



## Synthesis, structure, spectroscopic properties, electrochemistry, and DFT correlative studies of *trans*-[Ru(P-P)<sub>2</sub>Cl<sub>2</sub>] complexes



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### ABSTRACT

Five *trans*-[Ru(P-P)<sub>2</sub>Cl<sub>2</sub>] complexes were prepared by reacting RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub> with P-P ligands {P-P = 3-hexyl-1,3-bis(diphenylphosphino)propane (hdppp) (**1**); 1,3-bis(diphenylphosphino)propane (dppp) (**2**); 1,2-bis(diphenylphosphino)ethane (dppe) (**3**); 1,1'-bis(diphenylphosphino)methane (dppm) (**4**); 1,2-bis(diphenylphosphino)ethylene (depe) (**5**)}. The complexes were characterized by an elemental analysis, IR, <sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P{<sup>1</sup>H}NMR, FAB-MS and TG/DTA. These Ru(II) complexes showed Ru(III)/Ru(II) quasireversible redox couple. The molecular structures of the complexes **1** and **3** were determined by X-ray crystallography, and their spectroscopic properties were studied. Another polymorph of **3** was reported in literature, the reported polymorph of **3** in this work crystallizes in P1 space group, whereas, the previously reported polymorph crystallizes in C2/c space group. The two complexes adopt a distorted *trans* octahedral coordination and ruthenium(II) ions are located on a crystallographic centre of symmetry. Based on the optimized structures, computational investigations were carried out in order to determine the electronic structures of the complexes. The electronic spectra of **1** and **1\*** in dichloromethane were calculated with the use of time-dependent DFT methods, and the electronic spectra of the transitions were correlated with the molecular orbitals of the complexes.

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### 1. Introduction

Ruthenium(II) complexes with polydentate phosphines ligands have received much attention in the last decades due to their application in the field of homogeneous catalysis [1,2]. Several complexes of the general formula *cis*- and *trans*-[M(P-P)<sub>2</sub>X<sub>2</sub>] (P-P = C<sub>2</sub>H<sub>4</sub>(PR<sub>2</sub>)<sub>2</sub> (R = Me, Et or Ph), CH<sub>2</sub>(PPh<sub>2</sub>)<sub>2</sub>, and *o*-C<sub>6</sub>H<sub>4</sub>(PEt<sub>2</sub>)<sub>2</sub>; X = halogen, SCN<sup>-</sup>, H<sup>-</sup>, CN<sup>-</sup>) (M = Ru, Os) were prepared by Chatt and Hayter [3,4]. These complexes, *trans*-[Ru(P-P)<sub>2</sub>Cl<sub>2</sub>], could be used as starting materials to prepare bi- and pronuclear complexes [5,6]. Classical procedures for the syntheses of these complexes require the reflux conditions in acidic media [7] or the aqueous solution of K<sub>2</sub>[RuCl<sub>5</sub>(H<sub>2</sub>O)] [8]. Poor yields of complexes are obtained by these preparation procedures. For this reason, a study of the electronic structures of such complexes is valuable as a mean to predict their properties [9–11].

In this paper, we present the synthesis, crystal, molecular, the electronic structures, and the spectroscopic characterization

of five ruthenium(II) complexes with diphosphine ligands. The *trans*-[Ru(P-P)<sub>2</sub>Cl<sub>2</sub>] complexes, (P-P) {P-P = (Hdppp) = 3-hexyl-1,3-bis(diphenylphosphino)propane (**1**); (dppp) = 1,3-bis(diphenylphosphino)propane (**2**); (dppe) = 1,2-bis(diphenylphosphino)ethane (**3**) (dppe); (dppm) 1,1'-bis(diphenylphosphino)methane (**4**); 1,2-bis(diphenylphosphino)ethylene (**5**)}, were prepared from the reaction RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub> and the corresponding P-P ligand. These *trans* complexes have a poor solubility in many organic solvents. The solubility can be improved by modification of the diphosphine backbone chelating ligand with alkyl group. Hdppp is a newly prepared diphosphine ligand to improve the solubility of the *trans*-[Ru(P-P)Cl<sub>2</sub>] complexes. To probe the effect of the size of chelating ring of P-P on the electronic behavior *trans*-[RuCl<sub>2</sub>(P-P)<sub>2</sub>] complexes. In this work, we present and discuss the spectroscopic (IR, UV-Vis, <sup>1</sup>H NMR and <sup>31</sup>P NMR) and electrochemical (cyclic voltammetry) behavior of **1–5**, and report the X-ray structures for **1** and **3**. The absorption spectrum of complex **1** and **1\*** in dichloromethane have been modeled by time-dependent density functional theory (TD-DFT) using a mixed basis set, MWB/6-31+g(d,p) to correlate experimental findings with theoretical predictions.

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