Synthesis and Characterization of $[RuCl_3(P\text{-}P)(H_2O)]$ Complexes; P-P = Achiral or Chiral, Chelating Ditertiary Phosphine Ligands

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The reaction of the dinuclear $[RuCl_2(dppb)]_2(\mu\text{-dppb})$ (dppb = 1,4-bis(diphenylphosphino)butane) with Cl_2 in MeOH for ~30 min at room temperature gives the bright-red solid *mer*-$RuCl_3(dppb)(H_2O)$ (**1**); Cl_2 treatment for ~10 min affords the red-brown, mixed valence complex $[RuCl(dppb)]_2(\mu\text{-Cl})_3$ (**2**). Controlled bulk coulometric reduction of 50% of the content of a CH_2Cl_2 solution of **1** also produces **2**, formed by the reaction of **1** with "$RuCl_2$(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 $RuCl_2(diop)(PPh_3)$ or $[RuCl(diop)]_2(\mu\text{-Cl})_3$ as precursors. The $RuCl_3(P\text{-}P)L$ 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^{II}(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.[1,2] 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.[3] There are many examples of achiral and chiral "Ru(P-P)" catalyst systems. The $[RuCl(dppb)]_2(\mu\text{-Cl})_2$ complex catalyzes the hydrogenation of styrene,[4] the transfer hydrogenation (from propan-2-ol) of acetophenone,[5] and the H_2-hydrogenation of imines.[6] 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 $[RuCl(P\text{-}P)]_2(\mu\text{-Cl})_2$ (P-P = chiraphos, diop) species.[7] Subsequently, many "Ru(P-P)"-containing complexes (but with more emphasis on P-P = binap), such as $Ru_2Cl_4(P\text{-}P)_2(NEt_3)$,[2,8] $Ru(OAc)_2$(binap),[9] $[RuCl(arene)(P\text{-}P)]^+$,[10] $[RuH(P\text{-}P)(solvent)_3]^+$,[11] $Ru(P\text{-}P)(\pi\text{-allyl})_2$,[12] $RuCl_2(RCN)_2(P\text{-}P)$,[6,8e,13] $[RuX(P\text{-}P)]_2(\mu\text{-X})_2$ (*X* = halogen),[2,6,14,15] and $[RuX(P\text{-}P)]_2(\mu\text{-}$

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$X)_3$,[2,14,16] have been used as catalysts, and these have been synthesized generally via Ru^{II} precursors having Ru(arene),[10] Ru(diene),[8c,17,18] or Ru(η^3-allyl) moieties,[12,15,19] or via $RuCl_2(PR_3)_3$[2,6,14,16] or $RuCl_3(PR_3)_2$(*N*,*N*-dimethylacetamide) (R = Ph, *p*-tolyl).[2,14,16] Such types of complexes are extremely effective precursors for catalytic asymmetric hydrogenation of functionalized prochiral olefins, dienes, and ketones,[20,21] and certain prochiral imines.[22] The synthesized "Ru^{II}(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 $[RuCl(P\text{-}P)]_2(\mu\text{-}Cl)_3$, which under H_2 is reduced to the true Ru^{II} catalyst precursor $[RuCl(P\text{-}P)]_2(\mu\text{-}Cl)_2$.[6] The number of reported, isolated "Ru^{III}(P-P)" species is very limited,[16] and outside of the mixed-valence type, we are unaware of any containing chiral, chelating diphosphines.

In this paper, we report the synthesis of $RuCl_3$(P-P)L complexes [L = H_2O, MeOH, dimethyl sulfoxide (DMSO), P-P = dppb or diop], a new class of "Ru^{III}(P-P)" species, and include the structure of $RuCl_3(dppb)(H_2O)$ (**1**). A new route to the known, binuclear, mixed-valence $[RuCl(dppb)]_2$ $(\mu\text{-}Cl)_3$ complex (**2**)[14,16] from $[RuCl_2(dppb)]_2(\mu\text{-}dppb)$[14,23] is also described. Controlled potentiometric coulometry of **1** also produces **2**.

Experimental Section

Materials and Instrumentation. Except for the oxidation using Cl_2, 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. $RuCl_3 \cdot 3H_2O$ (~40% Ru) was obtained on loan from Johnson Matthey Ltd. or Colonial Metals Inc., or purchased from Degussa S.A. (São Paulo). $[RuCl_2(dppb)]_2(\mu\text{-dppb})$ (written subsequently as $Ru_2Cl_4(dppb)_3$),[3a,23] $[RuCl(P\text{-}P)]_2(\mu\text{-}Cl)_3$[14,16] (written subsequently as $Ru_2Cl_5(P\text{-}P)_2$, where P-P = dppb or diop), and $RuCl_2(diop)(PPh_3)$[13,14] were prepared according to literature procedures.

