

# Formation of Binuclear Ruthenium(II) Aqua Complexes and a Mononuclear Ammonia Complex Bearing P–P–O Facial Tridentate Ligands and Oxametallacycle Moieties

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The reaction of Ru( $\eta^6$ -cot)(dmfm)<sub>2</sub> (**1**; cot = 1,3,5-cyclooctatriene, dmfm = dimethyl fumarate) with water and dppe derivatives (dppe = 1,2-bis(diphenylphosphino)ethane) having two or four methoxy groups at the ortho positions of the phenyl rings, (*S,S*)-DIPAMP or *o*-MeO-dppe, afforded the unique binuclear Ru(II) aqua complexes **4a,b**, where two oxaruthenacycles are combined and hold a water molecule by coordination and hydrogen bonding, as revealed by X-ray crystallography. Although complex **4b** has a binuclear form in the solid state, disintegration occurred in solution to give the mononuclear aqua complex **4b'**. Complex **4b** was further treated with ammonia, resulting in the formation of the mononuclear Ru(II) ammonia complex **5** via ligand displacement with water. The water oxygen atom and ammonia nitrogen atom in these complexes can be regarded as chiral centers in the solid state, since they have four different groups, distinguished by coordination to ruthenium and nonequivalent hydrogen bondings.

## Introduction

The reactivity of low-valent transition-metal complexes toward water has recently attracted considerable attention, since this subject could lead to the development of novel, environmentally benign transition-metal-catalyzed reactions using water as a raw material.<sup>1</sup> Some electron-rich, low-valent late-transition-metal complexes such as Ru, Ir, and Pd complexes have been known to activate a water molecule to give the corresponding hydrido–hydroxo or  $\mu$ -oxo complexes.<sup>2–15</sup> On the other hand,

low-valent transition-metal aqua complexes, which can be regarded as an early stage in the oxidative addition of water, have also been reported. As for such Ru(0) complexes, Ru(methyl acrylate)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>O) (Sustmann et al.<sup>16</sup>) and [Ru(CO)(NO)(P<sup>t</sup>Bu<sub>2</sub>Me)<sub>2</sub>(H<sub>2</sub>O)][BAR<sub>4</sub>] (Ar = C<sub>6</sub>H<sub>3</sub>-3,5-(CF<sub>3</sub>)<sub>2</sub>; Caulton and co-workers<sup>17</sup>) have been described, as well as Ru(dppe)(dmfm)<sub>2</sub>(H<sub>2</sub>O) (**2**; dppe = 1,2-bis(diphenylphosphino)ethane, dmfm = dimethyl fumarate), which was prepared by the reaction of Ru( $\eta^6$ -cot)(dmfm)<sub>2</sub> (**1**; cot = 1,3,5-cyclooctatriene)<sup>18</sup> with H<sub>2</sub>O and dppe, and Ru(*S*)-QUINAP(dmfm)<sub>2</sub>(H<sub>2</sub>O) (**3**; QUINAP = 1-(2-diphenylphosphino-1-naphthyl)-isoquinoline), which was reported by our group (eq 1).<sup>19</sup>

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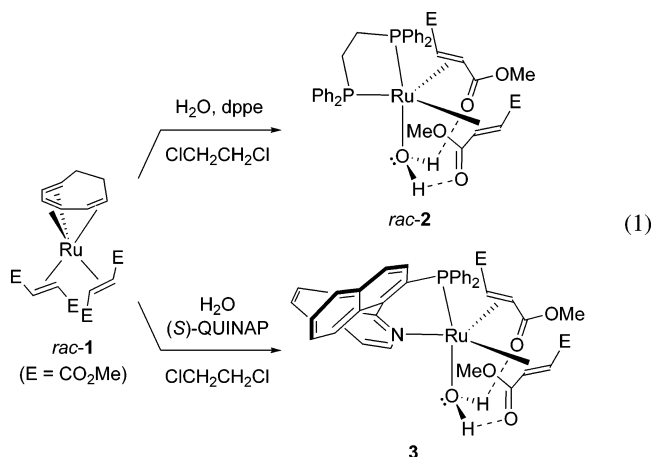
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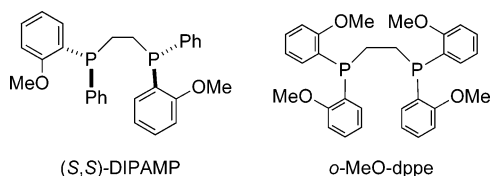
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Complexes **2** and **3** are stable enough to isolate in pure form without loss of the coordinated water molecule, since the two

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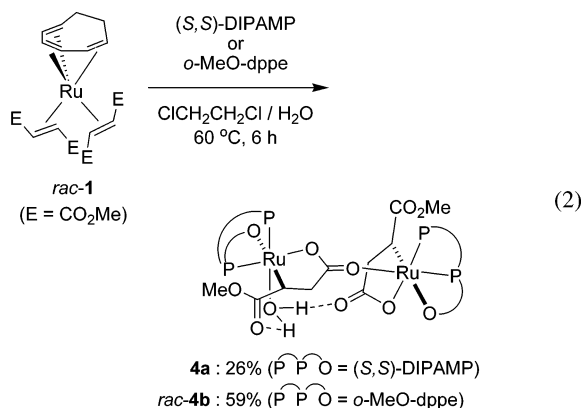
**Chart 1. Facial Tridentate dppe-Based Polymethoxy-Substituted Ligands**

intramolecular hydrogen bonds firmly hold the water, and can be synthesized on a gram scale.

In our ongoing study of aqua complexes and related reactions, the formation of unique binuclear oxaruthenacycle aqua complexes was observed using the facial tridentate polymethoxy-substituted dppe ligands (*S,S*)-DIPAMP and *o*-MeO-dppe (Chart 1) instead of dppe in eq 1. In this paper, we report the formation and structure of binuclear aqua complexes via an intriguing bond cleavage of dimethyl fumarate, which originally coordinated to the ruthenium in an  $\eta^2$  fashion, and the reactivity of the aqua complex with ammonia, which gives a mononuclear Ru(II) ammonia complex via disintegration of the binuclear constitution.

