

Unusual Ru(III) Chloro Complexes Containing Bis-dentate Ligands

Won K. Seok* and Li J. Zhang

Department of Chemistry, Dongguk University, Seoul 100-715, Korea. *E-mail: wonkseok@dongguk.edu

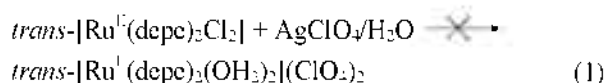
Received July 30, 2009. Accepted August 24, 2009

Key Words: Ru(III) dichloro complexes, Bis-dentate phosphine ligands, Crystal structure

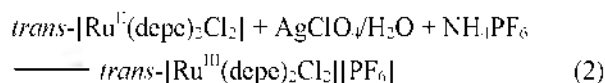
Redox chemistry of oxo and nitrido Ru or Os complexes containing polypyridine, Schiff base, or porphyrin ligands has been extensively studied.¹ Especially the polypyridyl complexes of ruthenium have been known as excellent photosensitizers in the use of photovoltaic cells based on nanocrystalline TiO₂ films as well.² Multiple bonding with O and/or N atoms of the oxo/nitrido ligands bonded to the metal stabilizes oxidants and promotes the conversion of organic and inorganic substrates *via* electron transfer, oxygen or nitrogen atom transfer, hydride transfer, and proton-coupled electron transfer pathways. Many researchers have endeavored to find out other sources of chelating ligands.³ We have been developed the synthetic chemistry of the reactive complexes of the diphosphine ligands coordinated to the ruthenium metal.

One of general methods for the preparation of reactive Ru-oxo complexes is using the oxidation of the corresponding Ru-aqua complexes, which can be obtained from the reaction of Ru-chloro complexes with Ag⁺ in water.¹ We applied it to the synthesis of the Ru-dioxo complexes surrounded by the diphosphine ligands. [Ru^{II}(dmpe)₂Cl₂] and [Ru^{II}(depe)₂Cl₂] complexes were isolated by the reactions of [Ru(PPh₃)₃Cl₂] with dmpe (1,2-bis(dimethylphosphino)ethane) and depe (1,2-bis(diethylphosphino)ethane), respectively, in acetone under refluxing, then aquated the corresponding Ru-dichloro complexes by AgClO₄ in H₂O.

We tried to prepare Ru(II) diaqua complexes, which have been known as the precursor to lead to Ru-dioxo complexes, however it turned out to be unsuccessful.



Rather we happened to obtain a blue crystalline solid as a final product, which identified an unexpected species of *trans*-[Ru^{III}(depe)₂Cl₂][PF₆] after precipitation by saturated NH₄PF₆ solution. The Ru(III) complex has been fully characterized with the aid of UV-Vis, FT IR, multi-nuclear NMR, and ESR spectrometers.



We were also able to isolate crystals of *trans*-[Ru^{III}(depe)₂Cl₂][PF₆] complex suitable for X-ray diffraction from the diffusion tube of acetone/water solution and to determine the crystal structure.

Figure 1 shows the perspective view of the *trans*-[Ru^{III}(depe)₂Cl₂]⁺ cation with atom labeling. The ruthenium atom is in six-coordinate with four phosphorous atoms in equatorial positions and two chlorine atoms *trans* each other. Due to the larger flexibility of the ethylene bridge and the less bulky substituents on the P-atoms, the coordination environment of the complex is slightly distorted from an octahedral environment.

Selected bond distances and angles shown in Table 1 indicate that mean Ru(III)-Cl distance is 2.34(4) Å and the bond angle formed by two chlorine and Ru atoms is linear with 178.0(1)°. The Ru-P bond distance ranges from 2.40(2) to 2.42(1) Å. Cl-Ru-P(1) and Cl-Ru-P(2) bite angles of the diphosphine ligand with the central ruthenium metal in the complex are 88.88(5)° and 90.40(5)°, which shows slight shrinking compared to those in *trans*-[Ru^{II}(depe)₂Cl₂] complex.⁴

Ru^{III}-Cl bond distance of *trans*-[Ru^{III}Cl₄(PPh₃)₂] and [Ru^{III}Cl₃(NH₃)(POMe₃)₂] complexes containing monodentate phosphine ligands spreads out from 2.34(1) to 2.38(1) Å.⁵ Only

