

## Synthesis and Characterization of [RuCl<sub>3</sub>(P-P)(H<sub>2</sub>O)] Complexes; P-P = Achiral or Chiral, Chelating Ditertiary Phosphine Ligands

Luis R. Dinelli,<sup>†</sup> Alzir A. Batista,<sup>\*,†</sup> Karen Wohnrath,<sup>†</sup> Marcio P. de Araujo,<sup>†</sup> Salete L. Queiroz,<sup>‡</sup> Marcos R. Bonfadini,<sup>‡</sup> Glaucius Oliva,<sup>‡</sup> Otaciro R. Nascimento,<sup>‡</sup> Paul W. Cyr,<sup>§</sup> Kenneth S. MacFarlane,<sup>§</sup> and Brian R. James<sup>\*,§</sup>

Departamento de Química, Universidade Federal de São Carlos, CEP 13565-905, São Carlos (SP), Brazil, Instituto de Física e Química, Universidade de São Paulo, CEP 13560-970, São Carlos (SP), Brazil, and Department of Chemistry, The University of British Columbia, Vancouver, BC, V6T 1Z1, Canada

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The reaction of the dinuclear [RuCl<sub>2</sub>(dppb)]<sub>2</sub>(μ-dppb) (dppb = 1,4-bis(diphenylphosphino)butane) with Cl<sub>2</sub> in MeOH for ~30 min at room temperature gives the bright-red solid *mer*-RuCl<sub>3</sub>(dppb)(H<sub>2</sub>O) (**1**); Cl<sub>2</sub> treatment for ~10 min affords the red-brown, mixed valence complex [RuCl(dppb)]<sub>2</sub>(μ-Cl)<sub>3</sub> (**2**). Controlled bulk coulometric reduction of 50% of the content of a CH<sub>2</sub>Cl<sub>2</sub> solution of **1** also produces **2**, formed by the reaction of **1** with "RuCl<sub>2</sub>(dppb)" produced in situ during the electrolysis. Complexes **1** and **2** were characterized by spectroscopic techniques [including electron spin resonance (ESR)], magnetic moments and cyclic voltammetry, and the structure of **1** was determined by X-ray diffraction. The structure shows that the aquo ligand forms hydrogen bonds with two *cis*-chlorine ligands of the neighboring molecule of the complex; this interaction gives rise to exchange coupling between two Ru(III) centers that is reflected in the ESR spectrum. A species **3** analogous to **1** has been obtained with the diop ligand [diop = (2*R*,3*R*)- or (2*S*,3*S*)-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane], on using RuCl<sub>2</sub>(diop)(PPh<sub>3</sub>) or [RuCl(diop)]<sub>2</sub>(μ-Cl)<sub>3</sub> as precursors. The RuCl<sub>3</sub>(P-P)L complexes (P-P = dppb, diop; L = dimethyl sulfoxide, MeOH) are readily synthesized from **1** or **3**.

### Introduction

For Ru complexes containing chelating ditertiary phosphine ligands, the 1:1 "Ru<sup>II</sup>(P-P)" moiety has been identified as the active component of catalysts within hydrogenation reactions, and this has motivated our ongoing interest in synthesizing Ru complexes that contain a single diphosphine ligand per metal center and examining their activities for the catalytic hydrogenation of unsaturated organics.<sup>1,2</sup> In cases where the catalyst precursor contains two chelating diphosphines per Ru, the active species in solution has been shown to contain a Ru(P-P) moiety, and indeed the excess (P-P) ligand inhibits the catalysis.<sup>3</sup> There are many examples of achiral and chiral "Ru(P-P)" catalyst systems. The [RuCl(dppb)]<sub>2</sub>(μ-Cl)<sub>2</sub> complex catalyzes the hydrogenation of styrene,<sup>4</sup> the transfer hydrogenation (from propan-2-ol) of acetophenone,<sup>5</sup> and the H<sub>2</sub>-hydrogenation of imines.<sup>6</sup> The first "Ru(P-P)" enantioselective catalyst system

reported was the hydrogenation of prochiral functionalized olefins such as (*Z*)-acetamidocinnamic acid to 97% enantiomeric excess using [RuCl(P-P)]<sub>2</sub>(μ-Cl)<sub>2</sub> (P-P = chiraphos, diop) species.<sup>7</sup> Subsequently, many "Ru(P-P)"-containing complexes (but with more emphasis on P-P = binap), such as Ru<sub>2</sub>Cl<sub>4</sub>(P-P)<sub>2</sub>(NEt<sub>3</sub>),<sup>2,8</sup> Ru(OAc)<sub>2</sub>(binap),<sup>9</sup> [RuCl(arene)(P-P)]<sup>+</sup>,<sup>10</sup> [RuH(P-P)(solvent)<sub>3</sub>]<sup>+</sup>,<sup>11</sup> Ru(P-P)(π-allyl)<sub>2</sub>,<sup>12</sup> RuCl<sub>2</sub>(RCN)<sub>2</sub>(P-P),<sup>6,8e,13</sup> [RuX(P-P)]<sub>2</sub>(μ-X)<sub>2</sub> (X = halogen),<sup>2,6,14,15</sup> and [RuX(P-P)]<sub>2</sub>(μ-

\* To whom correspondence should be addressed.