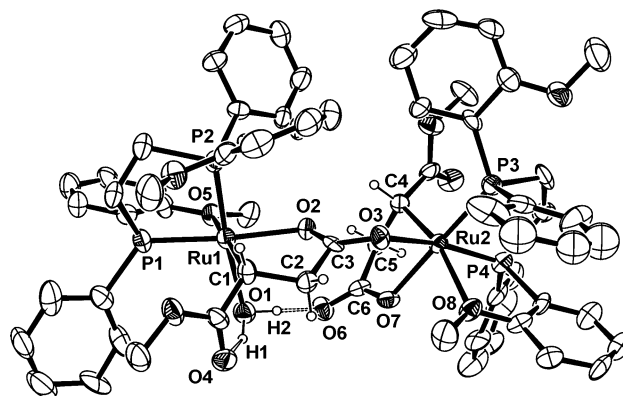
## Results and Discussion

**Formation and Structures of the Binuclear Ru(II) Aqua Complexes 4a,b.** The racemic form of complex **1** in 1,2-dichloroethane/H<sub>2</sub>O was treated with the phosphorus ligand (*S,S*)-DIPAMP or *o*-MeO-dppe at 60 °C for 6 h (eq 2). After



purification by alumina column chromatography, the novel binuclear Ru(II) aqua complexes **4** were obtained in 26% yield for **4a** and 59% yield for *rac*-**4b**, the solid-state structures of which were confirmed by single-crystal X-ray analyses.

Complex **4a** is a binuclear Ru(II) aqua complex, where (*S,S*)-DIPAMP ligands coordinate to the ruthenium centers in a facial tridentate manner (Figure 1 and Table 1). Notably, the oxaruthenacycle structures are formed via the apparent cleavage of an O-CH<sub>3</sub> bond in dimethyl fumarate. In the component of **4a** shown on the left-hand side of Figure 1, the water oxygen atom O1 is located at a trans position relative to the phosphorus atom P2, and the sp<sup>3</sup> carbon atom C1 in the oxametallacycle moiety



**Figure 1.** ORTEP drawing of **4a**. Hydrogen atoms, except for water and oxaruthenacycle moieties, are omitted for clarity. Thermal ellipsoids are given at the 30% probability level. The dashed lines for H1...O4 and H2...O6 indicate hydrogen bonds.

**Table 1.** Selected Bond Distances (Å) and Angles (deg) in **4a**

Ru1-P1	2.211(3)	Ru2-P3	2.242(4)
Ru1-P2	2.220(4)	Ru2-P4	2.174(3)
Ru1-O1	2.226(8)	Ru2-O3	2.186(6)
Ru1-O2	2.151(6)	Ru2-O7	2.147(8)
Ru1-O5	2.260(7)	Ru2-O8	2.298(9)
Ru1-C1	2.153(11)	Ru2-C4	2.129(11)
C1-C2	1.534(16)	C4-C5	1.539(18)
C2-C3	1.507(13)	C5-C6	1.546(16)
C3-O2	1.272(13)	C6-O7	1.262(17)
P1-Ru1-P2	83.42(15)	P3-Ru2-P4	81.66(13)
P1-Ru1-O1	101.3(2)	P3-Ru2-O3	97.2(2)
P1-Ru1-O5	80.51(18)	P3-Ru2-O8	94.0(2)
P1-Ru1-C1	103.9(2)	P3-Ru2-C4	102.4(3)
P2-Ru1-O2	92.7(2)	P4-Ru2-O7	100.6(2)
P2-Ru1-O5	95.4(2)	P4-Ru2-O8	81.1(2)
P2-Ru1-C1	91.3(4)	P4-Ru2-C4	98.1(2)
O1-Ru1-O2	82.5(3)	O3-Ru2-O7	79.7(2)
O1-Ru1-O5	84.3(3)	O3-Ru2-O8	84.9(2)
O1-Ru1-C1	88.8(4)	O3-Ru2-C4	95.9(3)
O2-Ru1-O5	94.6(2)	O7-Ru2-O8	82.7(3)
O2-Ru1-C1	81.5(3)	O7-Ru2-C4	81.1(4)
C3-O3-Ru2	129.2(7)		

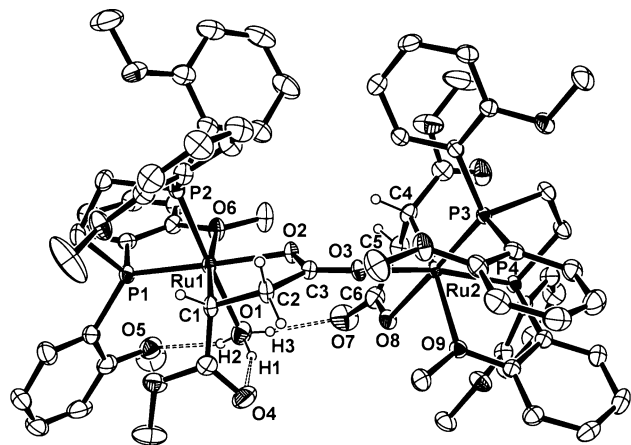
is trans to O5. On the other hand, in the component on the right-hand side, while (*S,S*)-DIPAMP coordinates in the same manner, the position of the oxametallacycle relative to the (*S,S*)-DIPAMP ligand is different from that in the component on the left side; i.e., in the right-hand component, the oxygen atom of the oxaruthenacycle O7 is located trans to the phosphorus atom P3, having a noncoordinated methoxyphenyl group. The carbonyl oxygen atom O3 binds to Ru2, and the coordinated water molecule is connected to the two carbonyl oxygen atoms O4 and O6. The distances O1...O4 and O1...O6 are 2.820(11) and 2.701(11) Å, indicating the existence of hydrogen bonds between H1...O4 and H2...O6, respectively. As a whole, the aggregation of the two P-P-O ligated oxaruthenacycle moieties is stabilized by coordination of the carbonyl oxygen and the hydrogen bond H2...O6. The oxygen atom of the water molecule O1 can be regarded as a chiral center in the solid state, since it has four different groups, i.e. ruthenium, an unshared electron pair, and two protons with different hydrogen bonds, as was observed in complexes **2** and **3**.<sup>19b</sup>

