



Mixed diphosphine/diamine ruthenium (II) isomers: Synthesis, structural characterization and catalytic hydrogenation of ketones



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ABSTRACT

The complexes *trans*-[RuCl₂(dppb)(cydn)] (**1**), *trans*-[RuCl₂(dppb)(opda)] (**2**) and *cis*-[RuCl₂(dppb)(cydn)] (**3**) were synthesized from {RuCl₂(dppb)}₂-μ-(dppb) {where: dppb = 1,4-bis(diphenylphosphino)butane; cydn = *cis* and *trans* (±) 1,2-diaminocyclohexane, and opda = *o*-phenylenediamine}. The complexes were characterized by nuclear magnetic resonance of phosphorus (³¹P{¹H} NMR), cyclic voltammetry (CV), infrared and ultraviolet/visible spectra (IR and UV/vis) as well as elemental analyses (CHN). The X-ray structures of (**1**) and (**3**) were determined and they are presented here. DFT calculations and experimental data showed that the *trans* isomers are obtained as thermodynamic products while the *cis* isomers are kinetic products. This behavior is different than described in the literature for similar complexes, where the *cis* isomer is obtained from the *trans* isomer. Additionally, the catalytic activity of the complexes (**1**), (**2**) and (**3**) was investigated, as pre-catalysts, in the reduction of the acetophenone and 4-methylacetophenone by transfer-hydrogenation.

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1. Introduction

The coordination chemistry of ruthenium (II) is closely related to the use of phosphines and chelating diphosphines ligands, due to their characteristic of coordination via the P-atom. Aromatic phosphines and diphosphines provide strong back-donation to the metal center, stabilizing a range of ruthenium oxidation states [1], mainly the +II state. The coordination sphere of ruthenium (II) diphosphine complexes is versatilely and can associate with a large number of other ligands, such as halogens, aryl groups [2,3], vinylidenes [4], carbenes [5], CO [6,7], NO [8], pyridines [7,9–11], porphyrins [12], dithiocarbamates [13], as well as H and H₂ [9], among others.

The use of diamine ligands associated with diphosphine in ruthenium (II) complexes can be determined by different synthetic routes, such as phosphine exchange, reduction of the metallic center and the choice of different starting complexes [14–17]. For example, the complex *trans*-[RuCl₂(dppb)(cydn)] (**1**) {where

dppb = 1,4-bis(diphenylphosphino)butane and cydn = 1,2-diaminocyclohexane} was first synthesized by Barata's group [14], and Warad's group [15], from the mononuclear [RuCl₂(dppb)(PPh₃)] precursor, where a dissociation of the PPh₃ is required. The complex *trans*-[RuCl₂(dppb)(opda)] (**2**) {where opda = *o*-phenylenediamine} was first synthesized by Batista's group [16], from the *mer*-[RuCl₃(dppb)(H₂O)] precursor by reduction of Ru (III) to Ru (II) in the presence of a reductive H₂ atmosphere.

Reacting the *mer*-[RuCl₃(dppb)(H₂O)] with opda produces a mixture of two different complexes with ³¹P{¹H} NMR signals at δ 47 and δ 26, which were assigned as *trans*-[RuCl₂(dppb)(opda)] and *trans*-[RuCl₂(dppb)(bqdi)] {bqdi = *o*-benzoquinonediimine}, respectively. There is no evidence of *cis* product formation in the reaction using the *mer*-[RuCl₃(dppb)(H₂O)] as precursor. However, the *trans*-[RuCl₂(dppb)(opda)] complex, in the presence of molecular oxygen, causes the slow oxidation of the coordinated opda to bqdi and, in such condition, a strong signal at δ 26 is observed, due to the formation of *trans*-[RuCl₂(dppb)(bqdi)], which can be quantitatively isolated [16].

