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The $RuCl_3(dppb)H_2O$ complex: A new metal-assisted oxidative dehydrogenation of the *o*-phenylenediamine ligand

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Abstract

The *trans*-[$RuCl_2$(dppb)(bqdi)] and *trans*-[$RuCl_2$(dppb)(opda)] complexes (dppb = 1,4-bis(diphenylphosphine)butane, bqdi = *o*-benzoquinonediimine, and opda = *o*-phenylenediamine) were synthesized from the reaction of the *mer*-[$RuCl_3$(dppb)(H_2O)] aqua-complex with the opda ligand. The X-ray structural and electrochemical characterizations of the isolated compounds showed that this aqua-complex induces the oxidative dehydrogenation of the amine species (opda) to the imine form (bqdi) of the *o*-phenylene ligand during the synthetic procedure. In the presence of oxygen, the $^{31}P\{^1H\}$ NMR experiments confirmed that the *trans*-[$RuCl_2$(dppb)(bqdi)] complex is the only product formed.

Keywords: Ruthenium complexes; 1,4-Bis(diphenylphosphine); *o*-Phenylene ligands; X-ray structures

Since the earlier works concerning the intrinsic electronic properties of *o*-phenylene ligands, a growth interest in the study of this class of ligands coordinated to metal centers has been observed [1–8]. Among these ligands, the redox species derived from *o*-phenylenediamine (opda) species have attracted special attention because of the magnetic properties of complexes prepared with metals of the first transition series [9].

The *mer*-[$Ru^{III}Cl_3$(dppb)(H_2O)] aqua-complex has shown to be a versatile compound as starting material for the production of species containing the "Ru^{II} Cl_2(dppb)" or "$Ru^{III}Cl_3$(dppb)" unit. Derivative species, such as *mer*-[$RuCl_3$(dppb)(L)] and *cis* or *trans*-[$RuCl_2$(dppb)$(L)_n$], where L = pyridine, 4-methylpyridine, dimethylsulfoxide, 2,2′–dithiobis(benzothiazole), 1,4-dithiane, and dppb = 1,4-bis(diphenylphosphine)butane, were synthesized and well characterized [10–13]. Particularly, the complexes with L = pyridine, 4-methylpyridine and dimethylsulfoxide produce triply bridged binuclear complexes of the type [(L)(dppb)Ru(μ-Cl)$_3$RuCl(dppb)] by reductive electrolysis [13]. Also, the aqua-complex has been used in the formation of mixed-valence complexes of general formula [(P–P)-ClRu(μ-Cl)$_3$RuCl(dppb)], where P–P = *o*-isopropylidene-2, 3-dihydroxy-1,4-bis(diphenylphosphine)butane, 2,2′-bis-(diphenylphosphine)1,1′-binaphthyl, triphenylphosphine, tri-*p*-tolylphosphine, and triphenylstibine [14]. Additionally, it is relevant to point out the catalytic activity presented by all these complexes, including the aqua-complex, toward the conversion of imines into amine [14].

Aiming to evaluate the reactivity of the *mer*-[Ru^{III} Cl_3(dppb)(H_2O)] compound as an oxidizing precursor of an *o*-phenylene ligand to obtain a ruthenium imine complex, we conducted the reaction of this aqua-complex with

