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Synthesis and Crystal Structure of a Cationic Trinuclear Ruthenium(II) Complex, $[Ru_3(\mu_2\text{-}Cl)_3(\mu_3\text{-}Cl)_2\{$1,2-bis(diphenylphosphino)benzene$\}_3]PF_6$

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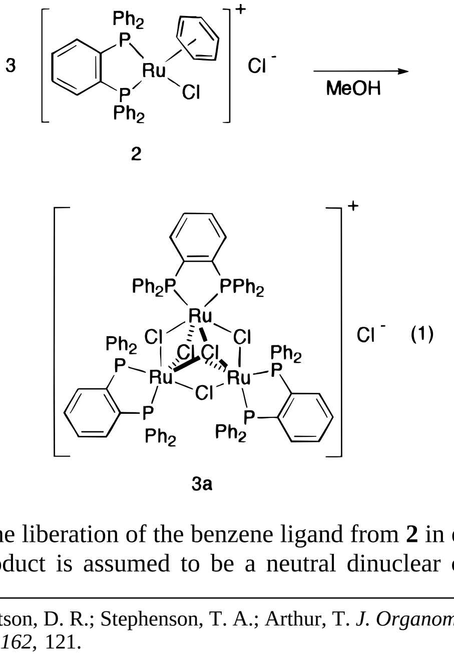
Introduction

Dinuclear ruthenium phosphine complexes bearing the face-sharing bioctahedral $Ru(\mu_2\text{-}Cl)_3Ru$ core have drawn considerable attention over past three decades because they have been readily prepared by the simple reaction of ruthenium chloride and *tert*-phosphine ligands.[1,2] These dinuclear complexes can be classified into three types on the basis of the formal oxidation states: Ru(II)Ru(II) complexes $L_3Ru(\mu_2\text{-}Cl)_3RuClL_2$[3,4] and $[L_3Ru(\mu_2\text{-}Cl)_3RuL_3]^+$,[5−8] Ru(II)Ru(III) complexes $L_2ClRu(\mu_2\text{-}Cl)_3RuClL$[9,10] and $LCl_2Ru(\mu_2\text{-}Cl)_3RuL_3$;[11] and Ru(III)Ru(III) complexes $L_2ClRu(\mu_2\text{-}Cl)_3RuCl_2L$ ($L = PR_3$).[6,12] Recently Cotton *et al.* reported linear trinuclear ruthenium complexes having the $Ru(\mu_2\text{-}Cl)_3Ru(\mu_2\text{-}Cl)_3Ru$ core.[12,13] Thus, ruthenium halide complexes have a tendency to form halide-bridged dinuclear and linear trinuclear complexes regardless of the oxidation state of ruthenium atoms. In 1978, Stephenson and Sime reported a cationic triangular halide-bridged ruthenium(II) complex $[Ru_3Cl_5(P(OEt)Ph_2)_9]^+$, although its structure has not been confirmed heretofore.[13,14] In 1991, we reported the first example of the structurally confirmed triangular complex $[Ru_3Cl_5((S)\text{-binap})_3]^+$ (**1**) (BINAP = 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl).[15,16] The characteristic feature of complex **1** is that **1** has the chelating peraryldiphosphine ligand. This is in sharp contrast to the observation that reactions of ruthenium halide with monodentate phosphine ligands as well as chelating diphosphine ligands having alkyl substituents on phosphorous atoms are prone to form dinuclear complexes.[9] The synthetic study of **1** prompted us to prepare another triangular trinuclear ruthenium complex by using 1,2-bis(diphenylphosphino)benzene (DPB) ligand, which is a peraryl chelating ligand and makes a 5-membered chelate ring instead of a 7-membered chelate ring in **1**. Thus, we report the synthesis and crystal structure of $[Ru_3Cl_5(dpb)_3]^+$ (**3**) and make a comparison between **1** and **3** in order to provide an insight into a triangular trinuclear cluster complex of ruthenium.