In complex **4b**, the main motif of the structure is similar to that in **4a** (Figure 2, Table 2). However, a remarkable difference was observed in the mode of hydrogen bonding. In **4b**, the coordinated water can have hydrogen bonds with not only the carbonyl oxygen atoms O4 and O7 but also the methoxy oxygen atom O5. The water molecule is disordered, and the positions of the water protons H1, H2, and H3 were determined on the

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**Figure 2.** ORTEP drawing of **4b**. Solvent molecules and hydrogen atoms, except for water and oxaruthenacycle moieties, are omitted for clarity. Thermal ellipsoids are given at the 30% probability level. The coordinated water molecule is described as disordered. The dashed lines for H1...O4, H2...O5, and H3...O7 indicate hydrogen bonds.

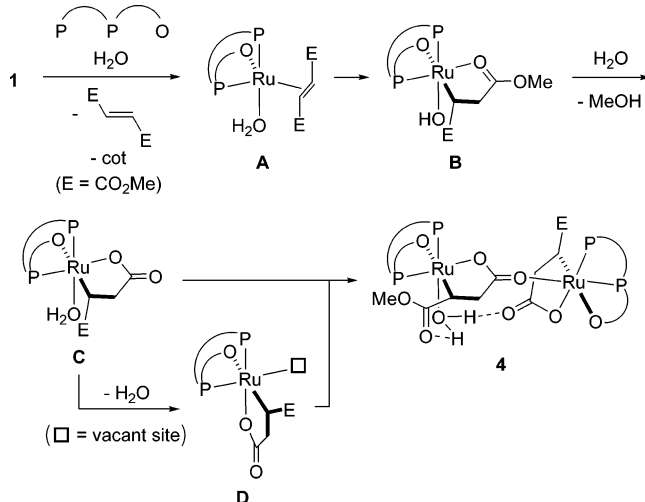
**Table 2.** Selected Bond Distances (Å) and Angles (deg) in **4b**

Ru1–P1	2.2046(15)	Ru2–P3	2.2431(13)
Ru1–P2	2.2521(13)	Ru2–P4	2.1916(12)
Ru1–O1	2.213(4)	Ru2–O3	2.192(3)
Ru1–O2	2.117(3)	Ru2–O8	2.141(4)
Ru1–O6	2.284(3)	Ru2–O9	2.310(3)
Ru1–C1	2.151(4)	Ru2–C4	2.131(4)
C1–C2	1.532(8)	C4–C5	1.536(8)
C2–C3	1.532(6)	C5–C6	1.506(8)
C3–O2	1.272(6)	C6–O8	1.270(7)
P1–Ru1–P2	83.78(5)	P3–Ru2–P4	82.14(4)
P1–Ru1–O1	96.77(13)	P3–Ru2–O3	96.49(10)
P1–Ru1–O6	80.83(11)	P3–Ru2–O9	92.44(10)
P1–Ru1–C1	103.84(14)	P3–Ru2–C4	100.56(16)
P2–Ru1–O2	97.34(10)	P4–Ru2–O8	99.88(10)
P2–Ru1–O6	95.49(10)	P4–Ru2–O9	80.90(9)
P2–Ru1–C1	90.41(14)	P4–Ru2–C4	97.32(14)
O1–Ru1–O2	81.75(16)	O3–Ru2–O8	81.25(14)
O1–Ru1–O6	81.12(15)	O3–Ru2–O9	85.97(12)
O1–Ru1–C1	92.89(17)	O3–Ru2–C4	95.92(16)
O2–Ru1–O6	93.21(13)	O8–Ru2–O9	86.62(13)
O2–Ru1–C1	82.04(16)	O8–Ru2–C4	80.52(18)
C3–O3–Ru2	134.9(3)		

basis of the Fourier map. The distances O1...O4, O1...O5, and O1...O7 are 3.086(6), 3.020(7), and 3.023(8) Å, respectively, which are longer than those in **4a** by ca. 0.3 Å. This can be explained by the low population of the water protons at each position: H1, H2, and H3. Further refinement of the water protons in **4a,b** was unsuccessful, and thus they were treated using the riding model with the least-squares method.

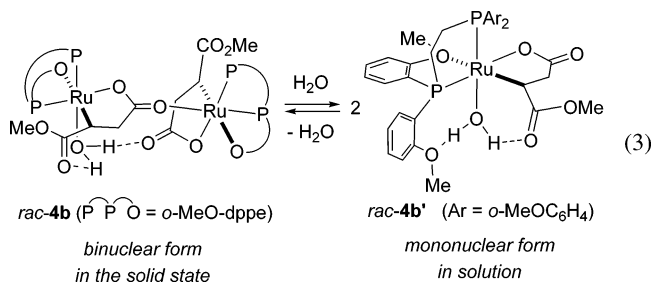
When the structures of **4a,b** were compared, although most bond distances were similar, several bond angles were quite different. The angle of P1–Ru1–O1 in **4b** is smaller by 4.5° than that in **4a**, due to the existence of the hydrogen bond H2...O5 in **4b**. P2–Ru1–O2 in **4b** is larger by 4.6° for the same reason, and thus, the P–P–O ligand of the left component in **4b** is revealed to incline slightly toward the aqua ligand compared with that in **4a**. On the other hand, O1–Ru1–C1 in **4b** is larger by 4.1°, which reflects that the hydrogen bond H1...O4 in **4b** is weakened. Similarly, the widened C3–O3–Ru2 angle in **4b** would be attributable to the lengthened hydrogen bond H3...O7. The torsion angles of the oxaruthenacycle moieties in the right-hand component (as shown in Figures 1 and 2) are also indicative of the weakening of the hydrogen bond H3...O7. There is a difference of 10.3° between the torsion

**Scheme 1.** Possible Formation Mechanism of **4**



angles of Ru2–O7–C6–O6 in **4a** (159.9(10)°) and Ru2–O8–C6–O7 in **4b** (170.2(5)°).