IR spectra (cm^{-1}) were recorded as CsI pellets in the 4000−200 cm^{-1} 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 λ_{max} or shoulder (nm)/ϵ_{max} ($M^{-1}cm^{-1}$). 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 (μ_{eff}) were determined at room temperature (~25° C) by the Gouy method, or by the Evans method using the paramagnetically shifted ^1H NMR signal of $CHCl_3$.[24] Cyclic voltammetry (CV) experiments were carried out at room temperature in CH_2Cl_2 containing 0.10 M $Bu_4N^+ClO_4^-$ (TBAP) (Fluka Purum) using a BAS-100B/W Bioanalytical Systems Instrument; the working and auxiliary electrodes were stationary Pt foils, and the reference electrode was Ag/AgCl, 0.10 M TBAP in CH_2Cl_2, a medium in which ferrocene is oxidized at 0.43 V (Fc^+/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*-$RuCl_3(dppb)(H_2O)$ (1).** All reactions with Cl_2 were performed in air *in a well-ventilated fume hood.* Cl_2 was generated by dropwise addition of concentrated HCl (10 mL) to ~6.0 g of magnetically stirred, solid $KMnO_4$ in a three-necked flask equipped with a 50-mL addition funnel, a stopper, and a rubber septum; the generated Cl_2 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_2 to bubble through the mixture before adding another drop of acid. Bubbling of Cl_2 through a suspension of $Ru_2Cl_4(dppb)_3$ (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_2O (3 × 10 mL), and dried under vacuum (72 mg; 92%). Anal. Calcd for $C_{28}H_{30}OCl_3P_2Ru$: C, 51.59; H, 4.64; Cl, 16.31. Found: C, 51.5; H, 4.7; Cl, 16.6. UV−vis (CH_2Cl_2): 534 (1650), 420 (1290), 352(1750). IR: ν_{OH} 3053 s, δ_{OH} 1620 s, ν_{Ru-Cl} 340, 303, 263. ESR: see text. μ_{eff} 2.19 μ_B. Crystals suitable for X-ray analysis were grown by slow diffusion of Et_2O into a CH_2Cl_2 solution of the complex. Complex **1** was also made by bubbling Cl_2 through a suspension of $Ru_2Cl_5(dppb)_2$ (**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_2O (5 × 1 mL) and dried under vacuum (15.5 mg; 52%).

$[RuCl(dppb)]_2(\mu\text{-}Cl)_3$ (2). Use of the procedure described above, but bubbling Cl_2 for 10 min through a C_6H_6 or CH_2Cl_2 solution (10 mL) of the $Ru_2Cl_4(dppb)_3$, gave a red-brown solution, which was then reduced in volume to ~1 mL; addition of Et_2O (10 mL) produced a red-brown product, which was filtered off, washed with hexanes, and vacuum-dried (66 mg; 90%). Anal. Calcd for $C_{56}H_{56}Cl_5P_4Ru_2$: C, 54.57; H, 4.59; Cl, 14.38. Found: C, 54.5; H, 4.6; Cl, 14.6. UV−vis/NIR ($CDCl_3$): 374 (9400), 436 (sh, 7300), 550 (sh, 4700), 980 (900), 2050 (1200).

$RuCl_3(dppb)(DMSO)$. Complex **1** (100 mg, 0.153 mmol) and DMSO (25 μL, 0.352 mmol) were stirred in CH_2Cl_2 (25 mL) at room temperature for 4 h; the solution volume was reduced to ~2 mL, when addition of Et_2O (10 mL) precipitated a red solid, which was collected, washed well with Et_2O, and dried under vacuum (88 mg, 79%). Anal. Calcd for $C_{30}H_{34}OCl_3P_2SRu$: C, 50.61; H, 4.81, S, 4.50. Found: C, 50.32; H, 4.92; S, 4.37. UV−vis (CH_2Cl_2): 532 (1670), 420 (1330), 356 (1750). IR: ν_{SO} 944 vs, ν_{Ru-Cl} 336, 261. ESR: g_1 2.974, g_2 1.985, g_3 1.518. μ_{eff} 2.08 μ_B.

