

A NEW HETEROBIMETALLIC RUTHENIUM(II) COMPLEX: SYNTHESIS, SPECTRAL STUDIES AND CATALYTIC ACTIVITY POTENTIAL IN THE TRANSFER HYDROGENATION OF KETONES

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Abstract

A new heterobimetallic ruthenium(II) complex with general formula $[\text{Ru}(\text{NCCH}_3)_2(\text{P}(\text{OMe})_2\text{Ph})_2(\text{dppf})][\text{BF}_4]_2$. $\{\text{NCCH}_3 = \text{acetonitrile } \text{P}(\text{OMe})_2\text{Ph} = \text{dimethylphenylphosphonite, dppf} = 1,1'\text{-bis}\{\text{diphenylphosphino}\}\text{ferrocene}\}$ was synthesized from a one pot reaction of $[\text{Ru}(\text{COD})-(\text{NCCH}_3)_4][\text{BF}_4]_2$, dimethylphenylphosphonite and 1,1'-bis{diphenylphosphino}ferrocene in dichloromethane under continuous stirring. The complex was characterized by NMR ($^{31}\text{P}\{^1\text{H}\}$, ^1H and ^{13}C), vibrational spectroscopy (FTIR) and elemental analysis. Catalytic performance of the complex in the transfer hydrogenation of cyclohexanone was investigated. An 80% conversion was achieved at a substrate to catalyst ratio of 1250 with 98% selectivity.

Keywords: Heterobimetallic ruthenium, transfer hydrogenation, cyclohexanone, 1,1'-bis{diphenylphosphino}ferrocene, dimethylphenylphosphonite.

1. Introduction

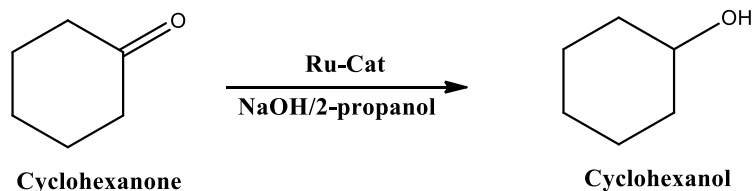
A wide range of active ruthenium compounds have been prepared using the polymer dichlorocyclooctadieneruthenium(II) ($[\{\text{Ru}-\text{Cl}_2(\text{COD})\}_x]$) as suitable precursor in the past [1-3]. Although the polymer itself is highly insoluble in most organic solvents; several techniques have been developed to obtain soluble derivatives that can be eventually applied to generate active ruthenium compounds [1,4]. One of such derivatives is $[\text{Ru}(\text{COD})(\text{NCCH}_3)_4][\text{BF}_4]_2$ which has been demonstrated to have a great potential as precursor for ruthenium organometallic compounds [5-7]. Conventional hydrogenation procedure involves the use of hydrogen and reducing agents under high pressure. Waste disposal from such reactions becomes very dangerous since these reducing agents are harmful to the environment [8]. Direct transfer of hydrogen to substrates from different hydrogen donor ligands has therefore become an interesting alternative, and a wide variety of organic functional groups have been transformed using transition metal catalysts [9]. Reduction of ketones, especially the enantioselective hydrogenation of prochiral ketones into

chiral alcohols via transfer hydrogenation procedure continue to receive continued attention [10,11]. Rhodium complexes are the most widely employed in this regard, but a number of ruthenium complexes with phosphinite and phosphonate ligands in particular have been applied with proven successes [8,12]. Generally, metal complexes bearing chiral bidentate ligands containing nitrogen donating atoms are the most widely employed in the transfer hydrogenation reactions [12]. Chiral bidentate ligands when compared to the monodentate ones are more expensive and not readily available. A highly efficient transfer hydrogenation catalyst with monodentate dimethylphenylphosphonite has been reported by our research group [12]. In this work, we report the reactivity of ruthenium starting material $[\text{Ru}(\text{COD})-(\text{CH}_3\text{CN})_4][\text{BF}_4]_2$ with 1,1'-bis{diphenylphosphino}ferrocene (dppf) and dimethylphenylphosphonite and its catalytic activity in the transfer hydrogenation of simple ketone, cyclohexanone.

2. Materials and methods

2.1. Materials

The chemical reagents used in this study were analytical grade, commercially sourced



Scheme 1: Schematic representation of the transfer hydrogenation reaction

3. Results and discussion

Treatment of the ruthenium(II) complex $[\text{Ru}(\text{COD})(\text{NCCH}_3)_4][\text{BF}_4]_2$ with 2 equivalents of $\text{P}(\text{OMe})_2\text{Ph}$ in dichloromethane at room temperature and in the presence of 1 equiv of dppf, generates the corresponding mononuclear bimetallic complex **3** as yellow crystalline solids. The compound is air-stable with a sharp melting point and the elemental analysis data agreed with the proposed stoichiometry. The proposed molecular structure is shown in Fig. 1.