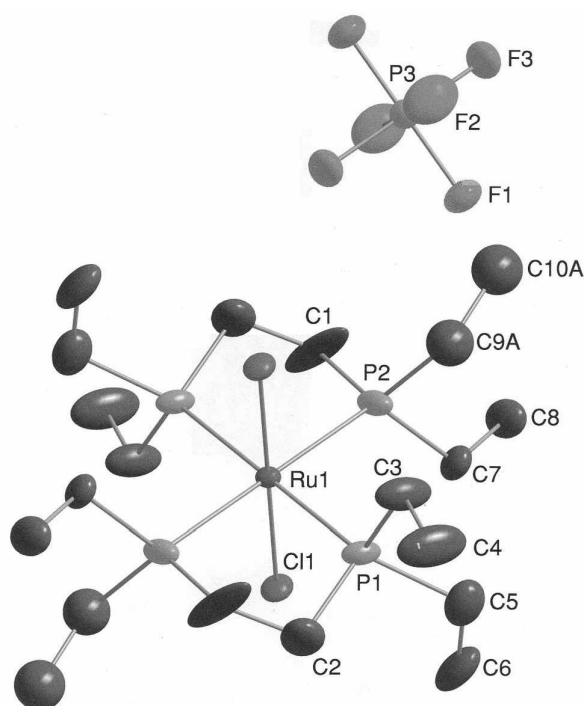


Figure 1. Molecular structure of *trans*-[Ru^{III}(depe)₂Cl₂][PF₆] in the crystals. Displacement ellipsoids are shown at the 50% probability level. Hydrogen atoms have been omitted for clarity.

Table 1. Selected bond distances (Å) and angles (°).

Ru(1)-Cl(1)	2.34(4)	Ru(1)-P(1)	2.418(8)	Ru(1)-P(2)	2.40(2)
P(1)-C(2)	1.77(1)	P(1)-C(3)	1.814(8)	P(1)-C(5)	1.92(2)
P(2)-C(1)	1.883(8)	P(2)-C(7)	1.82(3)	P(2)-C(9A)	1.96(2)
P(3)-F(1)	1.61(3)	P(3)-F(2)	1.588(4)	Cl(1)-Ru(1)-P(1)	88.88(5)
Cl(1)-Ru(1)-P(2)	90.40(5)	P(1)-Ru(1)-P(2)	97.71(5)	Ru(1)-P(1)-C(2)	107.6(3)
Ru(1)-P(1)-C(3)	116.0(2)	Ru(1)-P(1)-C(5)	122.6(2)	C(2)-P(1)-C(3)	107.0(3)
C(2)-P(1)-C(5)	104.0(3)	C(3)-P(1)-C(5)	98.2(3)	P(1)-C(5)-C(6)	117.0(5)
Ru(1)-P(2)-C(7)	115.8(4)	Ru(1)-P(2)-C(1)	105.3(2)	Ru(1)-P(2)-C(9A)	110.8(5)
C(1)-P(2)-C(7)	103.5(3)	C(1)-P(2)-C(9A)	122.3(6)	C(7)-P(2)-C(9A)	97.5(6)
P(2)-C(7)-C(8)	116.9(4)	F(1)-P(3)-F(2)	90.6(2)	F(1)-P(3)-F(3)	89.8(2)

Table 2. Comparison of bond distances [Å] and angles [°] for related ruthenium diphosphine complexes.

Complex	Ru-P(1)	Ru-P(2)	Ru-Cl	Cl-Ru-P(1)	Cl-Ru-P(2)	P(1)-Ru-P(2)	Ref.
Ru ^{II} (depe) ₂ Cl ⁺	2.372(2)	2.241(2)	2.395(2)	90.9(1)	92.1(1)	80.1(1)	6
<i>cis</i> -Ru ^{II} (depe) ₂ Cl ₂ ^a	2.352(2)	2.284(3)	2.484(2)	89.85(8)	90.77(8)	96.64(8)	7
<i>trans</i> -Ru ^{II} (depe) ₂ Cl ₂	2.338(1)	2.340(1)	2.427(1)	89.36(5)	92.63(4)	83.40(4)	4
<i>trans</i> -Ru ^{III} (DHBuPE) ₂ Cl ₂ ⁻	2.400(2)	2.400(2)	2.336(2)	86.98(5)	89.86(6)	82.06(6)	8
<i>trans</i> -Ru ^{III} (depe) ₂ Cl ₂ ⁺	2.418(8)	2.40(2)	2.34(4)	88.88(5)	90.40(5)	82.29(5)	This work

^aFor *cis*-Ru(depe)₂Cl₂ complex, each bond distance and angle is averaged and the P(1) atom is *trans* disposed to another P-donor atom.