$RuCl_3(dppb)(MeOH)$. Complex **1** (100 mg, 0.153 mmol) was refluxed in 10 mL of CH_2Cl_2/MeOH (1:1) for 8 h. The solution volume was reduced to ~2 mL, when addition of Et_2O precipitated a dark red solid, which was collected, washed with ether, and dried under vacuum (72 mg; 71%). Anal. Calcd for $C_{29}H_{32}OCl_3P_2Ru$: C, 52.30; H, 4.84. Found: C, 52.4; H, 4.6. UV−Vis (CH_2Cl_2): 530 (1780), 420 (1470), 356 (1900). IR: δ_{OH} 1634, ν_{Ru-Cl} 351, 266. ESR: g_1 2.828, g_2 2.106, g_3 1.645.

$RuCl_3(diop)(H_2O)$ (3). Bubbling of Cl_2 through a solution of $RuCl_2(diop)(PPh_3)$ (273 mg, 0.29 mmol) in CH_2Cl_2 (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_2O (30 mL) and the solution filtered to remove a small amount of the mixed

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Table 1. Crystallographic Data for *mer*-$RuCl_3$(dppb)(H_2O) (**1**)[a]

formula	$C_{28}H_{30}OCl_3P_2Ru$
fw	651.88
space group	orthorhombic, *Pbca*
a, Å	14.932 (2)
b, Å	18.133 (3)
c, Å	20.594 (2)
V, Å^3	5576.0(1)
Z	8
ρ_{calc}, g/cm^3	1.553
T, °C	25
μ (Mo Kα), cm^{-1}	9.850
F(000)	2648
no. of refined params	316
R1 [$I > 2\sigma(I)$]	0.046
wR2	0.094

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

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 $C_{31}H_{34}O_3Cl_3P_2Ru$: C, 51.43; H, 4.73. Found: C, 51.17; H, 4.76. UV−vis (CH_2Cl_2): 534 (1720), 428 (1480), 356 (1800). IR: ν_{OH} 3058 s, δ_{OH} 1596 s, ν_{Ru-Cl} 313, 274. ESR: g_1 2.782, g_2 2.137, g_3 1.721. μ_{eff} 2.21 μ_B. Complex **3** was also made by bubbling Cl_2 through a solution of $Ru_2Cl_5(diop)_2$ (25.5 mg, 0.018 mmol) in CH_2Cl_2 (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%).

$RuCl_3$(diop)(DMSO). Complex **3** (22.3 mg, 0.031 mmol) and DMSO (5 μL, 0.070 mmol) were stirred in CH_2Cl_2 (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 $C_{33}H_{38}O_3Cl_3P_2SRu$ requires: C, 50.55; H, 4.88. Found: C 50.21; H, 4.99. UV−vis (CH_2Cl_2): 530 (1680), 424 (1390), 358 (1750). IR: ν_{SO} 948 vs, ν_{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 l 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 Kα radiation (λ = 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 $\theta_{max} = 24.97°$, with a scan rate range 6.7−20° min^{-1}. The data were corrected for Lorentz and polarization, and the absorption effects were corrected empirically by a standard procedure.[25] The structure was solved by Patterson methods and difference Fourier techniques. Scattering factors for non-H atoms were taken from Cromer and Mann,[26a] with corrections for anomalous dispersion from Cromer and Liberman[26b] and for H atoms from Stewart et al.[27] All calculations were performed with the program SHELX-97.[28] 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.[28] The aromatic and CH_2 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 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.

Table 2. Selected Bond Lengths (Å) and Angles (deg)[a]

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)			

[a] Estimated standard deviations are given in parentheses.

Results and Discussion

The Ru(III) aquo, chelating diphosphine complexes of the type $RuCl_3$(P-P)(H_2O), where P-P = dppb (**1**) or diop (**3**), are readily synthesized by Cl_2-oxidation of the Ru(II) precursors Ru_2Cl_4(P-P)$_3$ or $RuCl_2$(P-P)(PPh_3), or the Ru(II)Ru(III) dinuclear species Ru_2Cl_5(P-P)$_2$; the source of the water for the aquo ligand could be the solvent or the Cl_2 supply. That the syntheses from Ru_2Cl_4(P-P)$_3$ proceed via Ru_2Cl_5(P-P)$_2$ 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 $RuCl_2$(diop)(PPh_3), in situ monitoring in the NIR region revealed the charge-transfer bands at 950 and 2050 cm^{-1}, characteristic of $Ru_2Cl_5(diop)_2$.[16] Finally, if the Cl_2-oxidation procedure is carried out for a shorter time scale, the $Ru_2Cl_5(dppb)_2$ complex (**2**) can be isolated in high yield on using $Ru_2Cl_4(dppb)_3$ as reactant.