Results and Discussion

Synthesis. Treatment of $[RuCl_2(\eta^6\text{-}C_6H_6)]_2$ with 2 equiv of 1,2-bis(diphenylphosphino)benzene in methanol at room temperature resulted in the formation of a cationic mononuclear complex $[RuCl(\eta^6\text{-}C_6H_6)(dpb)]Cl$ (**2**) whose structure was characterized by NMR spectroscopy (^1H and ^{31}P) together with the FAB mass spectrum. The ^1H NMR spectrum of **2** displayed a singlet at δ 6.23; the chemical shift value is typical of the $\eta^6\text{-}C_6H_6$ ligand coordinated to a ruthenium atom.[17,18] The benzene ligand of **2** was labile in protic solvent such as methanol, though inert in aprotic solvent such as benzene and dichloromethane. Thus, heating a methanol solution of **2** to 50 °C for 13 h caused liberation of the benzene ligand, resulting in the formation of a cationic trinuclear complex $[Ru_3(\mu_2\text{-}Cl)_3(\mu_3\text{-}Cl)_2(dpb)_3]Cl$ (**3a**) whose trinuclear core was revealed by a FAB mass spectrum. The ^1H NMR spectrum showed no signal assignable to $\eta^6\text{-}C_6H_6$ coordinated to the ruthenium atom. The $^{31}P\{^1H\}$ NMR spectrum of **3a** exhibited a singlet at δ 79.6, indicating that all phosphorous nuclei are magnetically equivalent. In order to procure a single crystal suitable for crystallographic study, a chloride anion of **3a** was replaced by a PF_6 anion. Thus, treatment of **3a** with $AgPF_6$ in a mixture of dichloromethane and methanol gave $[Ru_3(\mu_2\text{-}Cl)_3(\mu_3\text{-}Cl)_2(dpb)_3]PF_6$ (**3b**) as red crystalline solids. The ^1H and $^{31}P\{^1H\}$ NMR spectra of **3b** are almost the same as those of **3a**. The FAB mass spectrum together with the elemental analysis of **3b** supported this formulation, which was subsequently confirmed by a single crystal X-ray analysis (*vide infra*).



After the liberation of the benzene ligand from **2** in eq 1, the initial product is assumed to be a neutral dinuclear complex

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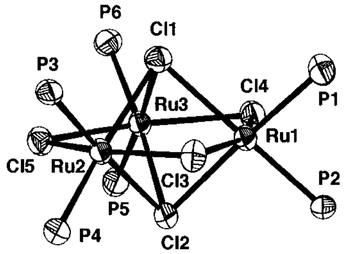
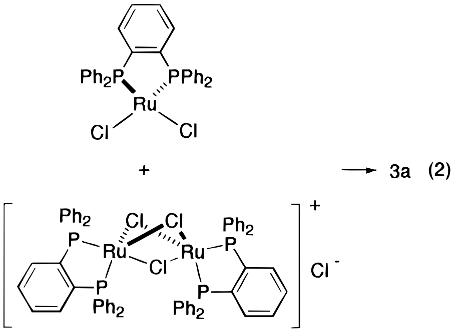


Figure 1. ORTEP drawing of a $Ru_3Cl_5P_6$ core part of **3b**.

$Ru_2Cl_4(dpb)_2$ (**4**), which is similar to the reported five-coordinated dinuclear complex $Ru_2Cl_2(\mu_2\text{-}Cl)_2(dppb)_2$ (dppb = bis(diphenylphosphino)butane),[19] though no intermediate has been observed in the reaction. In a protic solvent one chloride anion of **4** can presumably be outside of the coordination sphere of the ruthenium atom to give a cationic dinuclear species $[Ru_2Cl_3(dpb)_2]Cl$ (**5**). The cationic complex **5** is an electrophile and a nascent "$RuCl_2(dpb)$" is a nucleophile. Thus, reaction of **5** with $RuCl_2(dpb)$ afforded **3a**.[20]



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Electrochemistry of 3b. Cyclic voltammetry of **3b** in THF (0.1 M $TBABF_4$) showed a reversible one-electron oxidation process at +0.75 V *vs* Fc^+/Fc. In addition, a irreversible reduction occurred at −1.92 V. The oxidation potential of complex **3b** is comparable to that of the first oxidation of face-sharing bioctahedral Ru complexes such as $[Ru_2Cl_3(PEt_2Ph)_6]^+$ (+0.78 and +1.33 V *vs* Fc^+/Fc in which the potentials were converted from those *vs* Ag/AgCl, using a value of +0.42 V *vs* Ag/AgCl for the corresponding potential of ferrocene).[6] In the case of face-sharing bioctahedral Ru complexes, two oxidation processes were observed with the potential separation of ~0.5 V, indicating the strong interaction of Ru−Ru ions through strong delocalization of the charge. In the present trinuclear complex, attempts to detect the additional oxidation waves at more positive potentials were unsuccessful because of the experimental limits of the potential window. However, a substantial charge delocalization will be expected in **3b**. A wide gap between oxidation and reduction indicates a strong interaction between metal ions and the stabilization of the oxidation state of all Ru(II) ions in complex **3b**, which is attributed to the coordination of the chelating triarylphosphine ligand.