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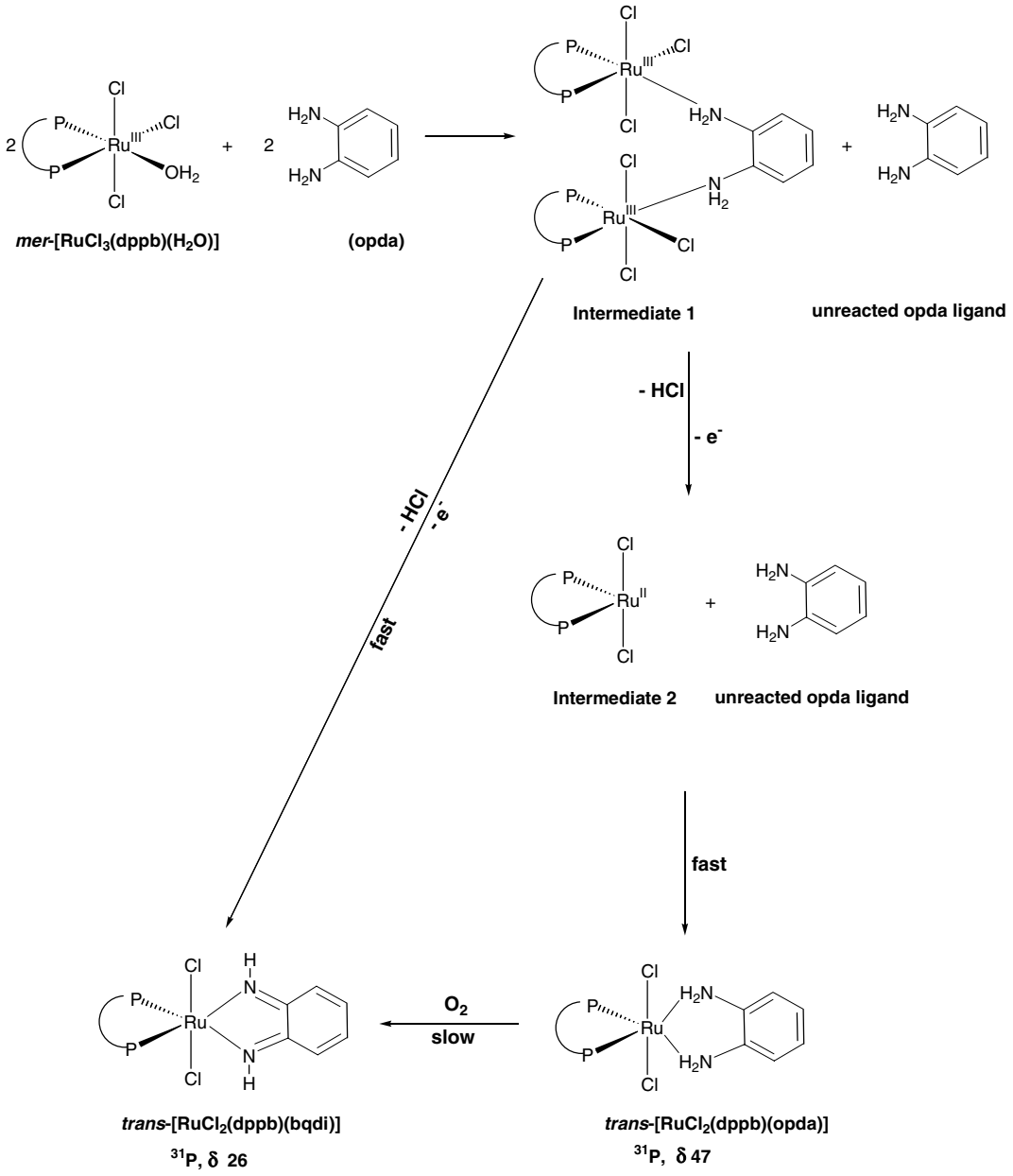
the *o*-phenylenediamine ligand. The synthesis was carried out under argon flow and stirring by using Schlenk techniques, at room temperature. The solvents used (methanol, dichloromethane, ethyl ether, hexane) were purified according to standard procedures [15]. $^{31}P\{1H\}$ (161 MHz) NMR spectra were acquired in a BRUKER DRX400 spectrometer, at 298 K, by using 85% H_3PO_4 as an external reference and $CDCl_3$ (Aldrich) as a solvent. The elemental analysis was performed in a Fison model EA 1108 equipment. Crystallographic data were performed with graphite monochromated Mo Kα ($\lambda = 0.71073$ Å) radiation on an Enraf-Nonius Kappa-CCD difractometer. Data were collected up to 50° in 2θ, with a redundancy of 4. The final unit cell parameters were based on all reflections. Data collections were made using the COLLECT program [16]; integration and scaling of the reflections were performed with the HKL Denzo–Scalepack system of programs [17]. Absorption corrections were carried out using the multi-scan method [18]. The structures were solved by direct methods with SHELXS-97 [19]. The model was refined by full-matrix least-squares on F^2 by means of SHELXL-97 [20]. All the hydrogen atoms were located on stereochemical grounds, stereochemically positioned and refined with the riding model [21]. Electron paramagnetic resonance (EPR) spectra were measured at 77 K using a Varian E-109 instrument operating at the X band frequency, within a rectangular cavity (E-248) fitted with a temperature controller. Electrochemical experiments were performed with an electrochemical analyzer BAS 100*W* from Bioanalytical system at 25 ± 0.2 °C in tetrabutylammonium perchlorate (TBAP) as supporting electrolyte. The half-wave formal potentials ($E_{1/2}$) for the $Ru^{III/II}$ redox process for the compounds were determined by cyclic voltammetry. These experiments were acquired in a conventional three-electrode glass cell with a platinum disk (0.0314 cm^2 of geometrical area) and foil as working and auxiliary electrodes, respectively. The potentials reported in this study were all converted to the normal hydrogen electrode (NHE), based on the ferrocene/ferrocenium ($Fc^{+/0}$) redox process, which was observed at 0.64 V in dichloromethane (CH_2Cl_2).