one crystal structure of Ru(III) containing bis-dentate phosphine ligand, *trans*-[Ru^{III}(DHBuPE)₂Cl₂]⁺ (DHBuPE = 1,2-bis(bis(hydroxybutyl)phosphino)ethane), was characterized. Its bond distances and angles are notably different from those of the other Ru(II) complexes as shown in Table 2.^{4,6-8}

The averaged Ru-Cl distance of *trans*-[Ru^{III}(depe)₂Cl₂][PF₆] is similar to that determined for *trans*-[Ru^{III}(DHBuPE)₂Cl₂][Cl] and displays considerably shorter bond distances than those of *cis*- and *trans*-[Ru^{II}(depe)₂Cl₂] complexes as expected. This is a consequence of the more shrinking size of the Ru(III) metal in comparison with the Ru(II) one. In contrast, the Ru-P bonds in Ru(III) complexes are longer than those in the related Ru(II) complexes. Ru-Cl bond distance of the five-coordinated Ru(II) cationic complex displays the average between those of the six-coordinated Ru(II) and Ru(III) complexes.⁶

Even though we initially expected Ru(II) diaqua complexes as the products from the reaction of Ru(II) dichloro complexes with AgClO₄ in water, it is not surprising to obtain the unusual Ru(III) dichloro complexes as the final products, considering that both *trans*-[Ru^{II}(depe)₂Cl₂] and *cis*-[Ru^{II}(depe)₂Cl₂] complexes exhibit chemically reversible one-electron oxidation to Ru(III) forms with low half-wave potentials around 0.14 to 0.25 V depending on the solvents used.^{4,7} However for the polypyridyl Ru(II) chloro system, once Ru(II) aqua complex was formed as a final product, it was not easy to be further oxidized by mild oxidant to give Ru(III) complex with relatively higher potential.^{1a,1b}

The *trans*-[Ru^{III}(dmpe)₂Cl₂][PF₆] and *trans*-[Ru^{III}(depe)₂Cl₂][PF₆] complexes were fully identified by elemental analyses and spectroscopic data. Each Ru(III) complex shows the broad strong LMCT band around 680 ~ 700 nm in the UV-Vis spectra, while no observable peak was obtained in this region

for each corresponding Ru(II) complex. The terminal chloro stretching frequency of the Ru(III) complex in FT IR spectra was observed around 335 cm⁻¹. On the basis of IR spectra for transition metal chloro complexes,⁹ these Ru(III) complexes are believed to be *trans* configuration.

The ESR spectra of the prepared Ru(III) complexes have been obtained. The *g*-tensors of the compounds studied were well matched with those of [Ru^{III}(dmpe)₂Cl₂][ClO₄] and [Ru^{III}(depe)₂Cl₂][ClO₄] prepared by the reaction of RuCl₃ with the corresponding diphosphine ligand, which indicated low-spin *d*⁵ systems with *trans* geometry.¹⁰ Broad resonance peaks at 1.53, -10.85, -14.26, and -14.54 ppm for protons directly attached to phosphorous atom in the ¹H NMR spectrum were observed and confirmed the presence of paramagnetic complex. And the peaks at 114.4, -8.6, and -23.6 ppm were also observed in the ¹³C NMR spectrum.

The ³¹P NMR spectroscopy was used to identify the prepared ruthenium complexes. The ³¹P NMR spectra for Ru(II) diphosphine complexes shows two well-resolved resonances at 59.0 and 47.4 ppm as triplet for a *cis* isomer and one resonance at 47.7 ppm as a singlet for a *trans* isomer.¹¹ The ³¹P NMR spectrum of each Ru(III) complex displays one signal. Because the phosphorous atoms in the ligand are in the proximity to the paramagnetic Ru(III) center, the signal is not well resolved. The peak at 146 ppm is shown as sharp quintet, which corresponds to the phosphorous atom in the PF₆ anion.

Although *trans*-[Ru^{III}(dmpe)₂Cl₂][PF₆] prepared by a method analogous to that used for *trans*-[Ru(depe)₂Cl₂][PF₆] except employing *trans*-[Ru(dmpe)₂Cl₂] as a starting material has been identified, we have been unable to grow crystals suitable for X-ray analysis, because of its relative instability in a diffusion tube compared to the depe analogue.⁷ Attempts were also made to obtain *cis*-[Ru^{III}(depe)₂Cl₂][PF₆] and *cis*-[Ru^{III}(dmpe)₂

Cl₂] by using the reaction of *cis*-[Ru^{II}(depe)₂Cl₂] or *cis*-[Ru^{II}(dmpe)₂Cl₂] with AgClO₄. However the final products always turned out to be *trans* Ru(III) complexes, presumably they isomerized to the more stable compound upon oxidation.¹²