Crystal Structure of 3b. The crystal structure of **3b** consists of a separated discrete cationic trinuclear part with a PF_6 anion and two dichloromethane molecules of solvation. The cationic part of **3b** has a triangular arrangement of three ruthenium atoms linked by three μ_2-bridging chloride atoms and two face-capped μ_3-chloride atoms, as shown in Figure 1. Selected bond distances and angles of **3b** are listed in Table 1. Each ruthenium atom is coordinated by four chlorine atoms and two phosphorus atoms in *cis* positions and adopts a pseudo-octahedral geometry as expected for Ru(II) complexes. The cationic fragment approximated D_3 symmetry. The structure of **3b** is closely related to that of $[Ru_3Cl_5(binap)_3]^+$ (**1**),[15,16] and the major difference is the size of the chelate rings: a five-membered ring for **3b** and a seven-membered ring for **1**. The interatomic Ru−Ru distances (3.219(3)−3.234(3) Å) of **3b** are shorter than those (3.294(3)−3.383(3) Å) found for **1**,[15,16] in accordance with bite angles of P−Ru−P (82.9(2)−84.6(3)°) for **3b** smaller than those (89.2(3)−91.8(3)°) found for **1**. The interatomic Ru−Ru distances in **3b** are comparable to those (3.115−3.40 Å) reported for face-sharing bioctahedral Ru complexes having the $Ru(\mu_2\text{-}Cl)_3Ru$ unit, *i.e.*, $(PEt_2Ph)_2ClRu(\mu_2\text{-}Cl)_3Ru(PEt_2Ph)_3$ (3.367 Å),[3] $(PBu_3)_2ClRu(\mu_2\text{-}Cl)_3RuCl(PBu_3)_2$ (3.115 Å),[10] (*S,S*-chiraphos)$ClRu(\mu_2\text{-}Cl)_3RuCl$(*S,S*-chiraphos) (3.25 Å),[9] $(PPh_3)_2(CS)Ru(\mu_2\text{-}Cl)_3RuCl(PPh_3)_2$ (3.35(2) Å),[4] $(PEt_2Ph)Cl_2Ru(\mu_2\text{-}Cl)_3Ru(PEt_2Ph)_3$ (3.28 Å),[11] $[(PR_3)_3Ru(\mu_2\text{-}Cl)_3Ru(PR_3)_3]^+$ (R = Me, 3.275 Å;[5] R = Bu, 3.395(1) Å;[6] PR_3 = PEt_2Ph, 3.443 Å;[7] $(PR_3)_3$ = bis(2-(diphenylphosphino)ethyl)phenylphosphine, 3.343(1) Å[8]), and $(PR_3)_2ClRu(\mu_2\text{-}Cl)_3RuCl_2(PR_3)$ (R = Bu, 3.18 Å;[12] R = Et, 3.20 Å[6]). The Ru−Ru bond distances are well out of the

