



# 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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## ARTICLE INFO

### Article history:

Received 22 April 2013

Accepted 16 June 2013

Available online 27 June 2013

### Keywords:

Ruthenium  
Diphosphine  
Electrochemistry  
DFT calculation

## 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**<sup>+</sup> 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>-1</sup>, H<sup>-1</sup>, CN<sup>-1</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**<sup>+</sup> 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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## 2. Experimental

### 2.1. Materials

The reagents: ruthenium trichloride hydrate, 1,3-bis(diphenylphosphino)propane (dppp), 1,2-bis(diphenylphosphino)ethane (dppe), 1,1'-bis(diphenylphosphino)methane (dppm); 1,2-cis-1,2-bis(diphenylphosphino)ethylene (depe), *n*-Butyllithium solution 1.6 M in hexane, Diphenylphosphine, and solvents (reagent grade) were purchased from Aldrich and were used as received, 1-chloro-2-(chloromethyl)octane was purchased from MolPort, Tetrabutylammonium hexafluorophosphate (TBAHF), purchased from Aldrich, was recrystallized twice from 1:1 ethanol/water solution and then vacuum dried at 110 °C. The synthesis of RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub> has been previously described [6].

### 2.2. Syntheses

#### 2.2.1. Synthesis of 2-hexyl-1,3-bis(diphenylphosphino)propane (Hdppp) ligand

The new ligand was prepared following published procedures [12,13]. A solution of *n*-BuLi in *n*-hexane (25 mL of a 1.6 M solution, 2.56 g) was added dropwise to a solution of diphenylphosphine, Ph<sub>2</sub>PH (7.44 g, 40.0 mmol) in dry THF (20 mL) at –5 °C over 5 h. The prepared red solution consisting of Ph<sub>2</sub>PLi was stirred for 2 hours at ambient temperature. Then a solution of 1-chloro-2-(chloromethyl)octane (3.94 g, 20.0 mmol) in dry THF (20 mL) was added dropwise within 40 min until all the red color was disappeared. The reaction temperature was kept at 0 °C during the addition and the solution was stirred for another 4 h to ensure that the reaction went to completion. To the colorless mixture, a degassed aqueous solution saturated with NH<sub>4</sub>Cl (100 mL) was added and the organic layer was separated. The solution was dried with Na<sub>2</sub>SO<sub>4</sub> and separated from the solid residue. After the evaporation of the volatile materials under vacuum, the crude product was distilled to yield highly viscous colorless air sensitive oil. Yield (8.0 g, 81%). UV–Vis in dichloromethane: λ<sub>max</sub> = 237 nm. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ (ppm), 0.7 (br, 3H, 1CH<sub>3</sub>), 1.0–2.1 (3 br, 11H, 5CH<sub>2</sub> and 1CH), 2.4 (m, 4H, 2PCH<sub>2</sub>), 6.8–7.9 (3 m, 20H, Phs). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ (ppm) –21.5. MS (EI): M<sup>+</sup> 496.2 (*m/z*). IR (KBr, cm<sup>-1</sup>): 3180 (*ν*<sub>PHH</sub>) and 2970 (*ν*<sub>CH</sub>), 1520 (*ν*<sub>C=C</sub>). Elemental Anal. Calc. for C<sub>33</sub>H<sub>38</sub>P<sub>2</sub>: C, 79.81; H, 7.71. Found: C, 79.63; H, 7.65%.

#### 2.2.2. General procedure for the syntheses of trans-[Ru(P-P)<sub>2</sub>Cl<sub>2</sub>] (1–5) complexes

Diphosphine ligand (2.0 mmol) was dissolved in 10 mL of dichloromethane and the solution was added dropwise to a stirred solution of RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub> (1.0 mmol) in 10 mL of dichloromethane. The reaction mixture was stirred approximately for 50 min at room temperature. The brown solution was filtered to remove the insoluble impurities. The solvent was reduced by a vacuum and the product was then precipitated by adding *n*-hexane. The yellow solid was filtered and washed three times with 20 mL of diethyl ether.