<sup>†</sup> Federal University of São Carlos.

<sup>‡</sup> University of São Paulo.

<sup>§</sup> University of British Columbia.

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X)<sub>3</sub>,<sup>2,14,16</sup> have been used as catalysts, and these have been synthesized generally via Ru<sup>II</sup> precursors having Ru(arene),<sup>10</sup> Ru(diene),<sup>8c,17,18</sup> or Ru( $\eta^3$ -allyl) moieties,<sup>12,15,19</sup> or via RuCl<sub>2</sub>(PR<sub>3</sub>)<sub>3</sub>,<sup>2,6,14,16</sup> or RuCl<sub>3</sub>(PR<sub>3</sub>)<sub>2</sub>(*N,N*-dimethylacetamide) (R = Ph, *p*-tolyl).<sup>2,14,16</sup> Such types of complexes are extremely effective precursors for catalytic asymmetric hydrogenation of functionalized prochiral olefins, dienes, and ketones,<sup>20,21</sup> and certain prochiral imines.<sup>22</sup> The synthesized “Ru<sup>II</sup>(P-P)” species are typically air-sensitive in solution, and clearly it would be advantageous for application in organic syntheses to use more air-stable complexes as catalyst precursors. We have noted, for example, the preferred use of the air-stable, Ru(III)/Ru(II) mixed-valence complex [RuCl(P-P)]<sub>2</sub>( $\mu$ -Cl)<sub>3</sub>, which under H<sub>2</sub> is reduced to the true Ru<sup>II</sup> catalyst precursor [RuCl(P-P)]<sub>2</sub>( $\mu$ -Cl)<sub>2</sub>.<sup>6</sup> The number of reported, isolated “Ru<sup>III</sup>(P-P)” species is very limited,<sup>16</sup> and outside of the mixed-valence type, we are unaware of any containing chiral, chelating diphosphines.

In this paper, we report the synthesis of RuCl<sub>3</sub>(P-P)L complexes [L = H<sub>2</sub>O, MeOH, dimethyl sulfoxide (DMSO), P-P = dppb or diop], a new class of “Ru<sup>III</sup>(P-P)” species, and include the structure of RuCl<sub>3</sub>(dppb)(H<sub>2</sub>O) (**1**). A new route to the known, binuclear, mixed-valence [RuCl(dppb)]<sub>2</sub>( $\mu$ -Cl)<sub>3</sub> complex (**2**)<sup>14,16</sup> from [RuCl<sub>2</sub>(dppb)]<sub>2</sub>( $\mu$ -dppb)<sup>14,23</sup> is also described. Controlled potentiometric coulometry of **1** also produces **2**.

## Experimental Section

**Materials and Instrumentation.** Except for the oxidation using Cl<sub>2</sub>, manipulations were carried out under purified Ar using standard Schlenk techniques. Reagent grade solvents were appropriately distilled and dried before use. The dppb was used as received from Aldrich. RuCl<sub>3</sub>·3H<sub>2</sub>O (~40% Ru) was obtained on loan from Johnson Matthey Ltd. or Colonial Metals Inc., or purchased from Degussa S.A. (São Paulo). [RuCl<sub>2</sub>(dppb)]<sub>2</sub>( $\mu$ -dppb) (written subsequently as Ru<sub>2</sub>Cl<sub>4</sub>(dppb)<sub>3</sub>),<sup>3a,23</sup> [RuCl(P-P)]<sub>2</sub>( $\mu$ -Cl)<sub>3</sub><sup>14,16</sup> (written subsequently as Ru<sub>2</sub>Cl<sub>5</sub>(P-P)<sub>2</sub>, where P-P = dppb or diop), and RuCl<sub>2</sub>(diop)(PPh<sub>3</sub>)<sup>13,14</sup> were prepared according to literature procedures.

IR spectra (cm<sup>-1</sup>) were recorded as CsI pellets in the 4000–200 cm<sup>-1</sup> region, on a Bomen-Michelson 102 instrument; UV–visible (UV–vis) and near-infrared (NIR) spectra were recorded in solution on Hewlett-Packard 8452A diode array or Cary 500 spectrophotometers, respectively, and are presented as  $\lambda_{\text{max}}$  or shoulder (nm)/ $\epsilon_{\text{max}}$  (M<sup>-1</sup>cm<sup>-1</sup>). ESR spectra were measured at –160 °C using a Varian E-109 instrument operating at the X band frequency, within a rectangular cavity (E-248) fitted with a temperature controller. Effective magnetic moments ( $\mu_{\text{eff}}$ ) were determined at room temperature (~25° C) by the Gouy method, or by the Evans method using the paramagnetically

shifted <sup>1</sup>H NMR signal of CHCl<sub>3</sub>.<sup>24</sup> Cyclic voltammetry (CV) experiments were carried out at room temperature in CH<sub>2</sub>Cl<sub>2</sub> containing 0.10 M Bu<sub>4</sub>N<sup>+</sup>ClO<sub>4</sub><sup>-</sup> (TBAP) (Fluka Purum) using a BAS-100B/W Bio-analytical Systems Instrument; the working and auxiliary electrodes were stationary Pt foils, and the reference electrode was Ag/AgCl, 0.10 M TBAP in CH<sub>2</sub>Cl<sub>2</sub>, a medium in which ferrocene is oxidized at 0.43 V (Fc<sup>+</sup>/Fc). In the controlled potentiometric coulometry, a Pt mesh was used as working electrode and the auxiliary electrode was separated from the solution by a sintered glass disk. Elemental analyses were performed in the Chemistry Departments at either the University of São Paulo or British Columbia.