Table 1. Selected Interatomic Distances (Å) and Angles (deg) of **3b**

Interatomic Distances (Å)			
Ru(1)−Ru(2)	3.234(3)	Ru(1)−Ru(3)	3.219(3)
Ru(2)−Ru(3)	3.231(3)	Ru(1)−P(1)	2.243(7)
Ru(1)−P(2)	2.228(7)	Ru(1)−Cl(1)	2.517(6)
Ru(1)−Cl(2)	2.487(6)	Ru(1)−Cl(3)	2.455(6)
Ru(1)−Cl(4)	2.413(6)	Ru(2)−P(3)	2.231(7)
Ru(2)−P(4)	2.236(7)	Ru(2)−Cl(1)	2.516(6)
Ru(2)−Cl(2)	2.498(6)	Ru(2)−Cl(3)	2.409(6)
Ru(2)−Cl(5)	2.432(6)	Ru(3)−P(5)	2.227(7)
Ru(3)−P(6)	2.225(7)	Ru(3)−Cl(1)	2.492(6)
Ru(3)−Cl(2)	2.524(6)	Ru(3)−Cl(4)	2.439(6)
Ru(3)−Cl(5)	2.388(6)		
Interatomic Angles (deg)			
Ru(2)−Ru(1)−Ru(3)	60.09(8)	Ru(1)−Ru(2)−Ru(3)	59.72(8)
Ru(1)−Ru(3)−Ru(2)	60.19(8)	P(1)−Ru(1)−P(2)	82.9(2)
P(1)−Ru(1)−Cl(1)	98.4(2)	P(1)−Ru(1)−Cl(2)	175.1(2)
P(1)−Ru(1)−Cl(3)	103.5(2)	P(1)−Ru(1)−Cl(4)	92.9(2)
P(2)−Ru(1)−Cl(1)	173.2(2)	P(2)−Ru(1)−Cl(2)	94.2(2)
P(2)−Ru(1)−Cl(3)	105.8(2)	P(2)−Ru(1)−Cl(4)	92.8(2)
Cl(1)−Ru(1)−Cl(2)	84.1(2)	Cl(1)−Ru(1)−Cl(3)	80.4(2)
Cl(1)−Ru(1)−Cl(4)	80.6(2)	Cl(2)−Ru(1)−Cl(3)	81.1(2)
Cl(2)−Ru(1)−Cl(4)	83.3(2)	Cl(3)−Ru(1)−Cl(4)	156.5(2)
P(3)−Ru(2)−P(4)	83.2(3)	P(3)−Ru(2)−Cl(1)	94.3(2)
P(3)−Ru(2)−Cl(2)	175.1(2)	P(3)−Ru(2)−Cl(3)	93.4(2)
P(3)−Ru(2)−Cl(5)	104.5(2)	P(4)−Ru(2)−Cl(1)	172.7(2)
P(4)−Ru(2)−Cl(2)	98.1(2)	P(4)−Ru(2)−Cl(3)	92.0(2)
P(4)−Ru(2)−Cl(5)	105.8(2)	Cl(1)−Ru(2)−Cl(2)	83.9(2)
Cl(1)−Ru(2)−Cl(3)	81.3(2)	Cl(1)−Ru(2)−Cl(5)	81.5(2)
Cl(2)−Ru(2)−Cl(3)	81.8(2)	Cl(2)−Ru(2)−Cl(5)	79.8(2)
Cl(3)−Ru(2)−Cl(5)	156.0(2)	P(5)−Ru(3)−P(6)	84.6(3)
P(5)−Ru(3)−Cl(1)	175.7(2)	P(5)−Ru(3)−Cl(2)	96.1(2)
P(5)−Ru(3)−Cl(4)	103.7(2)	P(5)−Ru(3)−Cl(5)	92.8(2)
P(6)−Ru(3)−Cl(1)	95.1(2)	P(6)−Ru(3)−Cl(2)	174.8(2)
P(6)−Ru(3)−Cl(4)	102.9(2)	P(6)−Ru(3)−Cl(5)	94.7(2)
Cl(1)−Ru(3)−Cl(2)	83.8(2)	Cl(1)−Ru(3)−Cl(4)	80.6(2)
Cl(1)−Ru(3)−Cl(5)	82.9(2)	Cl(2)−Ru(3)−Cl(4)	82.0(2)
Cl(2)−Ru(3)−Cl(5)	80.1(2)	Cl(4)−Ru(3)−Cl(5)	156.7(2)
Ru(1)−Cl(1)−Ru(2)	80.0(2)	Ru(1)−Cl(1)−Ru(3)	80.0(2)
Ru(2)−Cl(1)−Ru(3)	80.3(2)	Ru(1)−Cl(2)−Ru(2)	80.9(1)
Ru(1)−Cl(2)−Ru(3)	79.9(2)	Ru(2)−Cl(2)−Ru(3)	80.1(2)
Ru(1)−Cl(3)−Ru(2)	83.3(2)	Ru(1)−Cl(4)−Ru(3)	83.1(2)
Ru(2)−Cl(5)−Ru(3)	84.2(3)		

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Ru−Ru single bond range (2.805−2.994 Å) found for $[Cl_3Ru(\mu_2\text{-}Cl)_3Ru(\mu_2\text{-}Cl)_3RuCl_3]^{4-}$ (2.805(1) Å),[21] $(PBu_3)_2ClRu(\mu_2\text{-}Cl)_3Ru(\mu_2\text{-}Cl)_3RuCl(PBu_3)_2$ (2.854(2) Å),[12] and $(PR_3)_2ClRu(\mu_2\text{-}Cl)_3RuCl(PR_3)_2$ ($PR_3 = PMe_3$, 2.992(1) Å; $PR_3 = PMe_2Ph$, 2.9941(4) Å[6]). The Ru−Cl and Ru−P bond distances are normal. Angles involving the three ruthenium atoms lie in the range 59.72(8)−60.19(8)°, and thus **3b** is a regular triangular trinuclear ruthenium(II) complex. Although a number of such regular triangular trinuclear complexes have been found for $Ru_3(CO)_{12}$[22] and $Ru_3(O)(O_2CCH_3)_6(PPh_3)_3$,[23] complex **3b** is only the second example possessing a $Ru_3(\mu_2\text{-}Cl)_3(\mu_3\text{-}Cl)_2$ core. Complex **3b** has three five-membered chelating rings with puckered conformations, and the angles between the best plane defined by each Ru atom and its two associated phosphorus atoms and the plane defined by the two phosphorus atoms and the two carbon atoms in the chelate rings are 143.3(6), 147.8(6), and 157.4(7)°.

Experimental Section

General. All manipulations for air- and moisture-sensitive compounds were carried out by the use of the standard Schlenk techniques under an argon atmosphere. Each solvent was purified by distillation under argon after drying over the desiccant shown below: dichloromethane, calcium hydride; hexane and THF, sodium benzophenone ketyl; methanol, magnesium alkoxide; chloroform-*d*, phosphorus pentoxide. $[Ru(\eta^6\text{-}C_6H_6)Cl_2]_2$[24] and 1,2-bis(diphenylphosphino)benzene[25] were synthesized according to the literature.

