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Ru(II) xantphos complex as an efficient catalyst in transfer hydrogenation of carbonyl compounds

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ABSTRACT

In the transfer hydrogenation of aromatic/aliphatic carbonyl compounds using *iso*-propanol–potassium hydroxide mixture as hydrogen donor, a mixed ligand Ru(II) complex, prepared from xantphos ligand and $RuCl_2(dmso)_4$, was examined. Besides, the solid state structure of the Ru (II) complex was determined using X-ray single crystallography. The catalytic reactivity of the complex was remarkable (up to 99%) and the catalyst showed more efficiency in the reduction of ketones than aldehydes.

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Phosphines and their derivatives have aroused much interest in the recent years because of their reactivity, structural novelty and catalytic activity [1–6]. Recent understanding within the catalytic systems and the relationship between ligand properties and catalytic performance will give access to more catalysts via rational design of the ligands. An important aspect to design the ligands is based on their natural bite angle, introduced by Casey and Whiteker [7] and is one of the most extensively applied parameter for diphosphines. The metal complexes containing large bite angle ligands such as xantphos, [9, 9dimethyl-4, 5-bis (diphenylphosphino) xanthenel, and others with a relatively similar moiety exhibit noticeable coordination chemistry along with catalytic activity [8-10]. Over the last decades, the ruthenium catalyzed reactions directed to organic synthesis have got much attention and a large number of highly efficient synthetic approaches are well documented in literature [11–17]. Recently, extensive research has been assigned to the improvement of rutheniumcatalyzed hydrogenation of unsaturated polar bonds such as aldehydes and ketones [18-20]. Ru-P^N^P and Ru-P^O^P systems were found to be active and selective catalytic systems for wide range of substrates. Looking for an efficient and easily accessible complex, bis (phosphine) and mixed donor phosphine-amine complexes Ru^{II}(P^N)

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and Ru^{II} (P^N^N) have showed highly efficient catalysts for the hydrogenation of esters to alcohols (or conversely, the dehydrogenative coupling of alcohols to form esters)[21,22]. More recently, xantphos pincer complexes of the Ru [23] have also been reported to catalyze the transfer hydrogenation of carbonyl bonds with a high efficiency. As part of our ongoing study, we report here the synthesis and characterization of a ruthenium (II) complex of xantphos 1, containing dimethyl sulfoxides and the catalytic activity of 1 was also investigated in transfer hydrogenation reaction of variety of carbonyl compounds.

1 was synthesized by simple reaction between xantphos and $RuCl_2$ (dmso)₄ in methylene chloride ([24] See Scheme 1).

Complex **1** crystallizes in a monoclinic system with space group $P2_1/n$ where the Ru atom is located at the center of a distorted octahedral environment formed by two P donor and one O atom of xantphos ligand, one S atom of dmso ligand and two Cl atoms. The selected bond lengths and bond angles are presented in Fig. 1.

The longer bond length of Ru1—P1 (2.3298(6) Å) compared with Ru1—P2 (2.2991(7) Å) may point to a weaker interaction in the former and is likely to be dissociated during catalytic reaction. However, Ru—S (2.1919(7) Å) is another alternative for cleavage in the catalytic cycle. The shorter Ru—O bond length (2.1587(17) Å) is the hardest choice for cleavage during catalytic cycle. The natural bite angle, 111.7° of the free xantphos ligand reduces to 105.48° (bite angle, P1—Ru1—P2) upon coordination. The complex **1** exhibits some interesting intermolecular interactions which stabilized the packing of **1**. The interactions between these molecules are presented by

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Scheme 1. Synthetic route for synthesis of complex 1.

dotted lines and summarized in Fig. 2. The monomeric units of **1** show intermolecular C—H...O, C—H... π and C—H...Cl interactions. These are considered as weak to medium hydrogen bonds [25,26]. The hydrogen bondings are principally observed between one of the H atoms of the phenyl ring of the xantphos ligand and the Cl atom of the complex. Also, an additional hydrogen bonding detected between one hydrogen atom of methylene chloride solvent and Cl atoms of the complex. Another hydrogen bonding between two units of the complex by means of two dmso ligands plays a significant role in stabilization of the packing of **1** (see Fig. 2).