**mer-RuCl<sub>3</sub>(dppb)(H<sub>2</sub>O) (1).** All reactions with Cl<sub>2</sub> were performed in air in a well-ventilated fume hood. Cl<sub>2</sub> was generated by dropwise addition of concentrated HCl (10 mL) to ~6.0 g of magnetically stirred, solid KMnO<sub>4</sub> in a three-necked flask equipped with a 50-mL addition funnel, a stopper, and a rubber septum; the generated Cl<sub>2</sub> was vented through a Tygon tube equipped with a 1-mL syringe (with an 18G needle) at each end, one end being inserted through the septum. The syringe tip on the outlet end of the tubing was fitted to a short piece of plastic tubing which was inserted into the reaction mixture to prevent contamination by metal from the syringe. The bubbling rate was maintained by adding one drop of concentrated HCl and allowing the released Cl<sub>2</sub> to bubble through the mixture before adding another drop of acid. Bubbling of Cl<sub>2</sub> through a suspension of Ru<sub>2</sub>Cl<sub>4</sub>(dppb)<sub>3</sub> (97 mg, 0.06 mmol) in MeOH (10 mL) for 30 min at room temperature generated a bright red precipitate, which was collected by filtration, washed with Et<sub>2</sub>O (3 × 10 mL), and dried under vacuum (72 mg; 92%). Anal. Calcd for C<sub>28</sub>H<sub>30</sub>OCl<sub>3</sub>P<sub>2</sub>Ru: C, 51.59; H, 4.64; Cl, 16.31. Found: C, 51.5; H, 4.7; Cl, 16.6. UV–vis (CH<sub>2</sub>Cl<sub>2</sub>): 534 (1650), 420 (1290), 352(1750). IR:  $\nu_{\text{OH}}$  3053 s,  $\delta_{\text{OH}}$  1620 s,  $\nu_{\text{Ru-Cl}}$  340, 303, 263. ESR: see text.  $\mu_{\text{eff}}$  2.19  $\mu_{\text{B}}$ . Crystals suitable for X-ray analysis were grown by slow diffusion of Et<sub>2</sub>O into a CH<sub>2</sub>Cl<sub>2</sub> solution of the complex. Complex **1** was also made by bubbling Cl<sub>2</sub> through a suspension of Ru<sub>2</sub>Cl<sub>5</sub>(dppb)<sub>2</sub> (**2**) (see below; 28 mg, 0.023 mmol) in MeOH (3 mL) for ~10 min. Concentration of the red suspension in vacuo and filtration gave a bright red solid, which was washed with Et<sub>2</sub>O (5 × 1 mL) and dried under vacuum (15.5 mg; 52%).

**[RuCl(dppb)]<sub>2</sub>( $\mu$ -Cl)<sub>3</sub> (2).** Use of the procedure described above, but bubbling Cl<sub>2</sub> for 10 min through a C<sub>6</sub>H<sub>6</sub> or CH<sub>2</sub>Cl<sub>2</sub> solution (10 mL) of the Ru<sub>2</sub>Cl<sub>4</sub>(dppb)<sub>3</sub>, gave a red-brown solution, which was then reduced in volume to ~1 mL; addition of Et<sub>2</sub>O (10 mL) produced a red-brown product, which was filtered off, washed with hexanes, and vacuum-dried (66 mg; 90%). Anal. Calcd for C<sub>56</sub>H<sub>56</sub>Cl<sub>5</sub>P<sub>4</sub>Ru<sub>2</sub>: C, 54.57; H, 4.59; Cl, 14.38. Found: C, 54.5; H, 4.6; Cl, 14.6. UV–vis/NIR (CDCl<sub>3</sub>): 374 (9400), 436 (sh, 7300), 550 (sh, 4700), 980 (900), 2050 (1200).

**RuCl<sub>3</sub>(dppb)(DMSO).** Complex **1** (100 mg, 0.153 mmol) and DMSO (25  $\mu$ L, 0.352 mmol) were stirred in CH<sub>2</sub>Cl<sub>2</sub> (25 mL) at room temperature for 4 h; the solution volume was reduced to ~2 mL, when addition of Et<sub>2</sub>O (10 mL) precipitated a red solid, which was collected, washed well with Et<sub>2</sub>O, and dried under vacuum (88 mg, 79%). Anal. Calcd for C<sub>30</sub>H<sub>34</sub>OCl<sub>3</sub>P<sub>2</sub>SRu: C, 50.61; H, 4.81, S, 4.50. Found: C, 50.32; H, 4.92; S, 4.37. UV–vis (CH<sub>2</sub>Cl<sub>2</sub>): 532 (1670), 420 (1330), 356 (1750). IR:  $\nu_{\text{SO}}$  944 vs,  $\nu_{\text{Ru-Cl}}$  336, 261. ESR:  $g_1$  2.974,  $g_2$  1.985,  $g_3$  1.518,  $\mu_{\text{eff}}$  2.08  $\mu_{\text{B}}$ .