Physical Measurements. Nuclear magnetic resonance (^1H, ^{31}P NMR) spectra were measured on a JEOL JNM-GSX-270 spectrometer. All ^1H NMR chemical shifts were reported in ppm relative to proton impurity resonance in chloroform-*d* at δ 7.27. The ^{31}P NMR chemical shifts were reported in ppm relative to an external reference of 85% H_3PO_4 at δ 0.00. Mass spectra were recorded on a JEOL SX-102 spectrometer. Elemental analyses were performed at Elemental Analysis Center of Osaka University. UV−vis spectra were taken on a JASCO Ubest-30 in a sealed 1 mm cell. All melting points were measured in sealed tubes and were not corrected.

Electrochemical measurements were made at 20 °C with a BAS 100 B/W electrochemical workstation. The working electrode was a platinum disk electrode, and the auxiliary electrode was a platinum wire. The reference electrode was $Ag/AgNO_3$ (0.01 M in 0.1 M $TBABF_4$ CH_3CN), abbreviated as Ag/Ag^+. The $E_{1/2}$ value for the ferrocenium/ferrocene (Fc^+/Fc) couple is +0.19 V *vs* Ag/Ag^+. All potential values are reported *vs* Fc^+/Fc.

Preparation of $[RuCl(\eta^6\text{-}C_6H_6)\{1,2\text{-}(Ph_2P)_2C_6H_4\}]Cl$ (2). A suspension of $[Ru(\eta^6\text{-}C_6H_6)Cl_2]_2$ (110 mg, 0.22 mmol) and $1,2\text{-}(Ph_2P)_2C_6H_4$ (196 mg, 0.44 mmol) in methanol (50 mL) was stirred for 13 h at room temperature. A brown solution was filtered from a small amount of precipitates. All of the volatiles were removed to give **2** as a yellow-orange solid (289 mg, 85% yield): mp 202−212 °C dec; ^1H NMR ($CDCl_3$) δ 6.23 (s, 6H, C_6H_6), 6.92−7.96 (m, 24H, aromatic protons); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 64.6 (s); FAB mass spectrum, *m/z* 661 ($M^+ - Cl$). Anal. Calcd for $C_{36}H_{30}Cl_2P_2Ru\cdot(CH_3OH)$: C, 60.99; H, 4.70. Found: C, 61.10; H, 4.45.

Table 2. Crystal Parameters and Experimental Data for X-ray Diffraction Measured on **3b**

formula	$C_{90}H_{72}Cl_5F_6P_7Ru_3\cdot 2(CH_2Cl_2)$
formula weight	2134.71
crystal system	monoclinic
space group	$P2_1/c$
a, Å	19.436(1)
b, Å	15.4674(9)
c, Å	29.811(1)
β, deg	95.014(7)
V, Å^3	8928(1)
Z	4
D(calcd), g cm^{-3}	1.588
F(000)	4288
temperature, °C	20
scan range (ω), deg	$1.10 + 0.15\tan\theta$
collection region	$+h, +k, \pm l$
$2\theta_{max}$, deg	120.0
no. of measured reflections	13521
no. of unique reflections	13231
R_{int}	0.058
no. of reflections with $F_o > 5\sigma(F_o)$	4919
μ, cm^{-1}	8.40
T_{min}, T_{max}	0.6681, 1.0247
valiable parameters	540
R, R_w[a]	0.080, 0.073
S[b]	1.522
$\Delta\rho$(max,min), e Å^{-3}	1.46, −1.27

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$, $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$, $w = 1/\sigma^2(F_o)$. [b] $S = [\sum w(|F_o| - |F_c|)^2/(N_{obs} - N_{param})]^{1/2}$.

Preparation of $[Ru_3Cl_5\{1,2\text{-}(Ph_2P)_2C_6H_4\}_3]Cl$ (3a). A solution of **2** (94 mg, 0.14 mmol) in methanol (15 mL) was stirred at 50 °C for 13 h. A red solution was filtered from a small amount of precipitates. All of the volatiles were removed to give **3a** as an orange solid (63 mg, 75% yield): mp 200−220 °C dec; ^1H NMR ($CDCl_3$) δ 6.73−7.66 (m, 72H, aromatic protons); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 79.6 (s); FAB mass spectrum, *m/z* 1820 ($M^+ - Cl$).