The X-ray analysis revealed that complexes **4a,b** were both binuclear complexes in the solid state, as mentioned above. On the other hand, in solution (CD<sub>2</sub>Cl<sub>2</sub> or CDCl<sub>3</sub>), although **4a** gave <sup>1</sup>H and <sup>13</sup>C NMR spectra corresponding to a binuclear structure, the NMR spectra of **4b** showed only a single set of signals for a mononuclear species, indicating that a mononuclear aqua complex was cleanly formed via disintegration of the binuclear form. As shown in eq 3, capturing an external water molecule



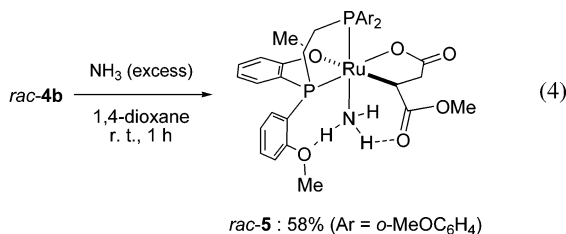
such as lattice water gives the mononuclear complex **4b'** in solution, and the reaction reversibly proceeds by recrystallization. Migration of the oxametallacycle moiety of the right-hand component in **4b** is involved in the complete formation of **4b'** from **4b**. The disintegration of **4b** in solution can be attributed to the weakened intercomponent hydrogen bonding (H3...O7, Figure 2) compared with that in **4a** (H2...O6, Figure 1) and to a slight increase in steric hindrance between the intercomponent phosphorus ligand moieties.

Since peak splitting of the coordinated water protons was observed in the <sup>1</sup>H NMR spectra of aqua complexes **2** and **3** upon cooling to –80 °C,<sup>19b</sup> VT <sup>1</sup>H NMR measurements of **4a,b** were also performed in CD<sub>2</sub>Cl<sub>2</sub>. Although slight upfield shifting and sharpening of the originally broad signal of the coordinated water protons were observed with a decrease in temperature, clear peak splitting was not detected.

**Possible Formation Mechanism of 4.** Although reaction intermediates have not yet been isolated, a possible pathway to **4** based on our previous investigation of the reactivity of **1** is proposed in Scheme 1. A bidentate phosphorus ligand, dpmm (bis(diphenylphosphino)methane), is known to react with **1** to give Ru( $\eta^4$ -cot)( $\eta^2$ -dmfm)( $\eta^2$ -dpmm).<sup>19a</sup> In the present binuclear complex formation, the reaction of **1** with a P–P–O ligand would be expected to afford the similar complex Ru( $\eta^4$ -cot)-

( $\eta^2$ -dmfm)( $\eta^2$ -P-P-O) at the initial stage. The oxygen atom of the P-P-O ligand then coordinates to ruthenium to form  $\text{Ru}(\eta^2\text{-cot})(\eta^2\text{-dmfm})(\eta^3\text{-P-P-O})$ , where P-P-O occupies three facial coordination sites. Ligand displacement between cot and  $\text{H}_2\text{O}$  affords the Ru(0) aqua complex **A**, which has a structure that is partially similar to that of **2** but the ruthenium center is more electron-rich, and thus oxidative addition of the coordinated  $\text{H}_2\text{O}$  should proceed and subsequent insertion of dimethyl fumarate into the formed Ru-H bond gives alkyl hydroxo intermediate **B**. From **B**, a nucleophilic attack of  $\text{H}_2\text{O}$  toward the carbonyl carbon with the assistance of ruthenium, which works as a Lewis acid, and the loss of MeOH would give the oxaruthenacycle aqua complex **C**,<sup>20</sup> corresponding to the left-hand component of **4**. Liberation of  $\text{H}_2\text{O}$  from **C** and migration of the oxaruthenacycle moiety gives the coordinatively unsaturated 16e intermediate **D**, which finally combines with **C** to afford **4**. The mechanism via the oxidative addition of  $\text{H}_2\text{O}$  as mentioned above seems to be likely, whereas protonation of the carbonyl oxygen by the water proton and electron transfer from ruthenium to dimethyl fumarate to form a Ru-C  $\sigma$  bond and subsequent enol-keto isomerization can also give **B**. An alternative pathway via  $\text{sp}^2$  C-H activation of dimethyl fumarate where an alkyl alkenyl complex is formed first<sup>21</sup> and successive hydrolysis of the complex might afford **B** can also not be ruled out.