**RuCl<sub>3</sub>(dppb)(MeOH).** Complex **1** (100 mg, 0.153 mmol) was refluxed in 10 mL of CH<sub>2</sub>Cl<sub>2</sub>/MeOH (1:1) for 8 h. The solution volume was reduced to ~2 mL, when addition of Et<sub>2</sub>O precipitated a dark red solid, which was collected, washed with ether, and dried under vacuum (72 mg; 71%). Anal. Calcd for C<sub>29</sub>H<sub>32</sub>OCl<sub>3</sub>P<sub>2</sub>Ru: C, 52.30; H, 4.84. Found: C, 52.4; H, 4.6. UV–Vis (CH<sub>2</sub>Cl<sub>2</sub>): 530 (1780), 420 (1470), 356 (1900). IR:  $\delta_{\text{OH}}$  1634,  $\nu_{\text{Ru-Cl}}$  351, 266. ESR:  $g_1$  2.828,  $g_2$  2.106,  $g_3$  1.645.

**RuCl<sub>2</sub>(diop)(H<sub>2</sub>O) (3).** Bubbling of Cl<sub>2</sub> through a solution of RuCl<sub>2</sub>(diop)(PPh<sub>3</sub>) (273 mg, 0.29 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (30 mL) for ~30 min at room temperature generated a red solution, which was then evaporated to dryness; the solid was then dissolved in Et<sub>2</sub>O (30 mL) and the solution filtered to remove a small amount of the mixed

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**Table 1.** Crystallographic Data for *mer*-RuCl<sub>3</sub>(dppb)(H<sub>2</sub>O) (1)<sup>a</sup>

formula	C <sub>28</sub> H <sub>30</sub> OCl <sub>3</sub> P <sub>2</sub> Ru
fw	651.88
space group	orthorhombic, <i>Pbca</i>
<i>a</i> , Å	14.932 (2)
<i>b</i> , Å	18.133 (3)
<i>c</i> , Å	20.594 (2)
<i>V</i> , Å <sup>3</sup>	5576.0(1)
<i>Z</i>	8
$\rho_{\text{calc}}$ , g/cm <sup>3</sup>	1.553
<i>T</i> , °C	25
$\mu$ (Mo K $\alpha$ ), cm <sup>-1</sup>	9.850
<i>F</i> (000)	2648
no. of refined params	316
<i>R</i> 1 [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.046
<i>wR</i> 2	0.094

$$^a R1 = \sum ||F_o| - |F_c|| / \sum |F_o|, wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}.$$

phosphine precursor. The red solution was concentrated to ~1 mL and hexanes (20 mL) were added to precipitate the product, which was collected, and dried under vacuum (53 mg; 25%). Anal. Calcd for C<sub>31</sub>H<sub>34</sub>O<sub>3</sub>Cl<sub>3</sub>P<sub>2</sub>Ru: C, 51.43; H, 4.73. Found: C, 51.17; H, 4.76. UV-vis (CH<sub>2</sub>Cl<sub>2</sub>): 534 (1720), 428 (1480), 356 (1800). IR:  $\nu_{\text{OH}}$  3058 s,  $\delta_{\text{OH}}$  1596 s,  $\nu_{\text{Ru-Cl}}$  313, 274. ESR:  $g_1$  2.782,  $g_2$  2.137,  $g_3$  1.721.  $\mu_{\text{eff}}$  2.21  $\mu_B$ . Complex **3** was also made by bubbling Cl<sub>2</sub> through a solution of Ru<sub>2</sub>Cl<sub>5</sub>(diop)<sub>2</sub> (25.5 mg, 0.018 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) for 10 min. Concentration of the red solution in vacuo to ~2 mL, followed by addition of hexanes (10 mL) precipitated a dark red solid, which was filtered off, washed with hexanes (3 × 3 mL) and dried under vacuum (13.3 mg; 50%).

**RuCl<sub>3</sub>(diop)(DMSO).** Complex **3** (22.3 mg, 0.031 mmol) and DMSO (5  $\mu$ L, 0.070 mmol) were stirred in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) at room temperature for 6 h, when the solution changed from dark red to pink. The volume was reduced to ~1 mL and hexanes (20 mL) were added to precipitate a solid, which was filtered off, washed with hexanes (3 × 3 mL), and dried in vacuo (13 mg, 58%). Anal. Calcd for C<sub>33</sub>H<sub>38</sub>O<sub>3</sub>Cl<sub>3</sub>P<sub>2</sub>SRu requires: C, 50.55; H, 4.88. Found: C 50.21; H, 4.99. UV-vis (CH<sub>2</sub>Cl<sub>2</sub>): 530 (1680), 424 (1390), 358 (1750). IR:  $\nu_{\text{SO}}$  948 vs,  $\nu_{\text{Ru-Cl}}$  325, 260. ESR:  $g_1$  2.982,  $g_2$  2.031,  $g_3$  1.584.