Such interactions provide an additional stabilization to crystal consistency and are basically attributable to the supramolecular nature of most inorganics. The catalytic activity of **1** was investigated for transfer hydrogenation of carbonyl compounds. The complex **1** was found to be highly efficient in the reduction of aldehyde and ketones to their corresponding alcohols (Scheme 2). Even though the large number of Ru(II) catalysts reported for this particular transformations, the use of Ru^{II} (P^O^P) systems are quite rare [27].

In the present study, the catalytic conversions of selected aldehydes and ketones are found in the range 84–>99% within the reaction time of 8–24 h (See Table 1). Although the catalytic activity of the complex displays slightly lower efficiency for the hydrogenation of aldehydes, it, however, shows higher activity for hydrogenation of ketones with respect to similar reported catalysts [23].In addition, *iso*–PrOH/KOH was used as hydrogen source because of the higher solubility of KOH in *iso*– PrOH rather than the cheaper sodium hydroxide. Notably, the catalytic efficiency of **1** decreased in presence of the large substituents on the substrate. This might be due to the steric hindrance caused by the bulky xantphos ligand around the metal center through substrate binding. These consequences can be justified according to the proposed mechanism represented in Scheme 3. As can be seen, the substrate should be coordinated to the metal center for further migratory insertion step. Ketones have more electron density on their oxygen due to the existence of alkyl groups. Satisfactorily, ketones with small alkyl groups would be better coordinated to the Ru center and can be reduced remarkably.

On the whole, the catalytic activity of **1** is higher than other structurally similar Ru (II) complexes, which may be due to the presence of the dmso ligand. In conclusion, the synthesis and characterization of the novel Ru(II) complex **1** has been performed.





Fig. 1. The coordination-sphere labeled diagram of [Ru (*P*,*O*,*P*-xantphos) (*S*-dmso) Cl₂]. Thermal ellipsoids are displayed at 50% probability level. Hydrogen atoms and the methylene chloride solvent molecule are omitted for clarity.

Fig. 2. MERCURY view of C—H...Cl hydrogen bonding (blue dashed line) and C—H... π interactions (magenta dashed line) in the packing of complex **1**.



Scheme 2. Transfer hydrogenation of aldehydes and ketones using basic *iso*-propanol catalyzed by complex 1.

Table 1

Catalytic transfer hydrogenation of carbonyl substrates by complexes 1^a.





The conversion was calculated based on starting substrate, by using GC and with comparison of authentic samples.

Intermolecular C—H...O, C—H... π and C—H...Cl interactions have been found to significantly stabilize the supramolecular structure of **1** in the crystalline state, as determined by single X-ray crystallography. **1** is found to be active in catalytic transfer hydrogenation of aldehydes and ketones. However, the complex shows much higher catalytic efficiency for the reduction of ketones than aldehydes.

Acknowledgment

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Appendix A. Supplementary material

CCDC#781165 contains the crystallographic data for **1**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre (CCDC) via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2011.04.013 or by direct contacting the authors.



Scheme 3. Proposed catalytic cycle for the reduction of carbonyl compounds.

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under vacuum and washed twice with diethyl ether (2 x 10 cm³). The resulting deep yellow compound was recrystallized from methylene chloride to give yellow powder (0.811 g, Yield = 97.8%). m, p = 334 °C (dec). IR (KBr, cm⁻¹): 1113 (S O, S bonded dmso). ¹H NMR (CDCl₃, ppm): 1.66 (s, 3H, CH₃), 1.71 (s, 3 H, CH₃), 3.13 (s, 3H, CH₃, S bonded dmso). ³¹P (¹H) NMR (CDCl₃, ppm): 14.8 (s, 2P). Elemental analyses; found (Calcd. for C₄₃H₄₂Cl₆O₂P₂-RuS): c, 51.96 (51.72), H, 4.26 (4.24).

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