The geometry around the metal center in the mixed biphosphino/diamine ruthenium complexes with general formula

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[RuCl₂(P–P)(N–N)] is normally distorted octahedral, because of the restricted bite angles of the surrounding bidentate ligands, providing the *trans* or *cis* isomers according to the position of the chlorido ligands. Several works describe the isomerization process from the *trans* isomer to the *cis* isomer, which can be labeled as kinetic and thermodynamic products, respectively. Only for sake of illustration, the *trans*-[RuCl₂(dppme)(cydn)] {where dppme = H₂C=C(CH₂PPh₂)₂} is a kinetic product, which is readily isomerizes to the *cis* isomer (thermodynamic product) [18]. The *trans*-[RuCl₂(dppb)(dimprp)] {where dimprp = 2,2-dimethyl-1,3-propanediamine} also isomerizes to the *cis* isomer within 20 h of reaction, which indicates that *cis* isomer is more stable than the *trans* isomer [19]. However, certain biphosphino/diamine complexes containing ruthenium do not present such isomerization process [19], such as in the *trans*-[RuCl₂(dppb)(diamph)] {where diamph = 2,3-diaminonaphthalene}.

Herein is described the synthesis and structural characterization of the *trans*-[RuCl₂(dppb)(cydn)] (**1**), *trans*-[RuCl₂(dppb)(opda)] (**2**), *cis*-[RuCl₂(dppb)(cydn)] (**3**) and *cis*-[RuCl₂(dppb)(opda)] (**4**), for the purpose of understanding the isomerization process involved. The complexes were synthesized from the [RuCl₂(dppb)]₂-μ-(dppb) complex, and the catalytic activity of (**1**), (**2**) and (**3**) as pre-catalysts in the transfer-hydrogenation of acetophenone and 4-methylacetophenone is discussed. Suitable crystals of (**1**) and (**3**), CH₂Cl₂ were obtained and the X-ray analyses are presented here.

2. Experimental

2.1. General considerations

All reactions were carried out under argon atmosphere using standard Schlenk techniques. Solvents were purified by standard methods [20] and all chemicals used were of reagent grade or comparable purity. Ruthenium trichloride, tetrabutylammonium hexafluorophosphate (TBAH), 1,4-bis(diphenylphosphino)butane (dppb), triphenylphosphine (PPh₃), *o*-phenylenediamine, *cis* and *trans* (±) 1,2-diaminocyclohexane, acetophenone, 4-methylacetophenone and hexadecane (Sigma-Aldrich) were used as received.

Ruthenium complexes were analyzed by ³¹P{¹H}-NMR on a Bruker Avance III 500 spectrometer operated at 11.75 T; ³¹P was observed at 202.46 MHz. The spectrometer was equipped with a broadband observe probehead (BBO). Samples were prepared under argon atmosphere and analyzed at variable temperature with a CD₂Cl₂ capillary and dichloromethane (CH₂Cl₂) as solvent. Chemical shifts are with respect 85% H₃PO₄ signal, as external reference.

Electrochemical data were obtained using a potentiostat/galvanostat μ-autolab type III. Solutions of the complexes (10⁻³ mol L⁻¹) were prepared in dichloromethane (CH₂Cl₂) using 0.1 mol L⁻¹ tetrabutylammonium hexafluorophosphate (TBAH) as the supporting electrolyte. Measurements were made with a three-electrode configuration cell. A platinum foil was used as the working and auxiliary electrodes and Ag/AgCl, 0.10 mol L⁻¹ TBAH in CH₂Cl₂ as the reference electrode. Under the conditions used, E⁰ for the one-electron oxidation of [Fe(η⁵-C₅H₅)₂], added to the test solutions as an internal calibrant, is +0.43 V.

Elemental analyses were performed with a Thermo Scientific CHNS–O FLASH 2000 micro analyzer.

Optical spectra were recorded on a Shimadzu spectrophotometer, model UV-1800, coupled with a thermoelectrically temperature controlled cell TCC-100 (at 25.0 ± 0.1 °C), using a quartz cell (1 cm), between 200 and 800 nm. IR spectra were recorded in a spectrometer FT-IR Frontier Single Range – MIR from Perkin Elmer coupled with an attenuated total reflectance (ATR) apparatus with diamond cell, in the 4000–200 cm⁻¹ range.