**X-ray Crystallographic Analysis of 1.** Selected crystallographic data appear in Table 1 together with some experimental details. A single crystal of approximate dimensions 0.12 × 0.30 × 0.60 mm was used for data collection and unit cell determination on an Enraf-Nonius CAD-4 diffractometer at room temperature with graphite monochromatized Mo K $\alpha$  radiation ( $\lambda$  = 0.710 73 Å). Unit-cell parameters were obtained from a least-squares refinement of the setting angles of 25 reflections in the range  $\theta$  = 10.2–18.9°. Intensity data were collected in the  $\omega$ -2 $\theta$  scan mode up to  $\theta_{\text{max}}$  = 24.97°, with a scan rate range 6.7–20° min<sup>-1</sup>. The data were corrected for Lorentz and polarization, and the absorption effects were corrected empirically by a standard procedure.<sup>25</sup> The structure was solved by Patterson methods and difference Fourier techniques. Scattering factors for non-H atoms were taken from Cromer and Mann,<sup>26a</sup> with corrections for anomalous dispersion from Cromer and Liberman<sup>26b</sup> and for H atoms from Stewart et al.<sup>27</sup> All calculations were performed with the program SHELX-97.<sup>28</sup> All non-H atoms of the structure were refined with anisotropic thermal parameters. The aromatic and methylene H atoms were set isotropic with a thermal parameter 20% greater than the equivalent isotropic displacement parameter of the associated C atom. All H atoms were stereochemically positioned and refined with the riding model.<sup>28</sup> The aromatic and CH<sub>2</sub> bond lengths were set equal to 0.93 and 0.97 Å, respectively, and the aromatic rings were treated as rigid groups. Selected bond lengths, and bond angles appear in Table 2. A complete

**Table 2.** Selected Bond Lengths (Å) and Angles (deg)<sup>a</sup>

Ru–P(1)	2.286(2)	Ru–Cl(2)	2.304(2)
Ru–P(2)	2.384(2)	Ru–Cl(3)	2.348(2)
Ru–Cl(1)	2.402(2)	Ru–O(W)	2.216(5)
O(W)···H(O1)	1.037(5)	Cl(3)···H(O1)	2.484(2)
O(W)···H(O2)	0.953(5)	Cl(3)···O(W)	3.346(3)
P–C 1.830(8)–1.843(8)			
P(1)–Ru–P(2)	93.53(7)	Cl(1)–Ru–O(W)	82.6(2)
P(1)–Ru–Cl(1)	92.09(7)	Cl(2)–Ru–Cl(3)	167.32(8)
P(1)–Ru–Cl(2)	95.66(8)	Cl(2)–Ru–O(W)	82.8(2)
P(1)–Ru–Cl(3)	96.43(7)	Cl(3)–Ru–O(W)	85.4(1)
P(1)–Ru–O(W)	174.4(2)	P(1)–C(1)–C(2)	115.9(5)
P(2)–Ru–Cl(1)	174.37(7)	C(1)–C(2)–C(3)	114.4(7)
P(2)–Ru–Cl(2)	89.14(7)	C(2)–C(3)–C(4)	116.5(7)
P(2)–Ru–Cl(3)	86.31(7)	P(2)–C(4)–C(3)	117.3(6)
P(2)–Ru–O(W)	91.8(2)	P(1)–C(111)–C(112)	116.6(6)
Cl(1)–Ru–Cl(2)	90.55(8)	P(1)–C(111)–C(116)	124.8(6)
Cl(1)–Ru–Cl(3)	92.83(7)	H(O1)–O(W)–H(O2)	100.0(4)
		O(W)–H(O1)–Cl(3)	140.0(3)
C–P–C 102.1(3)–103.0(3)			

<sup>a</sup> Estimated standard deviations are given in parentheses.

table of atomic coordinates and equivalent isotropic thermal parameters, crystallographic data, hydrogen atom parameters, anisotropic thermal parameters, bond lengths, and bond angles are included as Supporting Information.

## Results and Discussion

The Ru(III) aquo, chelating diphosphine complexes of the type RuCl<sub>3</sub>(P-P)(H<sub>2</sub>O), where P-P = dppb (**1**) or diop (**3**), are readily synthesized by Cl<sub>2</sub>-oxidation of the Ru(II) precursors Ru<sub>2</sub>Cl<sub>4</sub>(P-P)<sub>3</sub> or RuCl<sub>2</sub>(P-P)(PPh<sub>3</sub>), or the Ru(II)Ru(III) dinuclear species Ru<sub>2</sub>Cl<sub>5</sub>(P-P)<sub>2</sub>; the source of the water for the aquo ligand could be the solvent or the Cl<sub>2</sub> supply. That the syntheses from Ru<sub>2</sub>Cl<sub>4</sub>(P-P)<sub>3</sub> proceed via Ru<sub>2</sub>Cl<sub>5</sub>(P-P)<sub>2</sub> is apparent via visible monitoring of the reaction because the mixed valence species are red-brown, whereas **1** and **3** are bright red; also, during the synthesis of **3** from RuCl<sub>2</sub>(diop)(PPh<sub>3</sub>), in situ monitoring in the NIR region revealed the charge-transfer bands at 950 and 2050 cm<sup>-1</sup>, characteristic of Ru<sub>2</sub>Cl<sub>5</sub>(diop)<sub>2</sub>.<sup>16</sup> Finally, if the Cl<sub>2</sub>-oxidation procedure is carried out for a shorter time scale, the Ru<sub>2</sub>Cl<sub>5</sub>(dppb)<sub>2</sub> complex (**2**) can be isolated in high yield on using Ru<sub>2</sub>Cl<sub>4</sub>(dppb)<sub>3</sub> as reactant.