Preparation of $[Ru_3Cl_5\{1,2\text{-}(Ph_2P)_2C_6H_4\}_3]PF_6$ (3b). To a solution of **3a** (314 mg, 0.17 mmol) in a mixture of dichloromethane (9 mL) and methanol (10 mL) was added a suspension of $AgPF_6$ (80 mg, 0.32 mmol) in methanol (8 mL). The mixture was stirred for 1.5 h, and then precipitated AgCl was filtered off. Complex **3b** was obtained as red crystals (286 mg, 0.15 mmol, 88% yield) upon crystallization from a mixture of dichloromethane, methanol, and hexane: mp 200−220 °C dec; ^1H NMR ($CDCl_3$) δ 6.73−7.66 (m, 72H, aromatic protons); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 79.6 (s), −143.7 (septet, $J_{PF} = 713$ Hz); UV (MeOH) $\lambda_{max} = 310$ nm ($\epsilon = 3.3 \times 10^4$); FAB mass spectrum, *m/z* 1820 ($M^+ - PF_6^-$). Anal. Calcd for $C_{90}H_{72}Cl_5F_6P_7Ru$: C, 55.01; H, 3.69. Found: C, 54.88; H, 3.75.

Crystal Structure of 3b. Crystal data as well as details of the data collection and the method of refinement are summarized in Table 2. A red-orange crystal (crystal size: 0.47 × 0.23 × 0.13 mm) of complex **3b** was sealed in a glass capillary under an argon atmosphere and transferred to a goniostat on a Rigaku AFC-5R diffractometer with Cu Kα radiation ($\lambda = 1.541\,78$ Å). Cell constants and orientation matrices were determined using least-squares refinements of the angular coordinates of at least 25 accurately centered reflections ($22° < \theta < 29°$). Intensity data were collected by using the ω and $\omega - 2\theta$ scan ($\omega < 60°(2\theta) < \omega - 2\theta$) techniques. As a check of crystal stability, three representative reflections were measured every 200 data points. A linear correction factor was applied to the raw data (5.6% decay). The intensity data were corrected for Lorentz and

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Table 3. Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters for the Cationic Part of **3b**