The ground-state geometries were fully optimized without any symmetry constraints at the DFT level of theory, employing the B3LYP hybrid functional, with Becke's three-parameter hybrid functional [21] and correlational functional of Lee, Yang and Parr [22]. The basis set employed to build the molecular orbitals was LanL2DZ for ruthenium and 6-311 + G(d,p) for the remaining atoms. All structures possessed positive definite Hessian matrices, indicating that they were in a genuine minimum on the potential energy surface. All calculations were made using Gaussian 09 computational package [23].

The catalytic experiments were analyzed by gas chromatography with a Thermo Scientific Focus Gas Chromatograph equipped with an FID detector. An LM-120 column (polyethyleneglycol) (25 m long, 0.25 mm i. d., 0.25 μm film thickness) was used for the characterization of the catalytic products and N₂ was the gas carrier (1.0 mL min⁻¹). The temperature program ranged from 170 °C (2 min) to 200 °C at a heating rate of 10 °C min⁻¹.

2.2. Syntheses

2.2.1. *trans*-[RuCl₂(dppb)(cydn)] (**1**)

It was synthesized from 101.2 mg (62.3 μmol) of the [RuCl₂(dppb)]₂-μ-(dppb) [17] and 15.9 mg (129.2 μmol) of the *cis*

Table 1

Crystal data and structure refinement of the *trans*-[RuCl₂(dppb)(cydn)] (**1**) and *cis*-[RuCl₂(dppb)(cydn)] (**3**).

	(1)	(3), CH ₂ Cl ₂
Empirical formula	C ₃₄ H ₄₃ Cl ₂ N ₂ P ₂ Ru	C ₃₅ H ₄₄ Cl ₄ N ₂ P ₂ Ru
Formula weight	712.60	797.53
Temperature	296(2) K	296(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Triclinic
Space group	P2(1)/n	P-1
Unit cell dimensions		
<i>a</i> (Å)	15.1867(6)	9.6341(5)
<i>b</i> (Å)	10.9543(4)	13.3976(6)
<i>c</i> (Å)	21.8290(10)	16.0147(8)
α (°)	90°	68.412(2)°
β (°)	90.156(2)°	74.914(2)°
γ (°)	90°	73.098(2)°
<i>V</i> (Å ³)	3631.5(3)	1811.55(16)
<i>Z</i>	4	2
Density (calculated) (Mg/m ³)	1.320	1.462
Absorption coefficient (mm ⁻¹)	0.691	0.844
<i>F</i> (000)	1472	820
Crystal size (mm ³)	0.29 × 0.24 × 0.20	0.36 × 0.05 × 0.02
Theta range for data collection	1.63 to 25.21°	1.388 to 25.24°
Index ranges	-15 ≤ <i>h</i> ≤ 18 -13 ≤ <i>k</i> ≤ 12 -26 ≤ <i>l</i> ≤ 24	-11 ≤ <i>h</i> ≤ 11 -16 ≤ <i>k</i> ≤ 14 -19 ≤ <i>l</i> ≤ 19
Reflections collected	28970	22420
Independent reflections	6374 [R(int) = 0.0292]	6470 [R(int) = 0.0424]
Completeness to theta maximum (%)	θ 25.21°, 97.4%	θ 25.24°, 98.7%
Absorption correction [29]	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.7452 and 0.6834	0.7452 and 0.6828
Refinement method	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	6374/0/463	6470/0/397
Goodness-of-fit on <i>F</i> ²	1.247	1.064
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0642 <i>wR</i> 2 = 0.1502	<i>R</i> 1 = 0.0510 <i>wR</i> 2 = 0.1262
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0675 <i>wR</i> 2 = 0.1516	<i>R</i> 1 = 0.0741 <i>wR</i> 2 = 0.1409
Largest diff. peak and hole (e.Å ⁻³)	0.628 and -0.737	2.799 and -0.725

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