The complex has been characterized by means of standard spectroscopic techniques (IR and ^1H , $^{31}\text{P}\{^1\text{H}\}$, and $^{13}\text{C}\{^1\text{H}\}$ NMR) and elemental analysis. The IR spectrum of **3** contained weak $\nu(\text{CN})$ absorption band at 2062 cm^{-1} . The C_5H_4 of the dppf group displays two signals in the ^1H NMR spectrum of **3** at 3.9 and 4.1 ppm in the expected ratio of 4:4 [15]. The observed singlet at 2.48 ppm is assigned to the protons on the methoxy group on the $\text{P}(\text{OMe})_2\text{Ph}$ ligand while the acetonitrile methyl protons resonances appeared as a singlet at 1.50 ppm.

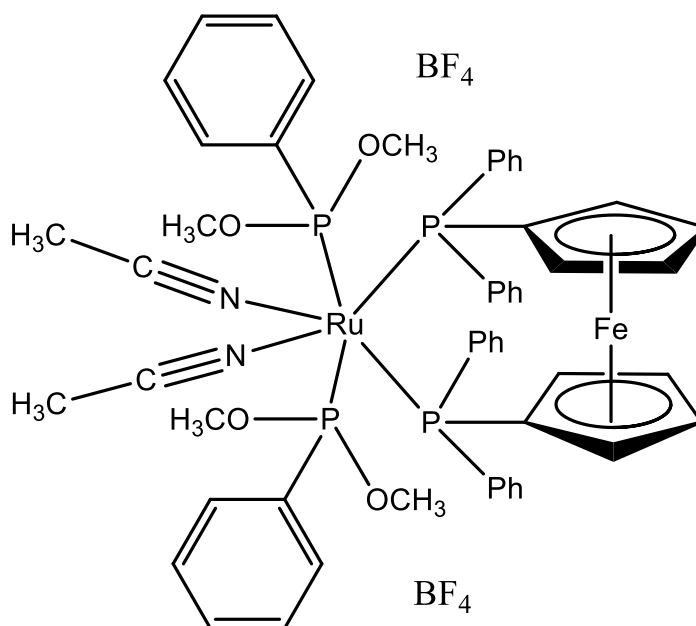


Fig. 1: Proposed chemical structure of 3

3.1. Structural characterization of 3

The phenyl group protons in both $\text{P}(\text{OMe})_2\text{Ph}$ and dppf appeared as a broad singlet at 7.20 ppm an indication that all the phenyl protons in **3** are equivalent. The C_5H_4 carbons on dppf were observed as four distinct lines between 72.60 and 76.97 ppm in its ^{13}C NMR spectrum in accord with literature values [15]. The methyl group on the acetonitrile appeared at 4.18 ppm while

the cyanide groups on the acetonitrile ligands appeared at the expected downfield chemical shifts at 128.28 ppm in the $^{13}\text{C}\{^1\text{H}\}$ NMR of **3**. The observed singlet signal at 26.54 ppm in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **3** is assigned to the equivalent phosphorus nuclei of the dppf ligand while a sharp signal at 154.19 ppm is assigned to the phosphorous atoms in the $\text{P}(\text{OMe})_2\text{Ph}$ ligands [12].

3.2. The catalytic transfer hydrogenation reactions

The isolated complex has a simple synthetic route and it is stable both in air and solution, this prompted us to investigate its catalytic activity in the transfer hydrogenation of cyclohexanone as a model study. This procedure for the reaction is as represented in Scheme 1, where the hydrogen for the transfer hydrogenation of cyclohexanone is obtained from isopropanol. In the presence of catalytic amounts of sodium hydroxide base in 2-propanol at 82°C, the complex efficiently catalyzed the hydrogenation of cyclohexanone to cyclohexanol. At a substrate to catalyst ratio of 1250, an 80% conversion was achieved with 98% selectivity for cyclohexanol in 4 h. In the absence of a base, no hydrogenation was observed.

The detailed mechanism of this reaction has not been studied, but literature evidence showed that the NaOH base facilitates the formation of ruthenium alkoxide by abstracting proton of the alcohol and the alkoxide undergoes β -elimination to give ruthenium hydride intermediate as the active species [12]. The mechanism thus involved the ketone coordinating to the hydride-ruthenium intermediates and the observed effects seem to indicate that the hydride transfer from the metal to the coordinated ketone is the turnover-limiting step in the catalytic cycle [16].

Conclusions

The ruthenium-organonitrile derivative, $[\text{Ru}(\text{COD})(\text{NCCH}_3)_4][\text{BF}_4]_2$, was successfully prepared from the highly insoluble polymer $\{\text{RuCl}_2(\text{COD})\}_x$. The desired compound was then obtained from this precursor through ligand exchange reactions with 1,1-Bis(diphenylphosphino)ferrocene and dimethylphenylphosphonite. The complex is stable in air and successfully catalyzed the transfer hydrogenation of cyclohexanone to cyclohexanol under an inert atmosphere using 2-propanol as the hydrogen source. Work is ongoing to obtain the molecular structure of this compound. This study therefore developed a simple but highly efficient transfer hydrogenation catalyst, bis-

(acetonitrile)bis(dimethylphenylphosphonite)((1,1-Bis[diphenylphosphino]ferrocene)ruthenium(II).

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