A 10 mg sample (0.092 mmol) of the opda ligand was added to a methanol solution containing an equimolar quantity of the *mer*-$[Ru^{III}Cl_3(dppb)(H_2O)]$ complex. Almost instantaneously, a violet color was developed. The mixture was stirred for 6 h in the absence of light, under Ar atmosphere, followed by concentration to near 1 mL, and addition of ethyl ether to promote the precipitation. The resulting solid was collected, washed with hot hexane, ethyl ether, and dried under vacuum.

The $^{31}P\{^1H\}$ NMR spectrum of the reaction product shows two singlet signals at δ 47 and δ 26. These signals presented almost the same intensity suggesting that a mixture of compounds is produced, and the formed species are roughly at same concentration. The slow evaporation of a freshly prepared solution containing this product mixture in CH_2Cl_2/Et_2O yielded blue crystals suitable for X-ray structure determination. Elemental analysis for this crystal: Anal. Calcd(%) $C_{34}H_{34}Cl_2N_2P_2Ru$: C: 57.96; H: 4.86; N: 3.98. Found(%): C: 58.05; H: 5.01; N: 4.25. The $^{31}P\{^1H\}$ NMR spectrum of the collected crystals showed only one signal at δ 26. One very first assignment is that the formed crystals are from the *trans*-$[RuCl_2(dppb)(bqdi)]$ complex formed as described in Scheme 1, where the coordinated *o*-phenylenediamine (opda) ligand is oxidized to *o*-benzoquinonediimine (bqdi). It is important to point out that in ruthenium–phosphine–amine complexes, where the phosphorus are *trans* to nitrogen, the $^{31}P\{^1H\}$ NMR chemical shift occurs around δ 45 [10,22]. Therefore, the signal at δ 47 that appears in the $^{31}P\{^1H\}$ NMR spectrum of the solid mixture product would be assigned to the formation of the *trans*-$[RuCl_2(dppb)(opda)]$ amine complex, where the nitrogen atoms are *trans* to the phosphorous atoms. Concomitantly with the reduction of the metal center (Scheme 1), the dissociation of the chlorine occurs and the *trans*-$[RuCl_2(dppb)(bqdi)]$ is formed to stabilize the non-innocent o-benzoquinone diimine ligand, which has never been isolated as a free molecule [5].