Experimental Section

The phosphorous ligands dmpe and depe were obtained from Stem Chemicals Co. and [Ru(PPh₃)₃Cl₂] was synthesized by literature method.⁴ Sealed ampoule acetone-*d*₆ and benzene-*d*₆ (99.9 atom % D) were obtained from the Aldrich. All other common reagents were ACS grade and were used without additional purification. All solvents were purified before use. Routine UV-Visible spectra were followed on a HP 8452A diode array spectrophotometer. FT IR spectra were obtained on a Bomem MB 100 spectrophotometer on KBr disc. ESR spectra were recorded with a Bruker ES 300E spectrometer. NMR spectra were collected on a JEOL 400 spectrometer. The chemical shift of ¹H and ¹³C NMR spectra were presented in parts per million (δ) and referenced to tetramethylsilane (TMS) and ³¹P NMR spectra to external 1% H₃PO₄ in D₂O. Elemental analyses were performed by the analytical laboratory of Basic Science Institute of Korea.

Preparation of [Ru(depe)₂Cl₂]. A solution of depe (2.6 g, 12.6 mmol) in dry acetone (10 mL) was added to a suspension of [Ru(PPh₃)₃Cl₂] (5.0 g, 5.2 mmol) in dry acetone (100 mL). The yellow solution was refluxed for 3 h and the residue was washed with hexane (2 × 10 mL) and dried under vacuum to give a bright yellow colored solid, which was recrystallized from acetone (2.26 g). Yield: 74%. m.p. 230 °C (dec.). Anal. Calc. for C₂₀H₄₈Cl₂P₄Ru: C, 41.1; H, 8.28. Found: C, 42.6; H, 8.58. ¹H NMR (acetone-*d*₆) δ 1.28 (m, 24 H, 8 × CH₂CH₃), 1.88 (s, 8 H, 2 × CH₂CH₂), 2.00 (m, 8 H, 8 × CHHCH₃), 2.56 (m, 8 H, 8 × CHHCH₃). ¹³C NMR (acetone-*d*₆) δ 9.9 (CH₂CH₃), 18.0 (CH₂CH₂), 21.4 (CH₂CH₃). ³¹P NMR (benzene-*d*₆) δ 47.7 (depe).

Preparation of *trans*-[Ru(depe)₂Cl₂][PF₆]. AgClO₄ (0.58 g, 2.79 mmol) in 20 mL of water was added into a solution of *trans*-[Ru(depe)₂Cl₂] (0.47 g, 0.80 mmol) in acetone/water (100 : 20 v/v) by dropwise. The reaction mixture was heated to reflux for 4 h, cooled to room temperature and filtered. To the filtrate was added saturated NH₄PF₆ to precipitate the products and filtered. The residue was washed with ether (2 × 10 mL) and dried at room temp to give a blue crystalline solid, which was recrystallized from acetone/water. Yield: 80%. Anal. Calc. for C₂₀H₄₈Cl₂F₆P₃Ru: C, 32.9; H, 6.63. Found: C, 31.6; H, 6.26. ESR (acetone) *g*₁ = 3.18, *g*₂ = 1.88, *g*₃ = 1.57. ¹H NMR (acetone-*d*₆) δ 1.53 (sharp s, 24H, 8 × CH₂CH₃), -10.85 (broad s, 8H, 2 × CH₂CH₂), -14.26 (broad s, 8H, 8 × CHHCH₃), -14.54 (broad s, 8H, 8 × CHHCH₃). ¹³C NMR (acetone-*d*₆) δ 114.4 (CH₂CH₃), -8.6 (CH₂CH₂), -23.6 (CH₂CH₃). ³¹P NMR (benzene-*d*₆) δ 146.0 (PF₆).

Crystal structure analysis. C₂₀H₄₈Cl₂F₆P₃Ru, monoclinic, space group *P*2₁/*n* (No. 14). *a* = 10.125(2), *b* = 11.237(2), *c* = 14.164(3) Å, β = 108.74(3)°, *V* = 1526.07(50) Å³, *Z* = 2, *T* = 200 K, *d*_{calc} = 1.587 g/cm³. A STOE IPDS instrument equipped

with an image plate area detector and employing graphite monochromated MoKα radiation (λ = 0.71073 Å) was used for data collection. A total of 4956 reflections were collected, which yielded 3890 reflections observed for [*I* > 2σ(*I*)]. The structure was solved by direct methods and subjected to a full-matrix least-squares refinement procedure for all non-hydrogen atoms. The final agreement factors were *R*₁ = 0.088 for [*I* > 2σ(*I*)] and *wR*₂ = 0.2011 for [*I* > 2σ(*I*)] (parameters, restraints). Crystallographic data in CIF format have been deposited at the Cambridge Crystallographic Data Centre, CCDC No. 622412.