atom	x	y	z	$U_{\mathrm{eq/iso}}$ (Å^2)^a	atom	x	y	z	$U_{\mathrm{eq/iso}}$ (Å^2)^a
Ru(1)	0.2838(1)	0.0634(1)	0.8454(1)	0.030(1)*	C(39)	−0.0234(14)	0.1611(17)	0.8616(9)	0.064(9)
Ru(2)	0.2276(1)	0.2533(1)	0.8154(1)	0.030(1)*	C(40)	−0.0414(14)	0.0943(16)	0.8337(10)	0.065(9)
Ru(3)	0.3041(1)	0.2228(1)	0.9148(1)	0.029(1)*	C(41)	−0.0143(15)	0.0782(16)	0.7950(10)	0.071(9)
P(1)	0.2345(3)	−0.0653(4)	0.8558(2)	0.039(4)*	C(42)	0.0358(13)	0.1404(15)	0.7798(8)	0.051(7)
P(2)	0.3694(3)	−0.0182(4)	0.8237(2)	0.033(4)*	C(43)	0.0831(12)	0.3908(13)	0.8113(7)	0.034(6)
P(3)	0.1185(3)	0.2880(4)	0.7931(2)	0.036(4)*	C(44)	0.1223(13)	0.4604(17)	0.8285(9)	0.062(8)
P(4)	0.2499(3)	0.3254(4)	0.7533(2)	0.037(4)*	C(45)	0.0934(14)	0.5365(16)	0.8397(9)	0.056(8)
P(5)	0.3979(3)	0.2907(4)	0.9452(2)	0.039(4)*	C(46)	0.0251(14)	0.5493(16)	0.8329(9)	0.063(8)
P(6)	0.2609(3)	0.2520(4)	0.9798(2)	0.036(3)*	C(47)	−0.0167(14)	0.4842(18)	0.8128(9)	0.068(9)
Cl(1)	0.1958(3)	0.1577(3)	0.8787(2)	0.035(4)*	C(48)	0.0101(14)	0.4077(15)	0.8006(9)	0.058(8)
Cl(2)	0.3473(3)	0.2016(3)	0.8381(2)	0.035(3)*	C(49)	0.3252(11)	0.2876(14)	0.7253(7)	0.034(6)
Cl(3)	0.2215(3)	0.1174(3)	0.7759(2)	0.039(4)*	C(50)	0.3199(13)	0.2197(15)	0.6935(8)	0.052(7)
Cl(4)	0.3343(3)	0.0701(3)	0.9223(2)	0.037(3)*	C(51)	0.3773(15)	0.1868(16)	0.6756(9)	0.061(8)
Cl(5)	0.2593(3)	0.3505(3)	0.8779(2)	0.037(4)*	C(52)	0.4395(14)	0.2215(17)	0.6900(9)	0.067(9)
C(1)	0.3064(11)	−0.1374(14)	0.8740(7)	0.034(6)	C(53)	0.4480(17)	0.2887(20)	0.7215(11)	0.096(11)
C(2)	0.3700(11)	−0.1156(13)	0.8594(7)	0.032(6)	C(54)	0.3884(15)	0.3210(16)	0.7378(9)	0.062(8)
C(3)	0.4294(12)	−0.1637(13)	0.8713(7)	0.037(6)	C(55)	0.2626(12)	0.4421(14)	0.7581(8)	0.043(7)
C(4)	0.4246(11)	−0.2392(14)	0.8956(8)	0.043(7)	C(56)	0.2346(13)	0.4956(16)	0.7212(9)	0.060(8)
C(5)	0.3622(13)	−0.2651(15)	0.9074(8)	0.055(8)	C(57)	0.2419(15)	0.5863(18)	0.7262(10)	0.082(10)
C(6)	0.3022(11)	−0.2169(13)	0.8959(7)	0.035(6)	C(58)	0.2750(15)	0.6183(16)	0.7627(10)	0.069(9)
C(7)	0.1727(12)	−0.0682(14)	0.8984(8)	0.038(6)	C(59)	0.3034(13)	0.5704(17)	0.7959(9)	0.063(8)
C(8)	0.1884(13)	−0.0922(14)	0.9435(9)	0.054(8)	C(60)	0.2991(13)	0.4803(16)	0.7938(8)	0.053(8)
C(9)	0.1369(16)	−0.0897(17)	0.9738(9)	0.073(9)	C(61)	0.3728(12)	0.3572(13)	0.9916(7)	0.033(6)
C(10)	0.0735(14)	−0.0632(17)	0.9587(9)	0.067(9)	C(62)	0.3080(12)	0.3446(14)	1.0050(8)	0.038(7)
C(11)	0.0573(14)	−0.0357(16)	0.9142(10)	0.064(9)	C(63)	0.2818(12)	0.3985(14)	1.0370(8)	0.044(7)
C(12)	0.1066(13)	−0.0409(15)	0.8854(8)	0.052(8)	C(64)	0.3232(14)	0.4649(16)	1.0568(9)	0.061(8)
C(13)	0.1880(12)	−0.1270(14)	0.8103(8)	0.043(7)	C(65)	0.3925(14)	0.4730(16)	1.0467(9)	0.064(9)
C(14)	0.1906(12)	−0.1006(14)	0.7657(8)	0.044(7)	C(66)	0.4168(13)	0.4201(16)	1.0164(9)	0.061(8)
C(15)	0.1648(12)	−0.1521(15)	0.7300(8)	0.047(7)	C(67)	0.4341(12)	0.3687(14)	0.9075(8)	0.037(6)
C(16)	0.1348(12)	−0.2273(15)	0.7390(8)	0.053(7)	C(68)	0.4713(13)	0.3390(16)	0.8749(9)	0.057(8)
C(17)	0.1298(12)	−0.2538(15)	0.7824(8)	0.050(7)	C(69)	0.4959(13)	0.3931(17)	0.8429(9)	0.060(8)
C(18)	0.1558(12)	−0.2035(15)	0.8190(8)	0.050(7)	C(70)	0.4844(15)	0.4804(18)	0.8439(10)	0.071(9)
C(19)	0.3575(12)	−0.0647(15)	0.7655(8)	0.048(7)	C(71)	0.4447(14)	0.5115(16)	0.8767(10)	0.071(9)
C(20)	0.3453(13)	−0.0066(15)	0.7296(9)	0.056(8)	C(72)	0.4186(12)	0.4563(15)	0.9105(8)	0.049(7)
C(21)	0.3325(13)	−0.0389(15)	0.6871(9)	0.055(8)	C(73)	0.4747(12)	0.2325(14)	0.9707(8)	0.046(7)
C(22)	0.3324(13)	−0.1270(17)	0.6804(9)	0.063(8)	C(74)	0.5436(14)	0.2582(16)	0.9650(8)	0.062(8)
C(23)	0.3499(13)	−0.1857(16)	0.7146(9)	0.061(8)	C(75)	0.5965(14)	0.2063(17)	0.9827(9)	0.067(9)
C(24)	0.3609(12)	−0.1537(15)	0.7581(8)	0.045(7)	C(76)	0.5828(16)	0.1345(20)	1.0052(10)	0.091(11)
C(25)	0.4578(11)	0.0241(12)	0.8297(8)	0.028(6)	C(77)	0.5192(15)	0.1101(16)	1.0164(9)	0.065(9)
C(26)	0.4950(16)	0.0265(17)	0.7917(10)	0.076(10)	C(78)	0.4642(12)	0.1561(15)	0.9945(8)	0.045(7)
C(27)	0.5642(17)	0.0616(19)	0.7968(11)	0.091(10)	C(79)	0.1705(12)	0.2783(15)	0.9786(8)	0.045(7)
C(28)	0.5884(15)	0.0963(17)	0.8374(11)	0.076(10)	C(80)	0.1445(14)	0.3486(16)	0.9579(9)	0.061(8)
C(29)	0.5536(14)	0.0947(16)	0.8727(9)	0.066(9)	C(81)	0.0727(17)	0.3694(19)	0.9520(11)	0.092(11)
C(30)	0.4853(13)	0.0576(16)	0.8696(9)	0.057(8)	C(82)	0.0275(15)	0.3165(19)	0.9671(10)	0.078(10)
C(31)	0.1139(12)	0.2963(13)	0.7326(7)	0.034(6)	C(83)	0.0512(17)	0.2462(21)	0.9915(11)	0.101(11)
C(32)	0.1760(11)	0.3112(12)	0.7106(8)	0.028(6)	C(84)	0.1239(16)	0.2256(18)	0.9976(10)	0.080(10)
C(33)	0.1732(14)	0.3207(15)	0.6651(9)	0.060(8)	C(85)	0.2740(13)	0.1686(16)	1.0247(9)	0.055(8)
C(34)	0.1127(15)	0.3168(16)	0.6389(9)	0.062(8)	C(86)	0.3132(14)	0.1838(16)	1.0666(10)	0.068(9)
C(35)	0.0526(15)	0.3042(17)	0.6575(10)	0.075(9)	C(87)	0.3248(14)	0.1199(17)	1.0988(9)	0.066(9)
C(36)	0.0521(14)	0.2932(16)	0.7054(9)	0.065(9)	C(88)	0.3004(15)	0.0392(17)	1.0871(10)	0.072(9)
C(37)	0.0540(11)	0.2110(14)	0.8093(8)	0.037(6)	C(89)	0.2632(14)	0.0186(17)	1.0487(10)	0.068(9)
C(38)	0.0247(12)	0.2231(14)	0.8476(8)	0.046(7)	C(90)	0.2513(14)	0.0866(17)	1.0172(9)	0.066(9)