**Formation of Mononuclear Ammonia Complex 5.** *rac-4b* was further reacted with an excess amount of  $\text{NH}_3$  in dioxane to give the racemic mononuclear ammonia complex **5**, the solid-state structure of which was confirmed by X-ray analysis (eq 4, Figure 3, Table 3). In the case of **5**, refinement of the



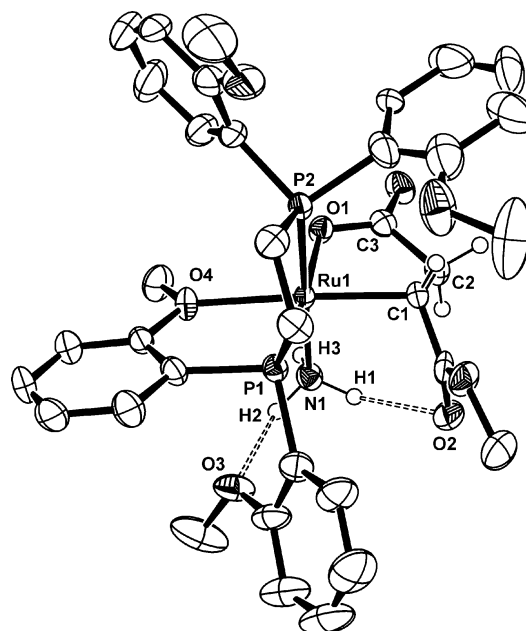
ammonia protons was successful, and the obtained hydrogen-bonding parameters are listed in Table 4. The hydrogen bonds  $\text{H1}\cdots\text{O2}$  and  $\text{H2}\cdots\text{O3}$  seem to be somewhat weak, according to the values of  $\text{H}\cdots\text{A}$  and  $\text{D}-\text{H}\cdots\text{A}$ . The distances  $\text{N1}\cdots\text{O2}$  (2.917(6) Å) and  $\text{N1}\cdots\text{O3}$  (2.955(6) Å) are shorter than those in **4b**. In **5**, the structural features, such as bond distances and angles, are consistent with those in the left-hand component of **4b**. However, the angles  $\text{O4}-\text{Ru1}-\text{N1}$  and  $\text{N1}-\text{Ru1}-\text{C1}$  in **5** are shifted by ca.  $3-4^\circ$  compared with the corresponding angles in **4b**, suggesting that the coordinated ammonia is fairly close to O2. The yield of **5** (58%) indicates that a certain amount of the right-hand component in **4b** isomerized and reacted with  $\text{NH}_3$  to give **5**. The overall signal patterns of  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra in **5** are consistent with those in **4b'**. The nitrogen atom of ammonia in **5** is also a chiral center in the solid state, since the three ammonia protons are differentiated from one another by the hydrogen bonds.<sup>19b</sup>

### Conclusion

The novel binuclear Ru(II) aqua complexes **4a,b**, bearing P-P-O facial tridentate ligands and oxaruthenacycle moieties,

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**Figure 3.** ORTEP drawing of **5**. The solvent molecule and hydrogen atoms, except for ammonia and oxaruthenacycle moieties, are omitted for clarity. Thermal ellipsoids are given at the 50% probability level. The dashed lines for  $\text{H1}\cdots\text{O2}$  and  $\text{H2}\cdots\text{O3}$  indicate hydrogen bonds.

**Table 3.** Selected Bond Distances (Å) and Angles (deg) in **5**

Ru1-P1	2.2058(14)	C1-C2	1.549(7)
Ru1-P2	2.2646(16)	C2-C3	1.526(7)
Ru1-O1	2.134(3)	C3-O1	1.291(5)
Ru1-O4	2.266(3)	N1-H1	0.90(7)
Ru1-N1	2.170(6)	N1-H2	0.79(6)
Ru1-C1	2.115(4)	N1-H3	0.86(6)
P1-Ru1-P2	83.32(5)	O1-Ru1-N1	82.85(18)
P1-Ru1-O4	80.88(9)	O1-Ru1-C1	81.88(16)
P1-Ru1-N1	97.88(15)	O4-Ru1-N1	84.16(15)
P1-Ru1-C1	103.70(14)	N1-Ru1-C1	88.5(2)
P2-Ru1-O1	96.00(11)	H1-N1-H2	114(7)
P2-Ru1-O4	96.50(10)	H1-N1-H3	106(7)
P2-Ru1-C1	90.73(16)	H2-N1-H3	96(5)
O1-Ru1-O4	93.66(12)		

**Table 4.** Hydrogen Bonding Parameters (Å, deg) in **5**

D-H $\cdots$ A	H $\cdots$ A (Å)	D $\cdots$ A (Å)	D-H $\cdots$ A (deg)
N1-H1 $\cdots$ O2	2.14(8)	2.917(6)	145(9)
N1-H2 $\cdots$ O3	2.38(5)	2.955(6)	131(5)

were synthesized and characterized. In these complexes, two mononuclear components cooperatively hold a water molecule through coordination and hydrogen bonding in the solid state. Complex **4b** was found to involve a unique hydrogen bonding mode, where three proton acceptors are closely located around the coordinated water and the water protons can interact with all of them. Disintegration of the binuclear form of **4b** occurred when it was dissolved in  $\text{CD}_2\text{Cl}_2$  or  $\text{CDCl}_3$ , to give the mononuclear aqua complex **4b'**. The coordinated water molecule in **4b** was replaced by ammonia to afford the mononuclear Ru(II) ammonia complex **5**, the structure of which was similar to that of **4b'**. In the solid state of **4a** and **5**, water and ammonia are fixed in chiral coordination sites, respectively, generating a chiral center on each central heteroatom. Thus, the water and ammonia protons could be distinguished from one another by being captured in chiral sites. We envisage that the results obtained here could aid in the further understanding of the reactivity of low-valent metal complexes toward water, and moreover, the chemistry of coordinated chiral water and

ammonia could contribute to developments in novel research areas concerning water and related chemistry.

## Experimental Section

**General Considerations.** NMR spectra were recorded on JEOL EX-400 (FT, 400 MHz ( $^1\text{H}$ ), 100 MHz ( $^{13}\text{C}$ ), 162 MHz ( $^{31}\text{P}$ )) spectrometers. Chemical shift values ( $\delta$ ) for  $^1\text{H}$  and  $^{13}\text{C}$  are referenced to internal solvent resonances and reported relative to  $\text{SiMe}_4$ . Chemical shifts for  $^{31}\text{P}$  are referenced to an external  $\text{P}(\text{OMe})_3$  resonance and reported relative to  $\text{H}_3\text{PO}_4$ . IR spectra were recorded on a Nicolet Impact 410 FT-IR spectrometer. Melting points were determined under argon on a Yanagimoto micro melting point apparatus. HR-MS spectra were recorded on JEOL SX102A spectrometers with *m*-nitrobenzyl alcohol (*m*-NBA) as a matrix. Elemental analyses were performed at the Microanalytical Center of Kyoto University.

