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Pd and Ru complexes bearing axially chiral ligands for the asymmetric hydrogenation of C=C and C=O double bonds

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ABSTRACT

Complexes composed of either Pd or Ru as central metal and ligands with axial chirality in all cases were used as hydrogenation catalysts. The ligands were (*R*)- and (*S*)-6,6′-dimethyl-2,2′-diaminobiphenyl, (*R*)-(+)-1-1′-Bi(2-naphtylamine), (*R*)-2,2′-Bis(diphenylphosphino)-1,1′-binaphthalene and (*R*)-2,2′-Bis(di-*p*-tolylphosphino)-1,1′-binaphthyl. The Pd(II) complexes had one diamine ligand and the Ru(II) complexes had one bisphosphine and one diamine ligand, forming seven member chelate rings with the metal center. The pro-chiral substrates used were itaconic acid, α-acetamidocinnamic acid and acetophenone. The Pd complexes showed 100% chemoselectivity toward the C=C bond, and toward the C=O bond in the case of Ru. The yield and enantiomeric excess versus time behavior was studied using a large substrate/catalyst ratio. The addition of an organic base to the reaction with Pd complexes enhanced yield and enantiomeric excess. Use of the (*S*)-diamine ligand in the complex favored the (*R*)-products. The best results with itaconic acid were 61% yield and 56% enantiomeric excess and 55% yield and 52% enantiomeric excess with α-acetamidocinnamic acid, both catalyzed by $Pd(OCOCF_3)_2$ ((*S*)-6,6′-dimethyl-2,2′-diaminobiphenyl) in 2,2,2-trifluoroethanol. In the case of the Ru catalysts, (*S*)-1-phenylethanol formed preferentially during hydrogenation of acetophenone. Potassium *tert*-butoxide stabilized the enantiomeric excess. The best result was 87% yield and 41% enantiomeric excess catalyzed by ((*R*)-2,2′-Bis(di-*p*-tolylphosphino)-1,1′-binaphthyl)-$RuCl_2$-((*R*)-(+)-1-1′-Bi(2-naphtylamine)).

1. Introduction

Pure enantiomers are widely used in pharmaceuticals, fine chemicals, agrochemicals and fragrances [1]. Standard chemical syntheses of enantiomers result in racemic mixtures, but their use is in most cases questionable because of the real or potential danger that one of the enantiomers may pose [2,3]. Industrial production of chiral molecules with high enantiomeric excess (ee) generally involves chiral resolution from the racemic mixture, a method that causes significant waste. Asymmetric catalysis, a potentially more efficient strategy, has been gaining momentum in recent years [4]. In this area, asymmetric hydrogenation of prochiral substrates is a powerful tool to obtain chiral compounds, either as final products, or as key intermediates in the synthesis of important chemicals [5]. A recent review on the scaling-up of asymmetric homogeneous hydrogenation is that of Ager et al. [6].

Extensive studies of the asymmetric hydrogenation of C=C and C=O groups [7–9] have been conducted with Pd, Ru or Rh as the active moiety of the catalyst. One alternative is to use the metal as supported nanoparticles interacting with a chiral modifier [7,10]; another option is to form a complex containing metal atoms bound to a chiral ligand [8,9], an idea that has already reached industrial application using 2,2′-Bis(diphenylphosphino)-1,1′-binaphthalene, BINAP, as the organic ligand [11]. BINAP has demonstrated its versatility in asymmetric hydrogenations and promoted the development and use of other bisphosphine ligands [8,11,12]. As an example, in the case of Pd, square-planar LQ-Pd-$(CF_3CO_2)_2$ complexes (where LQ is a bisphosphine ligand) have been prepared with DuPhos, SynPhos, SegPhos, BIPHEP, as well as BINAP, and tested satisfactorily in the enantioselective hydrogenation of functionalized ketones [13], and an assortment of imines [14–16].