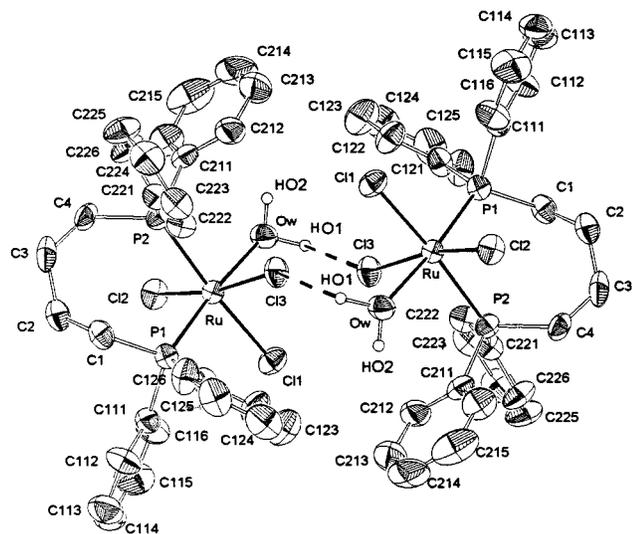
X-ray analysis of RuCl<sub>3</sub>(dppb)(H<sub>2</sub>O) (**1**) reveals a distorted octahedral structure with a *mer*-configuration of the Cl atoms with the aquo ligand necessarily *trans* to a P atom (Figure 1). Of interest, the aquo ligand forms H-bonds with two *cis*-chlorine ligands of the neighboring molecule of the complex, which is related by an inversion center. The water H atoms were identified from difference maps and were refined isotropically; the O–H(O1) and O–H(O2) distances are 1.037(5) and 0.953(5) Å, respectively, whereas the H(O1)···Cl(3) hydrogen-bonding distance is 2.484(2) Å. The distance of the O atom of one molecule to the Cl(3) from the centrosymmetrically related molecule is 3.346(3) Å, and the corresponding O–H(O1)···Cl(3) angle is 140.0(3)°. The H(O1)–O–H(O2) angle is 100.0(4)°. There is also a much weaker H-bonding interaction between H(O2) and Cl(1) with a separation of 3.217 Å. The Ru–Cl distances (2.304–2.402 Å) appear in the normal, well-established range for Ru(III) complexes<sup>29–31</sup>; the longest one is reasonably the bond *trans* to the P atom, whereas the Ru–Cl(3) of length 2.348(2) Å is possibly weakened compared with Ru–Cl(2), 2.304(2) Å, because of the H-bonding interaction with Cl(3). The Ru–P(1) and Ru–P(2) bonds, 2.286(2) Å and 2.384(2) Å, are *trans* to water and Cl, respectively, and are

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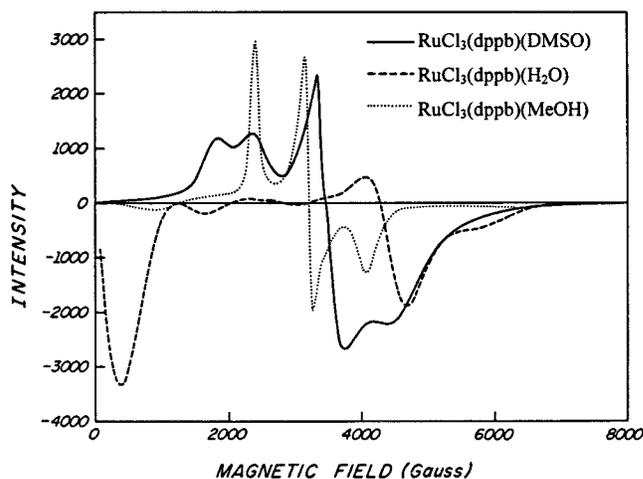


**Figure 1.** X-ray structure of *mer*-RuCl<sub>3</sub>(dppb)(H<sub>2</sub>O) (**1**), showing 50% probability thermal ellipsoids for the nonhydrogen atoms.

comparable to the Ru–P bond length in *mer*-RuCl<sub>3</sub>(PPh<sub>3</sub>)(1-methylimidazole)<sub>2</sub>, 2.326(2) Å, where the PPh<sub>3</sub> is *trans* to the methylimidazole.<sup>30</sup> As expected, for a relatively hard Ru(III) center, the Ru–OH<sub>2</sub> distance [2.216(5) Å] is shorter than the Ru–P distances, and being *trans* to a P-donor, the bond is longer than that of 2.101(4) Å found in RuCl<sub>3</sub>(dmp)<sub>2</sub>(H<sub>2</sub>O), where dmp is a N-donor pyrimidine derivative, and the aquo ligand is *trans* to a Cl atom.<sup>31</sup>

The magnetic moments of **1** and **3** (2.19 and 2.21 μ<sub>B</sub>, respectively), although somewhat high for low-spin d<sup>5</sup> (*S* = 1/2) systems, are not unusual for Ru(III) complexes.<sup>32</sup> Within these aquo complexes, the IR spectra show a sharp δ<sub>OH</sub> band of coordinated water in the 1600 cm<sup>-1</sup> region.<sup>33</sup> Three bands seen in the 340–260 cm<sup>-1</sup> range for **1** with *mer*-geometry could be associated with ν<sub>Ru–Cl</sub> stretches. For **3**, two stronger bands in this range are evident, but there are also several weaker bands that might be due to ν<sub>Ru–Cl</sub>; whether **3** is *mer* or *fac* is not known unambiguously, but similarities in UV–vis spectra of **1** and **3** imply a *mer*-configuration. The far-IR data for these particular complexes [or RuCl<sub>3</sub>(P–P)L, where L is another coordinating solvent, see below] do not readily distinguish between the *mer*- and *fac*-geometries.