**Materials and Methods.** All manipulations were performed under an atmosphere of argon. Reactions were performed by using standard Schlenk techniques. The reagents used in this study were dried and purified before use by standard procedures. Unless otherwise stated, all reagents were used as received from commercial suppliers.  $\text{Ru}(\eta^6\text{-cot})(\eta^2\text{-dmfm})_2^{18}$  and *o*-MeO-dppe $^{22}$  were prepared as described in the literature.

**Preparation of the Binuclear Aqua Complex 4a.** A mixture of complex **1** (203 mg, 0.41 mmol) and (*S,S*)-DIPAMP (199 mg, 0.43 mmol) in distilled 1,2-dichloroethane (12 mL)/ $\text{H}_2\text{O}$  (15 mL) was stirred at 60 °C for 6 h. After the solvent and water were evaporated, the residue was dissolved in distilled chloroform and then chromatographed on alumina. Elution with 2-propanol gave a yellow solution, from which the solvent was evaporated. The orange residue was recrystallized from chloroform/pentane to give **4a** (82 mg, 0.12 mmol, 29%).

Data for **4a** are as follows. Pale yellow solid. Mp: 124 °C dec. IR (KBr disk): 3054, 2947, 1707, 1686, 1647, 1434, 1315, 1166  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  8.96 (dd,  $J = 7.8, 14.2$  Hz, 1H,  $\text{H}_{\text{Ar}}$ ), 8.29 (t,  $J = 8.3$  Hz, 2H,  $\text{H}_{\text{Ar}}$ ), 7.72 (br s, 2H,  $\text{H}_{\text{Ar}}$ ), 7.63 (br s, 2H,  $\text{H}_{\text{Ar}}$ ), 7.46–6.54 (m, 27H,  $\text{H}_{\text{Ar}}$ ), 6.39 (t,  $J = 7.1$  Hz, 1H,  $\text{H}_{\text{Ar}}$ ), 6.24 (dd,  $J = 3.9, 8.3$  Hz, 1H,  $\text{H}_{\text{Ar}}$ ), 4.30 (br s, 2H,  $\text{H}_2\text{O}$ ), 4.20 (dd,  $J = 4.2, 12.0$  Hz, 1H, RuCH), 4.07 (s, 3H,  $\text{OCH}_3$ ), 3.75 (s, 3H,  $\text{OCH}_3$ ), 3.31 (s, 3H,  $\text{OCH}_3$ ), 3.21 (s, 3H,  $\text{OCH}_3$ ), 3.04–2.94 (m, 2H,  $\text{PCH}_2$ ), 2.92–2.72 (m, 2H,  $\text{PCH}_2$ ), 2.81 (s, 3H,  $\text{OCH}_3$ ), 2.56 (dd,  $J = 6.8, 17.6$  Hz, 1H, RuCHCH $_2$ ), 2.49–2.36 (m, 2H,  $\text{PCH}_2$ ), 2.17 (s, 3H,  $\text{OCH}_3$ ), 1.91 (d,  $J = 11.7$  Hz, 1H,  $\text{PCH}_2$ ), 1.87 (d,  $J = 12.2$  Hz, 1H, RuCHCH $_2$ ), 1.77 (dd,  $J = 8.5, 17.3$  Hz, 1H, RuCHCH $_2$ ), 1.70 (br d,  $J = 12.2$  Hz, 1H, RuCHCH $_2$ ), 1.41 (dd,  $J = 8.3, 16.1$  Hz, 1H, RuCH), 1.11–0.99 (m, 1H,  $\text{PCH}_2$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  192.4 (C=O), 188.9 (C=O), 188.7 (C=O), 187.4 (C=O), 163.1–110.2 ( $\text{C}_{\text{Ar}}$ ), 62.3 ( $\text{OCH}_3$ ), 56.6 ( $\text{OCH}_3$ ), 55.8 ( $\text{OCH}_3$ ), 55.4 ( $\text{OCH}_3$ ), 49.6 ( $\text{OCH}_3$ ), 48.4 ( $\text{OCH}_3$ ), 44.9 (RuCHCH $_2$ ), 42.9 (RuCHCH $_2$ ), 28.0 (dd,  $J_{\text{CP}} = 12.1, 32.9$  Hz,  $\text{PCH}_2$ ), 26.0 (dd,  $J_{\text{CP}} = 9.6, 34.6$  Hz,  $\text{PCH}_2$ ), 24.5 (dd,  $J_{\text{CP}} = 13.3, 35.0$  Hz,  $\text{PCH}_2$ ), 23.9 (dd,  $J_{\text{CP}} = 11.3, 32.9$  Hz,  $\text{PCH}_2$ ), 12.0 (RuCH), 11.8 (RuCH).  $^{31}\text{P}$  NMR (162 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  96.3 (d,  $J = 12.2$  Hz), 90.7 (d,  $J = 12.2$  Hz), 84.0 (br s), 79.8 (d,  $J = 30.4$  Hz). HR-MS (FAB-*m*NBA): calcd for  $\text{C}_{33}\text{H}_{35}\text{O}_6\text{P}_2\text{Ru}$   $m/z$  691.0952, found  $m/z$  691.0964 (0.5 $\text{M}^+$  –  $\text{H}_2\text{O}$ ) + H. Anal. Calcd for  $\text{C}_{66}\text{H}_{70}\text{O}_{13}\text{P}_4\text{Ru}_2 \cdot 0.2\text{CHCl}_3$ : C, 54.71; H, 5.11; Cl, 1.38. Found: C, 55.11; H, 5.04; Cl, 1.09.