2.2.2.1. *trans*-[Ru(Hdppp)<sub>2</sub>Cl<sub>2</sub>] (1). Yield (1.06 g, 91%). UV–Vis in dichloromethane: λ<sub>max</sub>(nm) (ε<sub>max</sub>, M<sup>-1</sup> cm<sup>-1</sup>): 465 (4.21 × 10<sup>2</sup>), 365 (4.95 × 10<sup>2</sup>), 340 (2.320 × 10<sup>3</sup>). IR (KBr, cm<sup>-1</sup>): 3160 (*ν*<sub>PHH</sub>) and 2960 (*ν*<sub>CH</sub>), 1520 (*ν*<sub>C=C</sub>), 450 (*ν*<sub>Ru-P</sub>). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ (ppm), 0.6 (2 br, 6 H, 2 CH<sub>3</sub>), 0.7–3.1 (4 br, 22 H, 10 CH<sub>2</sub> and 2 CH), 2.9 (m, 8 H, 4 PCH<sub>2</sub>), 6.5–7.8 (4 m, 20 H, PC<sub>6</sub>H<sub>5</sub>). <sup>31</sup>P{<sup>1</sup>H}(CDCl<sub>3</sub>): δ (ppm) 2.2. FAB-MS: M<sup>+</sup> 1165.3 (*m/z*). Elemental Anal. Calc. for C<sub>66</sub>H<sub>76</sub>Cl<sub>2</sub>P<sub>4</sub>Ru: C, 68.71; H, 7.61. Found: C, 68.83; H, 7.41%.

2.2.2.2. *trans*-[Ru(dppp)<sub>2</sub>Cl<sub>2</sub>] (2). Yield (0.86 g, 87%). UV–Vis in dichloromethane: λ<sub>max</sub> (nm) (ε<sub>max</sub>, M<sup>-1</sup> cm<sup>-1</sup>): 475 (3.88 × 10<sup>2</sup>), 375 (4.75 × 10<sup>2</sup>), 350 (2.097 × 10<sup>3</sup>). IR (KBr, cm<sup>-1</sup>): 3166 (*ν*<sub>PHH</sub>) and 2964 (*ν*<sub>CH</sub>), 1525 (*ν*<sub>C=C</sub>), 454(*ν*<sub>Ru-</sub>). 2.7 (m, 12 H, PCH<sub>2</sub>, PCH<sub>2</sub>), 7.01 (t, 16 H, PC<sub>6</sub>H<sub>5</sub>), 7.19 (t, 8 H, PC<sub>6</sub>H<sub>5</sub>), 7.37 (d, 16 H, PC<sub>6</sub>H<sub>5</sub>), <sup>31</sup>P {<sup>1</sup>H}(CDCl<sub>3</sub>): δ (ppm), 5.1. FAB-MS; [M<sup>+</sup>] 996.7 (*m/z*) Elemental Anal. Calc. for C<sub>54</sub>H<sub>52</sub>Cl<sub>2</sub>P<sub>4</sub>Ru: C, 65.06; H, 5.26. Found: C, 65.22; H, 5.40%.

2.2.2.3. *trans*-[Ru(dppe)<sub>2</sub>Cl<sub>2</sub>] (3). Yield (0.87 g, 90%). UV–Vis in dichloromethane: λ<sub>max</sub> (nm) (ε<sub>max</sub>, M<sup>-1</sup> cm<sup>-1</sup>): 447 (1.70 × 10<sup>2</sup>), 380 (3.4 × 10<sup>2</sup>), 312 nm (2.7 × 10<sup>4</sup>). IR (KBr, cm<sup>-1</sup>): 3155 (*ν*<sub>PHH</sub>) and 2957 (*ν*<sub>CH</sub>), 1517 (*ν*<sub>C=C</sub>), 445 (*ν*<sub>Ru-P</sub>). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ (ppm) 7.02–7.22 (3 m, 28 H, PC<sub>6</sub>H<sub>5</sub>), 2.73 (m, 8 H, 4 CH<sub>2</sub>), <sup>31</sup>P {<sup>1</sup>H}(CDCl<sub>3</sub>): δ (ppm) 44.9. FAB-MS; [M<sup>+</sup>] 968.8 (*m/z*). Elemental Anal. Calc. for C<sub>52</sub>H<sub>48</sub>Cl<sub>2</sub>P<sub>4</sub>Ru: C, 64.47; H, 4.99. Found: C, 64.56; H, 4.70%.

