chemical industries (pharmaceutical, agrochemical, fragrance etc) that produce fine chemicals for a variety of practical applications [5,6].

From the mechanistic point of view seminal contributions have been reported by Bäckvall [7], Morris [8] along with recent reports of Baratta [9]. So far, two well described mechanisms have been proposed, namely the inner sphere and the outer sphere mechanism differentiating depending on the substrate's interaction with the metal center [10]. Reinvestigation of the classical Noyori's "metal–ligand bifunctional catalysis mechanism" [11] has been recently proposed demonstrating that this issue remains a hot research topic [12].

An excellent review paper reported by Astruc [13] is highlighting the recent advances in the transfer hydrogenation reactions using transition metal catalysts.

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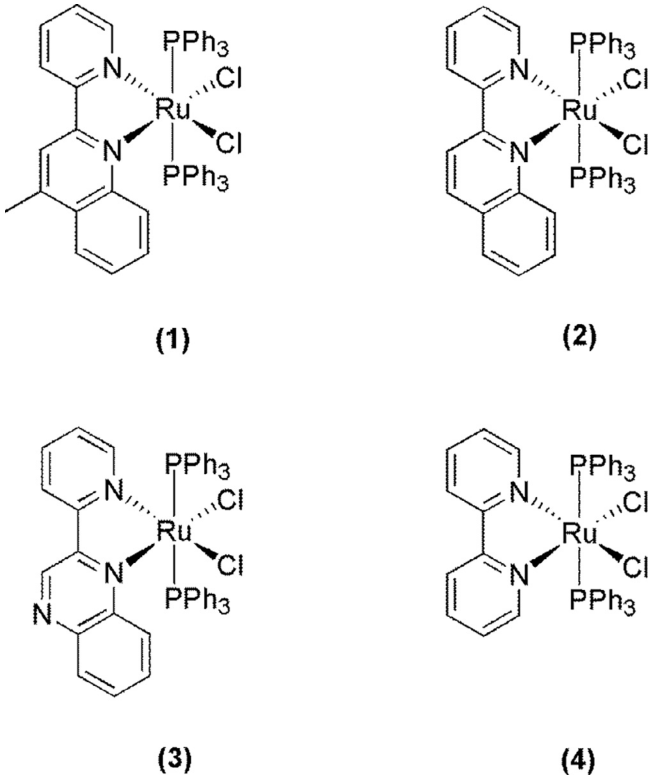

(1) (2)

(3) (4)

Scheme 1. Structures of the complexes **1**–**4** described in this work.

Among the plethora of prospective metal organic compounds for transfer hydrogenation reactions, ruthenium(II) complexes containing phosphine ligands constitute a special class that have been mainly proposed as catalyst precursors thereof [14].

As part of our ongoing research interest, we have started a systematic approach towards the preparation of new ruthenium(II) based catalyst precursors incorporating substituted pyridyl-quinoline ligands for the transfer hydrogenation of polarized unsaturated compounds (ketones, etc) [15,16].

With this in mind, we set out to examine the reaction of $[RuCl_2(PPh_3)_3]$ with 4-methyl-2-(2′-pyridyl)quinoline abbreviated as L1 within the text. Herein, we report on the synthesis and spectroscopic characterization of the new ruthenium(II) complex of the general structure *cis*-dichloride $[RuCl_2(PPh_3)_2(L1)]$ (**1**).

Complex **1** was evaluated in the transfer hydrogenation of benzophenone and acetophenone derivatives in 2-propanol at reflux in the presence of KOH. A comparison with the activity of the known catalyst precursors *cis*-dichloride $[RuCl_2(PPh_3)_2(L2)]$ (L2 = (2-(2′-pyridyl)quinoline) (**2**), *cis*-dichloride $[RuCl_2(PPh_3)_2(L3)]$ (L3 = 2-(2′-pyridyl)quinoxaline) (**3**) and *cis*-dichloride $[RuCl_2(PPh_3)_2(bipy)]$ (bipy **=** 2,2′-bipyridine) (**4**) is also reported (Scheme 1). Reactions of **1**–**4** with KO*i*Pr in excess provide RuH_2 species that have been isolated, characterized by NMR spectroscopy and proposed as the active catalysts.