In a parallel experiment, the reaction was conducted by the slow addition of the opda ligand to the aqua-complex solution until reaching the equimolar quantities of both reactants. In such conditions, a strong intensification of the signal at δ 26 in the $^{31}P\{^1H\}$ NMR spectrum was observed indicating that the *trans*-$[RuCl_2(dppb)(bqdi)]$ complex is preferentially produced. To reinforce the proposed mechanism, we conducted the reaction of the opda reduced ligand with the $[Ru^{II}Cl_2(dppb)(PPh_3)]$ complex. Since the ruthenium metal center is already in the reduced state, it will not promote any redox change in the ligand. Within this purpose, 15 mg (0.14 mmol) of the opda ligand was added to a benzene solution containing 100 mg (0.12 mmol) of the $[Ru^{II}Cl_2(dppb)(PPh_3)]$ complex. The reaction proceeded during 1 h, under argon, stirring and absence of light, at room temperature. The resulting solution was concentrated to near 1 mL, and the product was precipitated by the addition of ethyl ether. The solid was collected, washed with hot hexane, ethyl ether, and dried under vacuum. Yield: 86%. Anal. Calcd(%) for $[C_{34}H_{36}Cl_2N_2P_2Ru]$. $2(CH_2Cl_2)$: C: 49.43; H:4.61; N: 3.20. Found(%): C: 49.75; H: 4.75; N: 3.30. The $^{31}P\{^1H\}$ NMR spectrum of the reaction product shows one singlet δ 47 indicating the formation of the *trans*-$[RuCl_2(dppb)(opda)]$ complex. Thus, one can conclude that the complex produced from the reaction of the opda ligand with the $[RuCl_2(dppb)(PPh_3)]$ starting reagent is the *trans*-$[RuCl_2(dppb)(opda)]$ complex, which under air produces the *trans*-$[RuCl_2(dppb)(bqdi)]$ as final product. This oxidation process of the coordinated opda to bqdi ligand was previously used for synthesis of *o*-benzoquinone diimine complexes [5]. In fact, for the system in study, the opda complex is stable when the synthesis is carried out under inert atmosphere.

Aiming to detect the binuclear intermediate 1 (Scheme 1), the reaction of the aqua-complex with the opda ligand in



Scheme 1. Mechanism proposed for the production of the *trans*-[$RuCl_2$(dppb)(bqdi)] (collected crystals) and *trans*-[$RuCl_2$(dppb)(opda)] compounds from the reaction of the *mer*-[$Ru^{III}Cl_3$(dppb)(H_2O)] complex with the opda ligand.

CH_2Cl_2 was promoted being frozen in liquid nitrogen immediately after the mixture of the reagents. Unfortunately, we were not able to detect the desired intermediate 1 in the EPR experiments. Also, a signal close to the zero magnetic field, assigned to the *mer*-[$RuCl_3$(dppb)H_2O] complex [11], was not detected suggesting that this reaction is very fast indeed.

Crystal and molecular structure: Recrystallization of the *trans*-[$RuCl_2$(dppb)(bqdi)] and *trans*-[$RuCl_2$(dppb)(opda)] complexes from CH_2Cl_2/Et_2O solutions yielded suitable crystals for determination of X-ray structures, which are illustrated in Figs. 1 and 2, respectively. The structural parameters were: $a = 9.8564(4)$ Å, $b = 11.2311(4)$, $c = 15.4779(6)$ Å, $\alpha = 84.181(3)°$, $\beta = 73.913(2)°$, $\gamma = 70.456(3)°$, $V = 1551.36(10)$ Å^3, $Z = 2$, $T = 150(2)$ K, $F_W = 704.54$ g/mol for the *trans*-[$RuCl_2$(dppb)(bqdi)] complex, [$C_{34}H_{34}Cl_2N_2P_2Ru$], and $a = 8.6606(6)$ Å, $b = 15.9623(8)$, $c = 27.397(1)$ Å, $V = 3787.4(4)$ Å^3, $Z = 4$, $T = 120(2)$ K, $F_W = 873.98$ g/mol for the *trans*-[$RuCl_2$(dppb)(opda)] · 2(CH_2Cl_2) complex, [$C_{34}H_{36}Cl_2N_2P_2Ru$] · 2(CH_2Cl_2).