The aquo ligand in **1** and **3** is readily displaced by other solvent ligands (L) such as DMSO, MeOH, and MeCN. Complexes with DMSO and MeOH have been isolated; they show correct elemental analyses for the formulation RuCl<sub>3</sub>(P–P)L, and they have been partially characterized by spectroscopic and sometimes μ<sub>eff</sub> data. Similarities in UV–vis data to those of **1** again suggest *mer*-geometries. The ν<sub>SO</sub> values for the dppb/DMSO and diop/DMSO complexes (944 and 948 cm<sup>-1</sup>) suggest



**Figure 2.** ESR spectra (X-band frequency) of RuCl<sub>3</sub>(dppb)L complexes (L = H<sub>2</sub>O, DMSO, MeOH) at –160 °C in the solid state.

O-bonded sulfoxide.<sup>34</sup> Dissolution of **1** or **3** in MeCN gives UV–vis changes consistent with replacement of the aquo ligand by MeCN (see below).

Complexes **1** and **3**, and the RuCl<sub>3</sub>(P–P)L species, in CH<sub>2</sub>Cl<sub>2</sub> all show very similar UV–vis spectra having three bands in the 350–540 nm region with the middle band of somewhat lower intensity (see Figure S1). The spectra correspond closely to those reported earlier by one of our groups for dissolution of the dinuclear complex [RuCl<sub>3</sub>(dppb)]<sub>2</sub> in DMSO or MeCN,<sup>16</sup> consistent with formation of the corresponding RuCl<sub>3</sub>(dppb)L species. The new Ru(III) chemistry described here also partly clarifies the nature of the earlier suggested disproportionation of Ru<sub>2</sub>Cl<sub>5</sub>(dppb)<sub>2</sub> in coordinating solvents into “RuCl<sub>3</sub>(dppb)” and “RuCl<sub>2</sub>(dppb)”.<sup>16</sup>

The solid-state ESR spectrum measured for RuCl<sub>3</sub>(dppb)(H<sub>2</sub>O) (**1**) is markedly different from those determined for the corresponding DMSO and MeOH complexes (Figure 2). Those of the last two, with three *g* values in the 2.9, 2.0, and 1.5 regions, are typical of Ru(III) species with rhombic distortions,<sup>30</sup> whereas the spectrum of **1** shows a signal close to zero magnetic field, which is characteristic of complexes with coupling between paramagnetic species.<sup>35</sup> Presumably, such an interaction in **1** occurs via a pathway involving the intermolecular H-bonding of the coordinated water molecule with the Cl atoms of the neighboring molecule of the complex, as noted in the discussion of the crystal structure. The observed ESR spectrum is consistent with a spin–spin interaction giving a zero-field splitting energy (*J* value) of 0.309 cm<sup>-1</sup>. A conceptually similar exchange coupling between two Cu(II)-containing molecules via a very weak H-bond between a coordinated Cl atom and the NH proton of a pyrazole ligand (where Cl⋯H = 3.72 Å, compared with H⋯Cl = 2.48 Å within **1**) realized a *J* value about 100 times smaller.<sup>35</sup> The ESR of a frozen CH<sub>2</sub>Cl<sub>2</sub> solution of **1** (at –160 °C) shows the more typical three *g* value spectrum (*g* = 2.81, 2.11, and 1.71), implying the absence of coupling evident in the solid state. The ESR spectrum for **3**, the aquo/diop complex, is that of a typical Ru(III) species, implying the absence of strong H-bonding interactions in the solid-state structure; the ESR spectrum of a frozen MeCN solution of

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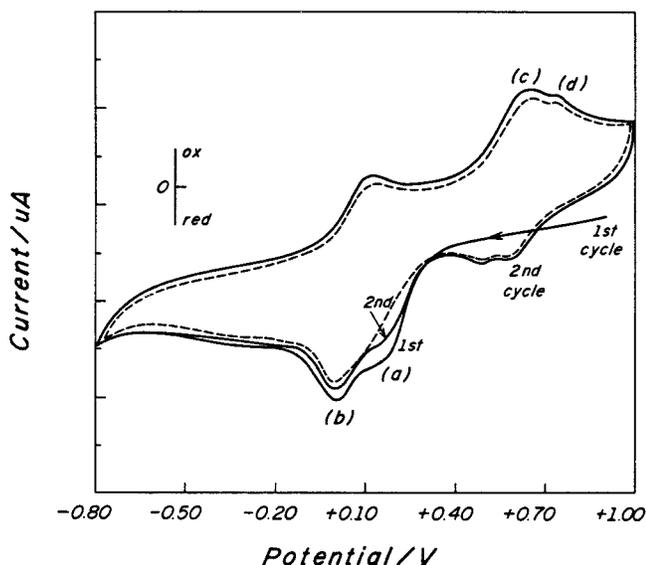
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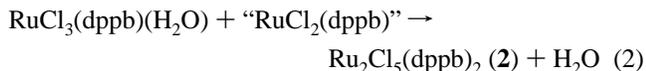
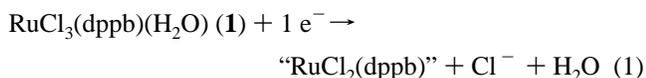