2. Materials and methods

2.1. Reagents and equipments

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; diethyl ether was pre-dried over $CaCl_2$ and then distilled over 4 Å molecular sieves under argon while hexanes were dried over 4 Å molecular sieves. C_6H_6 was dried upon standing over 4 Å molecular sieves and distilled prior to use. The substrates acetophenone, 4-methoxyacetophenone, 4-fluoroactophenone, 4-chloroacetophenone, 4-bromoacetophenone and benzophenone were purchased from Alfa Aesar, Sigma Aldrich and Acros Organics and used as received. The starting materials $[RuCl_2(PPh_3)_3]$ [17], *cis*-dichloride $[RuCl_2(PPh_3)_2(L2)]$ (L2 = 2-(2′-pyridyl)quinoline) (**2**) [16], *cis*-dichloride $[RuCl_2(PPh_3)_2(L3)]$ (L3 = 2-(2′-pyridyl)quinoxaline) (**3**) [15,18] and *cis*- dichloride $[RuCl_2(PPh_3)_2(bipy)]$ (bipy **=** 2,2′-bipyridine) (**4**) [19] were prepared according to literature procedures. The synthesis of L1 = 4-methyl-2-(2′-pyridyl) quinoline was made by slight modifications of the published procedure [20]. Infrared spectra were measured on a Shimadzu IR Affinity-1 spectrometer as potassium bromide pellets or Nujol mulls 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, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were recorded at 298 K on a Varian 300 MHz, on a Bruker Avance AV-400 MHz and/or on a Varian 200 MHz spectrometers respectively using $CDCl_3$ and C_6D_6 as the solvent containing TMS as internal standard, at 25 °C. *J* values are given in Hz. The ^{31}P NMR spectra were calibrated against an external 85% aqueous H_3PO_4 solution, which was filled in a capillary 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 CH_2Cl_2. 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) as previously reported [15,16].

2.2. Synthetic procedure and spectral data

2.2.1. Synthesis of 4-methyl-2-(2′-pyridyl)quinoline (*L1*)

In a round bottom two necked flask and under argon, 2-aminoacetophenone (203 mg, 1.5 mmol) and 2-acetylpyridine (182 mg, 1.5 mmol) were dissolved in dry ethanol (5 mL), followed by the addition of 3 drops of an aqueous KOH solution (66% w/w). The mixture was refluxed for 18 h and then was cooled at ambient temperature. The reaction mixture was treated with aqueous HCl solution (1 M) until neutral pH and then ethanol was rotary evaporated. The aqueous phase was extracted by CH_2Cl_2 (3×10 mL) and the organic layer was treated with anhydrous $MgSO_4$, filtered off and the clear filtrate was evaporated to dryness to give a yellow oily residue. This was purified by column chromatography on silica gel ($R_f = 0.7$, ethyl acetate:petroleum ether 4:1 (v:v)) affording a light yellow solid. Yield: 55% (180 mg). M.p. = 56 °C. IR (KBr, $\tilde{\nu}$, cm^{-1}): 3061 (w, C—H arom), 2918 (w, C—H aliph), 1597 (vs ν (C═N)), 1434 (s, ν (C═C)), 798 (vs γ(C—H)), 781 (vs γ (C—H)), 760 (vs γ (C—H)), 741 (vs γ (C—H). ^1H NMR ($CDCl_3$, 300 MHz, 298 K) δ (ppm): 2.81 (s, 3H, CH_3), 7.36 (t, $^3J_{HH} = 6$ Hz, H4′), 7.58 (t, $^3J_{HH} = 9$ Hz, H5′), 7.73 (t, $^3J_{HH} = 9$ Hz, H6), 7.88 (t, $^3J_{HH} = 6$ Hz, H7), 8.03 (d, $^3J_{HH} = 9$ Hz, H8), 8.20 (d, $^3J_{HH} = 9$ Hz, H5), 8.42 (s, H3), 8.66 (d, $^3J_{HH} = 6$ Hz, H6′), 8.75 (d, $^3J_{HH} = 6$ Hz, H3′). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz, 298 K) δ(ppm): 156.50, 155.67, 149.09, 147.81, 145.07, 136.96, 130.39, 129.26, 128.28, 126.52, 123.98,