**Preparation of the Binuclear Aqua Complex 4b.** A mixture of complex **1** (298 mg, 0.60 mmol) and *o*-MeO-dppe (310 mg, 0.60 mmol) in distilled 1,2-dichloroethane (12 mL)/ $\text{H}_2\text{O}$  (9 mL) was stirred at 60 °C for 6 h. After the solvent and water were evaporated, the residue was dissolved in distilled chloroform and then chromatographed on alumina. Elution with chloroform gave

a brown solution which was discarded, and subsequent elution with chloroform/2-propanol (4/1 to 1/2) gave a yellow solution, from which the solvent was evaporated. The orange residue was recrystallized from chloroform/pentane to afford **4b** (244 mg, 0.18 mmol, 59%).

Data for **4b** are as follows. Pale yellow solid. Mp: 154–155 °C dec. IR (KBr disk): 2939, 2909, 1657, 1589, 1572, 1475, 1430, 1245  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.72 (dd,  $J = 7.1, 12.9$  Hz, 1H,  $\text{H}_{\text{Ar}}$ ), 7.56 (br t,  $J = 7.8$  Hz, 1H,  $\text{H}_{\text{Ar}}$ ), 7.45 (t,  $J = 7.6$  Hz, 1H,  $\text{H}_{\text{Ar}}$ ), 7.30 (t,  $J = 7.8$  Hz, 1H,  $\text{H}_{\text{Ar}}$ ), 7.24 (t,  $J = 7.8$  Hz, 1H,  $\text{H}_{\text{Ar}}$ ), 7.19 (t,  $J = 7.8$  Hz, 1H,  $\text{H}_{\text{Ar}}$ ), 7.11 (t,  $J = 7.1$  Hz, 3H,  $\text{H}_{\text{Ar}}$ ), 7.03 (br t,  $J = 9.0$  Hz, 1H,  $\text{H}_{\text{Ar}}$ ), 6.94–6.89 (m, 2H,  $\text{H}_{\text{Ar}}$ ), 6.85 (dd,  $J = 7.3, 12.2$  Hz, 1H,  $\text{H}_{\text{Ar}}$ ), 6.79 (dd,  $J = 3.7, 8.1$  Hz, 1H,  $\text{H}_{\text{Ar}}$ ), 6.65 (d,  $J = 6.8$  Hz, 1H,  $\text{H}_{\text{Ar}}$ ), 4.52 (br s, 2H,  $\text{H}_2\text{O}$ ), 4.41 (s, 3H,  $\text{OCH}_3$ ), 3.76 (s, 3H,  $\text{OCH}_3$ ), 3.50–3.15 (m, 2H,  $\text{PCH}_2$ ), 3.43 (s, 3H,  $\text{OCH}_3$ ), 3.33 (s, 3H,  $\text{OCH}_3$ ), 2.65–2.43 (m, 1H,  $\text{PCH}_2$ ), 2.49 (s, 3H,  $\text{OCH}_3$ ), 2.19 (br d,  $J = 11.6$  Hz, 1H, RuCHCH $_2$ ), 1.57–1.39 (m, 2H, RuCH and RuCHCH $_2$ ), 1.16–1.00 (m, 1H,  $\text{PCH}_2$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  186.0 (2C, C=O), 163.6–109.9 ( $\text{C}_{\text{Ar}}$ ), 61.2 ( $\text{OCH}_3$ ), 56.6 ( $\text{OCH}_3$ ), 55.2 ( $\text{OCH}_3$ ), 55.1 ( $\text{OCH}_3$ ), 50.0 ( $\text{OCH}_3$ ), 38.5 (RuCHCH $_2$ ), 27.5 (d,  $J_{\text{CP}} = 31.5$  Hz,  $\text{PCH}_2$ ), 25.9 (d,  $J_{\text{CP}} = 30.7$  Hz,  $\text{PCH}_2$ ), 10.1 (RuCH).  $^{31}\text{P}$  NMR (162 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  84.8 (br s), 74.4. Anal. Calcd for  $\text{C}_{70}\text{H}_{78}\text{O}_{17}\text{P}_4\text{Ru}_2 \cdot 0.5\text{CHCl}_3 \cdot \text{H}_2\text{O}$ : C, 53.08; H, 5.09; Cl, 3.33. Found: C, 53.39; H, 5.05; Cl, 3.35.

**Preparation of Ammonia Complex 5.** To complex **4b** (100 mg, 0.072 mmol) was added 0.5 M  $\text{NH}_3$  in dioxane (2.0 mL, 1.0 mmol) at room temperature. After the mixture was stirred for 1 h, the obtained pale yellow precipitates were collected by filtration under Ar, washed with dry dioxane (1.0 mL) and pentane (20 mL), and dried under vacuum to give the title complex **5** (63 mg, 0.083 mmol, 58%).