The *trans*-[$RuCl_2$(dppb)(bqdi)] and *trans*-[$RuCl_2$(dppb)(opda)] complexes crystallize in the P1 triclinic and $P2_12_12_1$ orthorhombic space group, respectively, with the ruthenium environments adopting a distorted octahedral geometry. The bite angles of 76.59(10)° and 77.3(2)° observed for the *trans*-[$RuCl_2$(dppb)(bqdi)] and *trans*-[$RuCl_2$(dppb)(opda)] complexes, respectively, are consistent with the bidentate coordination of the *o*-phenylene

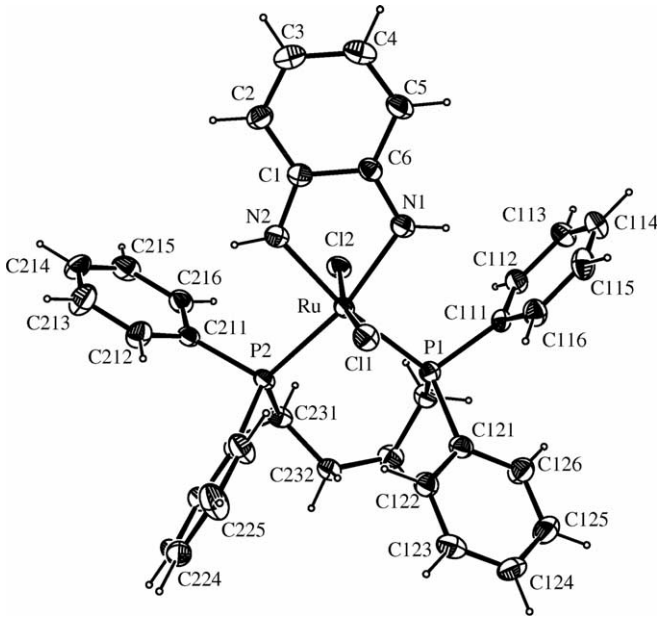


Fig. 1. ORTEP [21] view of the asymmetric unit of the *trans*-[$RuCl_2$(dppb)(bqdi)] complex, showing the atoms labeling and the 50% probability ellipsoids. Selected bond lengths (Å) and angles (°): Ru–N(1) 2.103(2), Ru–N(2) 2.056(3), Ru–P(2) 2.3051(8), Ru–P(1) 2.3431(9), Ru–Cl(1) 2.3994(9), Ru–Cl(2) 2.4130(9), N(2)–C(1) 1.351(4), N(1)–C(6) 1.349(4), N(2)–Ru–N(1) 76.59(10).