Acknowledgments. We are deeply indebted to Professors Konstantin L. Karaghiosoff, Thomas M. Klapötke and Peter Klüfers and Dr. Peter Mayer of Ludwig-Maximilian University of Munich for their discussions and generous allocation of diffraction time.

References

1. a) Seok, W. K.; Kim, M. Y.; Yokomori, Y.; Hodgson, D. J.; Meyer, T. J. *Bull. Korean Chem. Soc.* **1995**, *16*, 619. b) Groves, J. T. *Proc. Nat. Acad. Sci.* **2003**, *100*, 3589. c) Huynh, M. H. V.; Meyer, T. J.; Jameson, D. L. *Inorg. Chem.* **2005**, *44*, 3657. d) Bales, B. C.; Brown, P.; Dehestani, A.; Mayer, J. M. *J. Am. Chem. Soc.* **2005**, *127*, 2832. e) Zhang, J.; Liang, J.-L.; Sun, X.-R.; Zhou, H.-B.; Zhu, N.-Y.; Chan, P. W. H.; Che, C.-M. *Inorg. Chem.* **2005**, *44*, 3942. f) Concepcion, J. J.; Jurss, J. W.; Templeton, J. L.; Meyer, T. J. *J. Am. Chem. Soc.* **2009**, *130*, 16462.
2. a) Bolink, H.; Cappelli, L.; Coronado, E.; Gratzel, M.; Nazeeruddin, Md. K. *J. Am. Chem. Soc.* **2006**, *128*, 46. b) Obare, S. O.; Ito, T.; Meyer, G. J. *J. Am. Chem. Soc.* **2006**, *128*, 712. c) Seok, W. K.; Gupta, A. K.; Roh, S.-J.; Lee, W.; Han, S.-H. *Bull. Korean Chem. Soc.* **2007**, *28*, 1311.
3. a) Espinet, P.; Soulantica, K. *Coord. Chem. Rev.* **1999**, *193*, 499. (b) Menges, F.; Neuburger, M.; Pfaltz, A. *Org. Lett.* **2002**, *4*, 4713. (c) Pickett, T. E.; Roca, F. X.; Richards, C. J. *J. Org. Chem.* **2003**, *68*, 2592.
4. Buys, I. E.; Field, L. D.; George, A. V.; Hambley, T. W.; Purches, G. R. *Aust. J. Chem.* **1995**, *48*, 27.
5. a) Bruce, M. I.; Kelly, D. A.; McLaughlin, G. M.; Robertson, G. B.; Tomkins, I. B.; Wallis, R. C. *Aust. J. Chem.* **1980**, *33*, 195. b) Polam, J. R.; Porter, L. C. *J. Coord. Chem.* **1993**, *28*, 297.
6. Chin, B.; Lough, A. J.; Morris, R. H.; Schweitzer, C. T.; D'Agostino, C. *Inorg. Chem.* **1994**, *33*, 6278.
7. Winter, R. F.; Brunner, B. M.; Scheiring, T. *Inorg. Chim. Acta* **2000**, *310*, 21.
8. Baxley, G. T.; Miller, W. K.; Lyon, D. K.; Miller, B. E.; Nieckarz, G. F.; Weakley, T. J. R.; Tyler, D. R. *Inorg. Chem.* **1996**, *35*, 6688.
9. Taquikhan, M. M.; Mohiuddin, R. *J. Coord. Chem.* **1977**, *6*, 171.
10. a) Kneubuhl, F. K. *J. Chem. Phys.* **1960**, *33*, 1074. b) Chatt, J.; Leigh, G. J.; Mingos, D. M. P. *J. Chem. Soc. A* **1960**, 1674.
11. Bautista, M. T.; Cappellani, E. P.; Drouin, S. D.; Morris, R. H.; Schweitzer, C. T.; Sella, A.; Zubkowski, J. *J. Am. Chem. Soc.* **1961**, *113*, 4876.
12. a) Sullivan, B. P.; Meyer, T. J. *Inorg. Chem.* **1982**, *21*, 1037. b) Antberg, M.; Dahlenburg, L. *Inorg. Chim. Acta* **1986**, *111*, 73. c) Guedes da Silva, M. F. C.; Pombeiro, A. J. J.; Amatore, C.; Verpauw, J.-N. *Inorg. Chem.* **1988**, *37*, 2344.