Although amine and phosphine groups are isoelectronic, and hence can form similar compounds, the use of chiral diamine ligands has received significantly less attention than bisphosphines. Thomas and co-workers [17] reported the use of a Pd complex with a diamine ligand to hydrogenate C=C (α-phenylcinnamic) and C=O (methyl benzoylformate) double bonds with good results. They argued there was an advantage for catalysts having diamine ligands stemming from their stability and low cost when compared with bisphosphines, although this argument is applicable when only one organic ligand is required. Other examples of the benefits when using diamine ligands are found in the case of Ru. The BINAP-Ru system was able to hydrogenate functionalized ketones,

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but hydrogenation of simple ketones was ineffective [18]. This limitation was overcome by the addition of a diamine ligand to the BINAP-Ru catalyst [19]. Furthermore, by changing the chelate ring formed by the diamine with Ru, new substrates were hydrogenated [20] and the performance of the catalyst was enhanced [21].

We are interested in understanding and in making use of axial chirality, or atropoisomerism, present in some simple diamine ligands. Axial chirality involves a rotational barrier, in contrast to the requirement of a stereogenic atom present in the majority of the chiral diamine ligands used so far. We have done previous work with such a ligand, 6,6′-dimethyl-2,2′-diaminobiphenyl (MAB) [22]. It forms a seven member chelate ring with the metal, similar to the structure formed by most of the main bisphosphine ligands. MAB is also an efficient ligand in the Pd-catalyzed Suzuki–Miyaura and Mizoroki–Heck coupling reactions [23] and in the CuI-catalyzed Sonogashira coupling reaction [24]. We report here the syntheses of several new Pd and Ru complexes containing MAB and other axially chiral ligands and their catalytic evaluation in the asymmetric hydrogenation of substrates containing C=C or C=O double bonds.

2. Experimental

To characterize the complexes we used Nuclear Magnetic Resonance (NMR) and Infrared (IR) spectroscopies. ^{1}H and ^{31}P NMR was performed in a Bruker spectrometer (Avance III 500, ^{1}H resonance frequency of 500 MHz). The experiments were carried out in the liquid phase using $CDCl_3$ as solvent for the Ru complexes and DMSO-d_6 for the Pd complexes. The IR spectra were acquired in a Bruker FTIR spectrometer (Tensor 27). The samples were diluted in KBr and then compressed to form tablets.

During synthesis, all the manipulations were carried out with Schlenk equipment inside a glove bag purged several times with N_2. (*R*)-2,2′-Bis(diphenylphosphino)-1,1′-binaphthalene ((*R*)-BINAP), (*R*)-2,2′-Bis(di-*p*-tolylphosphino)-1,1′-binaphthyl ((*R*)-Tol-BINAP), $RuCl_2(C_6H_6)$ dimer, $PdCl_2{\cdot}(CH_3CN)_2$, $Pd(OCOCF_3)_2$, (*R*)-(+)-1-1′-Bi(2-naphtylamine) ((*R*)-DABN), acetophenone, itaconic acid (IA), α-acetamidocinnamic acid (AA), potassium *tert*-butoxide (*t*-BuOK), potassium hydroxide (KOH), benzylamine (BA), N,N-dimethylformamide (DMF), isopropyl alcohol (IPA), hexane, acetone, methanol (MeOH), 2,2,2-trifluoroethanol (TFE), and dichloromethane (DCM) were purchased from Aldrich with the highest purity available and/or anhydrous. MAB was synthesized and then resolved into (*R*) and (*S*) enantiomers according to previous reports [25,26].

2.1. Syntheses of the complexes

In Figs. 1 and 2 we show the Pd and Ru complexes synthesized in this paper.

2.1.1. $PdCl_2$ ((*S*)-6,6′-dimethyl-2,2′-diaminobiphenyl) or S-MCl

The synthesis of this complex was adapted from [27]. $PdCl_2{\cdot}(CH_3CN)_2$ (0.1 mmol) and (*S*)-MAB (0.12 mmol) were mixed in a Schlenk flask and then dichloromethane was poured in (10 mL).

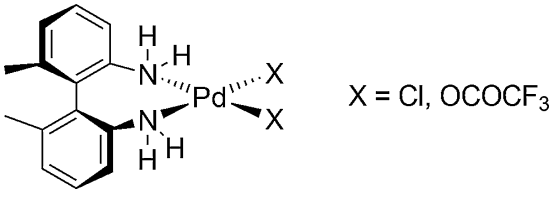

Fig. 1. Pd complexes synthesized for the asymmetric hydrogenation of prochiral C=C bonds.