X-ray analysis of $RuCl_3$(dppb)(H_2O) (**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[29−31]; 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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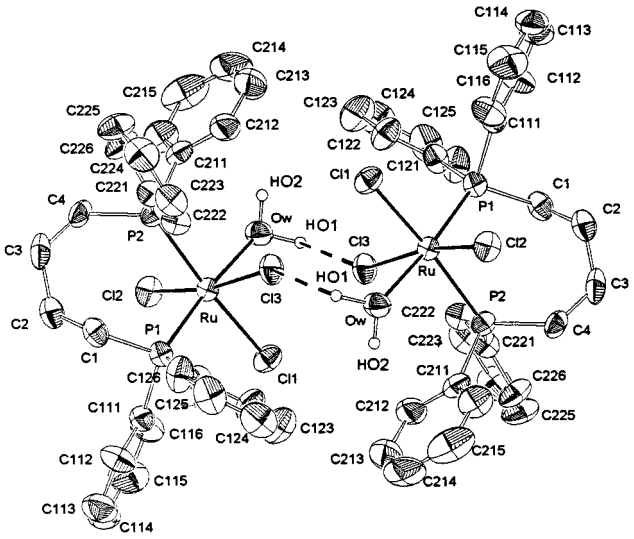

Figure 1. X-ray structure of *mer*- $RuCl_3(dppb)(H_2O)$ (**1**), showing 50% probability thermal ellipsoids for the nonhydrogen atoms.

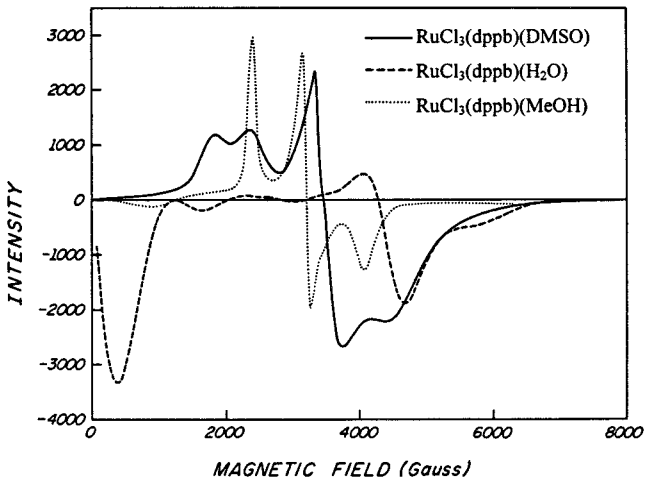

Figure 2. ESR spectra (X-band frequency) of $RuCl_3(dppb)L$ complexes (L = H_2O, DMSO, MeOH) at −160 °C in the solid state.

comparable to the Ru−P bond length in *mer*-$RuCl_3(PPh_3)$(1-methylimidazole)$_2$, 2.326(2) Å, where the PPh_3 is *trans* to the methylimidazole.[30] As expected, for a relatively hard Ru(III) center, the Ru−OH_2 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 $RuCl_3(dmtp)_2(H_2O)$, where dmtp is a N-donor pyrimidine derivative, and the aquo ligand is *trans* to a Cl atom.[31]

The magnetic moments of **1** and **3** (2.19 and 2.21 μ_B, respectively), although somewhat high for low-spin d^5 ($S = {}^1/_2$) systems, are not unusual for Ru(III) complexes.[32] Within these aquo complexes**,** the IR spectra show a sharp δ_{OH} band of coordinated water in the 1600 cm^{-1} region.[33] Three bands seen in the 340−260 cm^{-1} range for **1** with *mer*-geometry could be associated with ν_{Ru-Cl} stretches. For **3**, two stronger bands in this range are evident, but there are also several weaker bands that might be due to ν_{Ru-Cl}; 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 $RuCl_3$(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 $RuCl_3$(P-P)L, and they have been partially characterized by spectroscopic and sometimes μ_{eff} data. Similarities in UV−vis data to those of **1** again suggest *mer*-geometries. The ν_{SO} values for the dppb/DMSO and diop/DMSO complexes (944 and 948 cm^{-1}) suggest O-bonded sulfoxide.[34] 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 $RuCl_3$(P-P)L species, in CH_2Cl_2 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 $[RuCl_3(dppb)]_2$ in DMSO or MeCN,[16] consistent with formation of the corresponding $RuCl_3(dppb)L$ species. The new Ru(III) chemistry described here also partly clarifies the nature of the earlier suggested disproportionation of $Ru_2Cl_5(dppb)_2$ in coordinating solvents into "$RuCl_3(dppb)$" and "$RuCl_2(dppb)$".[16]