2.2.2.4. *trans*-[Ru(dppm)<sub>2</sub>Cl<sub>2</sub>] (4). Yield. (0.77 g, 82%). UV–Vis in dichloromethane: λ<sub>max</sub> (nm) (ε<sub>max</sub>, M<sup>-1</sup> cm<sup>-1</sup>): 483 (1.95 × 10<sup>2</sup>), 429 (2.8 × 10<sup>2</sup>), 320 (2.4 × 10<sup>3</sup>). IR (KBr, cm<sup>-1</sup>): 3150 (*ν*<sub>PHH</sub>) and 2955 (*ν*<sub>CH</sub>), 1525 (*ν*<sub>C=C</sub>), 455 (*ν*<sub>Ru-P</sub>). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ (ppm) 4.0 (m, 4 H, PCH<sub>2</sub>), 7.01 (t, 16 H, PC<sub>6</sub>H<sub>5</sub>), 7.18 (t, 8 H, PC<sub>6</sub>H<sub>5</sub>), 7.41 (m, 16 H, PC<sub>6</sub>H<sub>5</sub>), <sup>31</sup>P{<sup>1</sup>H}(CDCl<sub>3</sub>): δ (ppm) –7.1. FAB-MS; [M<sup>+</sup>] 940.5 (*m/z*). Elemental Anal. Calc. for C<sub>50</sub>H<sub>44</sub>Cl<sub>2</sub>P<sub>4</sub>Ru: C, 63.84; H, 4.71. Found: C, 63.56; H, 4.50%.

2.2.2.5. *trans*-[Ru(depe)<sub>2</sub>Cl<sub>2</sub>] (5). Yield. (0.77 g, 82%). UV–Vis in dichloromethane: λ<sub>max</sub> (nm) (ε<sub>max</sub>, M<sup>-1</sup> cm<sup>-1</sup>): 400 (3.96 × 10<sup>2</sup>), 350 (2.54 × 10<sup>3</sup>). IR (KBr, cm<sup>-1</sup>): 3155 (*ν*<sub>PHH</sub>) and 2955 (*ν*<sub>CH</sub>), 1517 (*ν*<sub>C=C</sub>), 447 (*ν*<sub>Ru-P</sub>), 318 (*ν*<sub>Ru-Cl</sub>). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ (ppm) 6.80 (d, 4 H, PCH), 7.0–7.21 (3m, 20 H, PC<sub>6</sub>H<sub>5</sub>), <sup>31</sup>P {<sup>1</sup>H}(CDCl<sub>3</sub>): δ (ppm) 53.7 FAB-MS; [M<sup>+</sup>] 964.7 (*m/z*). Elemental Anal. Calc. for C<sub>52</sub>-H<sub>44</sub>Cl<sub>2</sub>P<sub>4</sub>Ru: C, 64.74; H, 4.60. Found: C, 64.56; H, 4.40%.

### 2.3. Instrumentation

<sup>1</sup>H NMR (400 MHz) and <sup>31</sup>P NMR (162 MHz) spectra were measured on a Bruker Avance III 400 spectrometer as CDCl<sub>3</sub> solutions at room temperature. All chemical shifts are reported in ppm downfield of TMS (1H) or 85% phosphoric acid (<sup>31</sup>P) and referenced using the chemical shifts of residual solvent resonances. IR spectra were measured by FT-IR JASCO model 420. Elemental analyses were carried out on an Eurovector E.A.3000 instrument using copper sample-tubes. FAB-MS data were obtained on a Bruker IFS 48 FT-IR spectrometer and Finnigan 711A (8 kV), modified by AMD and reported as mass/charge (*m/z*), respectively. UV–Vis/NIR spectra were recorded on a TIDAS fiberoptic diode array spectrometer (combined MCS UV/NIR and PGS NIR instrumentation) from j & m in HELMA quartz cuvettes with 0.1 cm optical path lengths. Electrochemical measurements were performed in dichloromethane (Aldrich, HPLC grade) using BAS CV-27. All electrochemical experiments were done in a home-built cylindrical vacuum-tight one-compartment cell. A spiral-shaped Pt wire and an Ag wire as the counter and thin pseudo-reference electrodes are sealed into glass capillaries via standard joints and fixed by Quickfit screws. A platinum electrode is introduced as the working electrode through the top central port via a Teflon screw cap with a suitable fitting. It is polished with first 1 μm and then 0.25 μm diamond pastes before measurements. The cell was attached to a conventional Schlenk line via a side arm equipped with a Teflon screw valve and allows experiments to be performed under argon atmosphere with approximately 5 mL of analyte solution. Tetrabutylammonium hexafluorophosphate (0.1 M) was twice recrystallized and vacuum dried at 120 °C, and used as the supporting electrolyte. The temperature was controlled (at 25.0 ± 0.1 °C) by a Haake D8-C

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