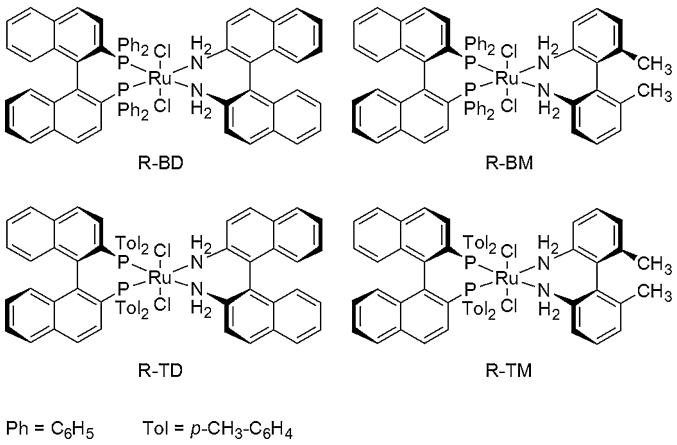

Fig. 2. Bisphosphine/diamines Ru complexes used as catalysts in the asymmetric hydrogenation of acetophenone.

The solution was heated and kept under reflux during 8 h before cooling to room temperature. The solution was concentrated under vacuum and the Pd complex precipitated by adding hexane. Hexane was then removed under vacuum atm room temperature to obtain a light brown powder. The yield of the synthesis was 93%. No additional purification of the powder was performed.

2.1.2. $Pd(OCOCF_3)_2$ ((*S*)-6,6′-dimethyl-2,2′-diaminobiphenyl) or S-MF

We followed a procedure similar to the one used in [13]. $Pd(OCOCF_3)_2$ (0.1 mmol), (*S*)-MAB (0.12 mmol) and acetone (15 mL) were poured in a Schlenk Flask. The solution was stirred for 1 h at room temperature. The solvent was removed under vacuum at room temperature to give a yellow powder. The yield was also 93%. No further purification of the complex was made.

2.1.3. ((*R*)-2,2′-Bis(diphenylphosphino)-1,1′-binaphthalene)-$RuCl_2$-((*R*)-(+)-1-1′-Bi(2-naphtylamine)) or R-BD

Synthesis of all the Ru complexes was done adapting the techniques reported in [20,28]. (*R*)-BINAP (0.3 mmol) and $RuCl_2(C_6H_6)$ dimer (0.15 mmol) were mixed in a Schlenk flask and DMF (12 mL) was then added. The solution was heated to 115 °C during 3 h and then cooled to room temperature. To this mixture, (*R*)-DABN (0.3 mmol) was added and left under stirring overnight. DMF was removed under vacuum at 40 °C. A dark red powder was obtained and no further purification of the complex was performed. The yield was 90%.

The same procedure was followed to synthesize the remaining Ru complexes, by just exchanging the corresponding ligands.

2.1.4. ((*R*)-2,2′-Bis(di-p-tolylphosphino)-1,1′-binaphthyl)-$RuCl_2$-((*R*)-(+)-1-1′-Bi(2-naphtylamine)) or R-TD

Ligands: (*R*)-Tol-BINAP and (*R*)-DABN. The yield was 92%.

2.1.5. ((*R*)-2,2′-Bis(diphenylphosphino)-1,1′-binaphthalene)-$RuCl_2$-((*R*)-6,6′-dimethyl-2,2′-diaminobiphenyl) or R-BM

Ligands: (*R*)-BINAP and (*R*)-MAB. The yield was 87%.

2.1.6. ((*R*)-2,2′-Bis(di-p-tolylphosphino)-1,1′-binaphthyl)-$RuCl_2$-((*R*)-6,6′-dimethyl-2,2′-diaminobiphenyl) or R-TM

Ligands: (*R*)-Tol-BINAP and (*R*)-MAB. The yield was 88%.