[a] Anisotropically refined atoms were given in the isotropic equivalent thermal parameters defined as $U_{\mathrm{eq}} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*(\mathbf{a}_i\cdot\mathbf{a}_j)$. Values for anisotropically refined are denoted by an asterisk.

polarization factors, and an empirical absorption correction based on reflection measurements was applied to the raw data.

The structure was solved by using direct methods (SHELXS-86)[26] and Fourier techniques. The positional parameters and thermal parameters of non-hydrogen atoms were refined against F_o using a full-matrix least-squares method (ANYBLK program).[27] The extinction parameter γ was introduced in the refinement of **3b** as $|F_c(\mathrm{cor})| = |F_c(\mathrm{raw})|/(1 + \gamma L_p|F_c(\mathrm{raw})|^2)^{1/2}$. The ruthenium, chlorine, and phosphorus atoms of the cationic part were anisotropically refined. All carbon atoms of the cationic part were isotropically refined. The carbon and chlorine atoms of the two solvating methylene chloride and the phosphorus and fluorine atoms of the anionic part were isotropically refined. Hydrogen atoms were included as fixed contributions in their idealized positions with C−H = 1.08 Å (sp^3-hybridized geometry), C−H = 0.95 Å (sp^2-hybridized geometry), and $B_{\mathrm{iso}} = 4.69$ Å^2. Atomic scattering factors were taken from a standard source,[28] and the effects of anomalous dispersions were included for the Ru, Cl, and P atoms by using $\Delta f'$ and $\Delta f''$

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(26) Sheldrick, G. M. In *Crystallographic Computing 3*; Sheldrick, G. M., Krüger, C., Goddard, R., Eds.; Oxford University Press: Oxford, U.K., 1985; p 179.

(27) Imoto, H. *ANYBLK; 'Program for Least-Squares Refinement'*; Department of Chemistry, Faculty of Science, The University of Tokyo: Tokyo 113, Japan.

values of Cromer and Ibers.[29] All calculations were performed with UNICS programs on NEC ACOS S-3700 computer and NEC EWS 4800/350 workstation at the Research Center for Protein Engineering Institute for Protein Research, Osaka University. Final atomic coordinates of **3b** are summarized in Table 3.

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Supporting Information Available: Listings of atomic coordinates, bond distances and angles, and anisotropic thermal parameters and a figure for **3b** (11 pages). Ordering information is given on any current masthead page.

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(28) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 99−101, Table 2.2B.

(29) Cromer, D. T.; Ibers, J. A. *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 145−150, Table 2.3.1.