The solid-state ESR spectrum measured for $RuCl_3(dppb)(H_2O)$ (**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,[30] whereas the spectrum of **1** shows a signal close to zero magnetic field, which is characteristic of complexes with coupling between paramagnetic species.[35] 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^{-1}. 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.[35] The ESR of a frozen CH_2Cl_2 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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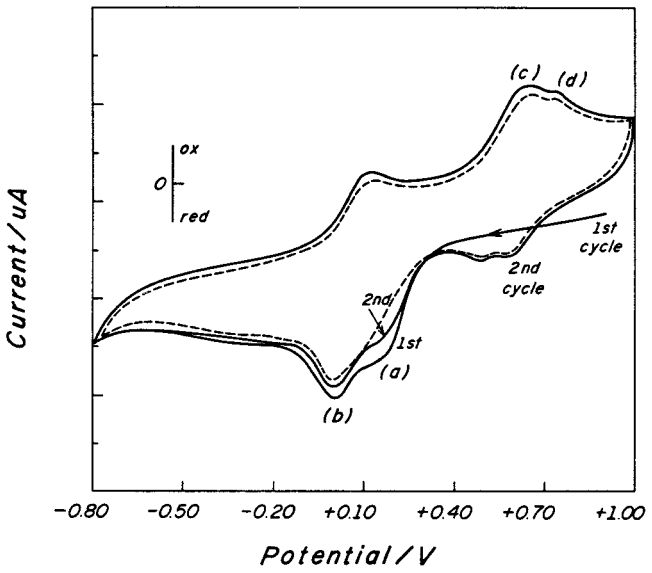

Figure 3. Cyclic voltammograms of $RuCl_3$(dppb)(H_2O) (**1**) (*2*), and Ru_2Cl_5(dppb)$_2$ (**2**) (− − −); 0.001 M in CH_2Cl_2 with 0.10 M TBPA; scan rate 100 mV/s.

$RuCl_3$(diop)(MeCN) formed in situ from **3** was essentially identical with that of **3**.

Cursory examination of the ^{1}H NMR spectra of several of the isolated $RuCl_3$(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^5 Ru species have been reported.[31,36]

Cyclic voltammetric measurements on [$RuCl_3$(dppb)(H_2O)] (**1**) (Figure 3) show the intermediacy of Ru_2Cl_5(dppb)$_2$ (**2**) in the overall reduction to "$RuCl_2$(dppb)", which exists as the known dimer [RuCl(dppb)]$_2$(μ-Cl)$_2$.[2,14] The CV data are readily rationalized in terms of eqs 1−3:

$$RuCl_3(dppb)(H_2O)\ (\mathbf{1}) + 1\ e^- \rightarrow \text{“}RuCl_2(dppb)\text{”} + Cl^- + H_2O \quad (1)$$

$$RuCl_3(dppb)(H_2O) + \text{“}RuCl_2(dppb)\text{”} \rightarrow Ru_2Cl_5(dppb)_2\ (\mathbf{2}) + H_2O \quad (2)$$

$$Ru_2Cl_5(dppb)_2\ (\mathbf{2}) + 1\ e^- \rightarrow Ru_2Cl_4(dppb)_2 + Cl^- \quad (3)$$

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_2Cl_2, filtering off the TBAP, and adding Et_2O to precipitate the mixed-valence complex. The air-sensitive Ru_2Cl_4(dppb)$_2$ complex has been made previously by H_2-reduction of **2**,[2,14] and presumably could be made electrochemically (eq 3). The CV behavior of $RuCl_3$(diop)(H_2O) (**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[16] 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 $CDCl_3$ shows bands at 970 and 2050 nm of comparable intensity (ϵ = 890 and 1180, respectively). Heath's group more recently has shown that the single isomer, mixed valence, cationic, triply choro-bridged complexes [$Ru_2Cl_3L_6$]$^{2+}$ (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.[37] 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,[38] 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_3 ligand in the dications, a factor that again will relatively stabilize Ru(III) and lead to a lower potential.[38] Both types of complexes are of the delocalized classification.[16,37] 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-initated 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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