**Figure 3.** Cyclic voltammograms of RuCl<sub>3</sub>(dppb)(H<sub>2</sub>O) (**1**) (—) and Ru<sub>2</sub>Cl<sub>5</sub>(dppb)<sub>2</sub> (**2**) (---); 0.001 M in CH<sub>2</sub>Cl<sub>2</sub> with 0.10 M TBPA; scan rate 100 mV/s.

RuCl<sub>3</sub>(diop)(MeCN) formed in situ from **3** was essentially identical with that of **3**.

Cursory examination of the <sup>1</sup>H NMR spectra of several of the isolated RuCl<sub>3</sub>(P-P)L complexes revealed relatively weak, paramagnetically upfield-shifted, broad signals that could be attributed generally to the phenyl or alkyl protons, but the NMR studies were not pursued, although such data on such low-spin d<sup>5</sup> Ru species have been reported.<sup>31,36</sup>

Cyclic voltammetric measurements on [RuCl<sub>3</sub>(dppb)(H<sub>2</sub>O)] (**1**) (Figure 3) show the intermediacy of Ru<sub>2</sub>Cl<sub>5</sub>(dppb)<sub>2</sub> (**2**) in the overall reduction to “RuCl<sub>2</sub>(dppb)”, which exists as the known dimer [RuCl(dppb)]<sub>2</sub>(μ-Cl)<sub>2</sub>.<sup>2,14</sup> The CV data are readily rationalized in terms of eqs 1–3:



The CV reveals an irreversible Ru(III)/Ru(II) process with  $E_{pc}$  0.14 V (point *a*), which is attributed to eq 1; this peak is absent in subsequent cycles because the electrochemistry is followed by the formation of **2** according to eq 2. The process at 0.06 V (point *b*) is due to reduction of the Ru(III) center of **2**, as confirmed by CV on a chemically synthesized sample of

**2** (Figure 3). Controlled bulk coulometry to 50% reduction of **1** readily allows for isolation of **2**; this was accomplished by evaporating the product solution to dryness, dissolving the red-brown residue in CH<sub>2</sub>Cl<sub>2</sub>, filtering off the TBAP, and adding Et<sub>2</sub>O to precipitate the mixed-valence complex. The air-sensitive Ru<sub>2</sub>Cl<sub>4</sub>(dppb)<sub>2</sub> complex has been made previously by H<sub>2</sub>-reduction of **2**,<sup>2,14</sup> and presumably could be made electrochemically (eq 3). The CV behavior of RuCl<sub>3</sub>(diop)(H<sub>2</sub>O) (**3**) is very similar to that of **1**; peaks corresponding to those of *a*–*d* are seen at 0.20, 0.14, 0.66, and 0.82 V, respectively, the consistently higher values revealing slight, relative stabilization of the Ru(II) state in the diop vs corresponding dppb species.

The two peaks at  $E_{1/2}$  0.52 and 0.73 V (points *c* and *d*, respectively) are attributed to Ru(III)/Ru(II) Ru(III)/Ru(III) couples, one implication being that, in this solution, **2** could exist as two isomers. Earlier, UV–vis and NIR data from one of our groups<sup>16</sup> had been interpreted in terms of the existence of two isomers within complexes such as **2**, such a conclusion being based partly on the presence of two charge-transfer bands in the NIR region solution spectra; for example, **2** in CDCl<sub>3</sub> shows bands at 970 and 2050 nm of comparable intensity ( $\epsilon = 890$  and 1180, respectively). Heath's group more recently has shown that the single isomer, mixed valence, cationic, triply choro-bridged complexes [Ru<sub>2</sub>Cl<sub>3</sub>L<sub>6</sub>]<sup>2+</sup> (where L is a terminal, monodentate, tertiary phosphine) exhibit two bands in this region of the spectrum but, in contrast to **2**, the higher energy band has much stronger intensity.<sup>37</sup> The closeness of the two  $E_{1/2}$  values argues for the existence of isomers within the solution of **2**. These potentials are about 1.0 V below the corresponding one of the dicationic species,<sup>38</sup> which seems reasonable considering the 2+ difference in charges on the complexes; comparison of each Ru environment in the two types of complexes shows that **2** has a terminal Cl atom versus a terminal PR<sub>3</sub> ligand in the dications, a factor that again will relatively stabilize Ru(III) and lead to a lower potential.<sup>38</sup> Both types of complexes are of the delocalized classification.<sup>16,37</sup> An alternative explanation for the presence of the *c* and *d* peaks (suggested by one of the reviewers) is that the second isomer is generated via a redox-initiated process after generation of the species giving rise to peak *c*; further CV studies on these dinuclear Ru species are needed to unravel these details.

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**Supporting Information Available:** Complete tables of crystallographic data, final atomic coordinates and equivalent isotropic parameters, hydrogen atom parameters, anisotropic thermal parameters, bond lengths and bond angles for **1**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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