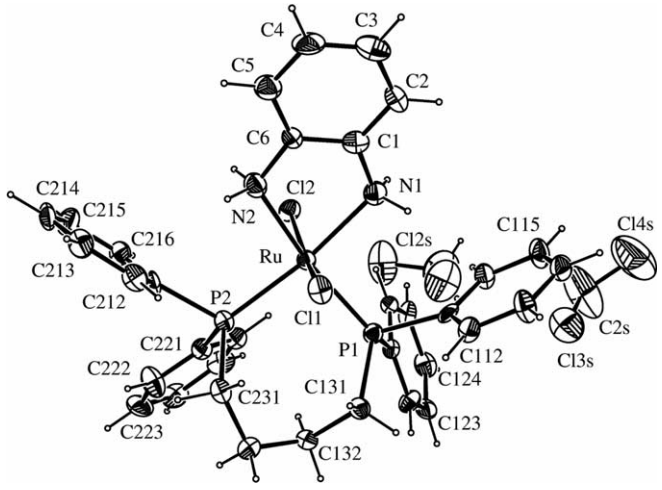


Fig. 2. ORTEP [21] view of the asymmetric unit of the *trans*-[$RuCl_2$(dppb)(opda)] complex, showing the atoms labeling and the 50% probability ellipsoids. Selected bond lengths (Å) and angles (°): Ru–N(1) 2.139(6), Ru–N(2) 2.124(6), Ru–P(2) 2.2919(19), Ru–P(1) 2.298(2), Ru–Cl(1) 2.4145(19), Ru–Cl(2) 2.4110(19), N(1)–C(1) 1.409(10), N(2)–C(6) 1.415(9), N(2)–Ru–N(1) 77.3(2).

ligands [23] as suggested by the $^{31}P\{^1H\}$ NMR experiments mentioned previously.

For the *trans*-[$RuCl_2$(dppb)(bqdi)] complex, the C–C bond lengths within the *o*-phenylene ring are well different (C(1)–C(2) 1.424(4), C(1)–C(6) 1.436(4), C(2)–C(3) 1.362(4), C(3)–C(4) 1.411(5), C(4)–C(5) 1.353(5), C(5)–C(6) 1.420(4)) thus indicating a localized charge distribution which is consistent with the quinone form. On the other hand, the C–C bond lengths of the *o*-phenylene ring observed for the *trans*-[$RuCl_2$(dppb)(opda)] complex are only of marginal difference (C(1)–C(2) 1.377(10), C(1)–C(6) 1.390(10), C(2)–C(3) 1.403(12), C(3)–C(4) 1.361(12), C(4)–C(5) 1.351(11), C(5)–C(6) 1.404(11)) suggesting a strongly delocalized charge distribution that is an indicative of the catechol form. Also, the average C–N bond lengths of 1.350(4) and 1.412(10) Å for the *trans*-[$RuCl_2$(dppb)(bqdi)] and *trans*-[$RuCl_2$(dppb)(opda)] complexes, respectively, confidently confirms that the *o*-phenylene ligands are in its fully oxidized and reduced forms in these compounds.

The half-wave formal potentials ($E_{1/2}$) of the $Ru^{III/II}$ redox process were observed at almost the same potential, 0.74 V, for the *trans*-[$RuCl_2$(dppb)(bqdi)] and *trans*-[$RuCl_2$(dppb)(opda)] complexes. Similar behavior was also observed for amine and imine iron and ruthenium complexes [5].

The $^{31}P\{^1H\}$ NMR experiments confirmed that the *trans*-[$RuCl_2$(dppb)(bqdi)] complex is the only product of the ruthenium-assisted reaction of the opda with the *mer*-[$Ru^{III}Cl_3$(dppb)(H_2O)] complex in the presence of oxygen. The oxidation process of the *trans*-[$RuCl_2$(dppb)(opda)] complex is slow and, under inert atmosphere, this species can be easily isolated with high level of purity from the reaction of the [$Ru^{II}Cl_2$(dppb)(PPh_3)] complex with the opda ligand. Therefore, the data collected here suggest that the *mer*-[$RuCl_3$(dppb)(H_2O)] complex is a suitable precursor for the conversion of the *o*-phenylenediamine to *o*-benzoquinonediimine ligand. This conclusion reinforces the application possibility of the *mer*-[$RuCl_3$(dppb)(H_2O)] aqua-complex as starting reagent in a wide range of synthetic routes.

Supplementary material

Complete tables of bond lengths and angles, final atomic coordinates and equivalent isotropic thermal parameters, calculated hydrogen parameters, anisotropic thermal parameters, and structure factors for the structures were deposited with the Cambridge Crystallographic Data Center (CCDC). The respective numbers for the *trans*-[$RuCl_2$(dppb)(bqdi)] and *trans*-[$RuCl_2$(dppb)(opda)] complexes are CCDC 275198 and 275199.

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