Data for **5** are as follows. Pale yellow solid. Mp: 141–142 °C dec. IR (KBr disk): 3067, 2944, 2903, 2836, 1663, 1585, 1574, 1475, 1432, 1245, 752  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  8.80 (dd,  $J = 7.6, 13.2$  Hz, 1H,  $\text{H}_{\text{Ar}}$ ), 7.69 (t,  $J = 7.8$  Hz, 1H,  $\text{H}_{\text{Ar}}$ ), 7.44 (t,  $J = 7.8$  Hz, 1H,  $\text{H}_{\text{Ar}}$ ), 7.33 (t,  $J = 7.6$  Hz, 1H,  $\text{H}_{\text{Ar}}$ ), 7.26 (t,  $J = 7.6$  Hz, 1H,  $\text{H}_{\text{Ar}}$ ), 7.18–7.10 (m, 3H,  $\text{H}_{\text{Ar}}$ ), 7.05 (br t,  $J = 8.8$  Hz, 1H,  $\text{H}_{\text{Ar}}$ ), 7.01 (t,  $J = 7.6$  Hz, 1H,  $\text{H}_{\text{Ar}}$ ), 6.87–6.78 (m, 5H,  $\text{H}_{\text{Ar}}$ ), 6.70 (d,  $J = 7.6$  Hz, 1H,  $\text{H}_{\text{Ar}}$ ), 4.22 (s, 3H,  $\text{OCH}_3$ ), 3.69 (s, 3H,  $\text{OCH}_3$ ), 3.57–3.30 (m, 2H,  $\text{PCH}_2$ ), 3.45 (s, 3H,  $\text{OCH}_3$ ), 3.15 (s, 3H,  $\text{OCH}_3$ ), 2.81 (br s, 3H,  $\text{NH}_3$ ), 2.59–2.48 (m, 1H,  $\text{PCH}_2$ ), 2.53 (s, 3H,  $\text{OCH}_3$ ), 2.16 (dd,  $J = 9.4, 19.8$  Hz, 1H, RuCHCH $_2$ ), 1.45–1.36 (m, 2H, RuCH and RuCHCH $_2$ ), 0.99–0.86 (m, 1H,  $\text{PCH}_2$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  188.8 (C=O), 186.9 (C=O), 162.5–109.7 ( $\text{C}_{\text{Ar}}$ ), 60.0 ( $\text{OCH}_3$ ), 55.8 ( $\text{OCH}_3$ ), 55.2 ( $\text{OCH}_3$ ), 55.1 ( $\text{OCH}_3$ ), 49.9 ( $\text{OCH}_3$ ), 39.7 (RuCHCH $_2$ ), 29.4 (dd,  $J_{\text{CP}} = 12.5, 32.5$  Hz,  $\text{PCH}_2$ ), 25.0 (dd,  $J_{\text{CP}} = 10.8, 33.4$  Hz,  $\text{PCH}_2$ ), 8.8 (RuCH).  $^{31}\text{P}$  NMR (162 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  73.6 (d,  $J = 18.4$  Hz), 72.5 (br s). HR-MS (FAB-*m*NBA): calcd for  $\text{C}_{35}\text{H}_{41}\text{NO}_8\text{P}_2\text{-Ru}$   $m/z$  767.1351, found  $m/z$  767.1372 ( $\text{M}^+$ ); calcd for  $\text{C}_{35}\text{H}_{39}\text{O}_8\text{P}_2\text{-Ru}$   $m/z$  751.1164, found  $m/z$  751.1198 ( $[\text{M} - \text{NH}_2]^+$ ).

**Crystallographic Study of Complexes 4a,b and 5.** The crystal data and experimental details for **4a,b** and **5** are summarized in Table 5. Crystals that were stable for X-ray diffraction measurements and were obtained by recrystallization as described above were mounted on glass fibers. All measurements were made on a Rigaku Saturn 70 CCD area detector with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71069$  Å) with the oscillation technique. The structures were solved by direct methods using SIR92 $^{23}$  and expanded using Fourier techniques (DIRDIF99). $^{24}$  Hydrogen atoms were refined using the riding model, except for the ammonia protons

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Table 5. Summary of Crystal Data, Collection Data, and Refinement Details of 4a,b and 5

	4a	4b	5
formula	C <sub>66</sub> H <sub>70</sub> O <sub>13</sub> P <sub>4</sub> Ru <sub>2</sub>	C <sub>70</sub> H <sub>78</sub> O <sub>17</sub> P <sub>4</sub> Ru <sub>2</sub> ·CHCl <sub>3</sub> ·H <sub>2</sub> O	C <sub>35</sub> H <sub>41</sub> NO <sub>8</sub> P <sub>2</sub> Ru·CHCl <sub>3</sub>
fw	1397.31	1654.80	886.11
cryst size, mm	0.20 × 0.20 × 0.20	0.20 × 0.20 × 0.20	0.40 × 0.10 × 0.10
cryst syst	monoclinic	triclinic	monoclinic
space group	C2 (No. 5)	P $\bar{1}$ (No. 2)	P2 <sub>1</sub> /n (No. 14)
a, Å	22.045(6)	13.222(4)	16.3423(13)
b, Å	18.270(5)	13.403(4)	11.7192(11)
c, Å	20.120(5)	24.012(7)	21.574(3)
α, deg	90	103.559(4)	90
β, deg	107.6940(13)	90.982(4)	109.319(5)
γ, deg	90	95.869(4)	90
V, Å <sup>3</sup>	7720(4)	4111(2)	3899.1(7)
Z	4	2	4
D(calcd), g cm <sup>-3</sup>	1.202	1.337	1.509
data collec temp, °C	-100	-60	-110
μ(Mo Kα), cm <sup>-1</sup>	5.257	6.034	7.398
2θ <sub>max</sub> , deg	55.0	55.0	55.0
no. of meas rflns	30 546	32 109	30 149
no. of unique rflns	13 774 (R <sub>int</sub> = 0.065)	17 826 (R <sub>int</sub> = 0.023)	8611 (R <sub>int</sub> = 0.080)
no. of obsd rflns (I > 2σ(I))	7280	14 834	5429
no. of variables	822	965	491
R1 <sup>a</sup> (I > 2σ(I))	0.073	0.079	0.061
wR2 <sup>a</sup> (I > 2σ(I))	0.139	0.228	0.096
GOF	0.955	1.030	1.152

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

in **5**, which were refined isotropically. Neutral atom-scattering factors were taken from Cromer and Waber.<sup>25</sup> Anomalous dispersion effects were included in  $F_c$ ;<sup>26</sup> the values for  $\Delta f'$  and  $\Delta f''$  were those of Creagh and McAuley.<sup>27</sup> The values for the mass attenuation coefficients were those of Creagh and Hubbell.<sup>28</sup> All calculations were performed using the CrystalStructure<sup>29,30</sup> crystallographic software package.

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**Supporting Information Available:** X-ray crystallographic data as CIF files for complexes **4a,b** and **5**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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