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Synthesis, Structure, and Reactivity of a Stable Zerovalent Ruthenium Aqua Complex

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A novel ruthenium(0) aqua complex, Ru(dimethyl fumarate)$_2$(dppe)(H_2O) (**4**), was synthesized via the reaction of Ru(η^6-1,3,5-cyclooctatriene)(dimethyl fumarate)$_2$ (**3**) with dppe in 1,2-dichloroethane/water, which is a quite rare example of a stable and isolable ruthenium(0) aqua complex. The X-ray crystallography of **4** indicated that coordination of a water molecule to the ruthenium center was stabilized by two hydrogen bonds with the carbonyl oxygen atoms of dimethyl fumarate ligands.

Introduction

Investigation of the reactivity of transition-metal complexes toward H_2O is very important because H_2O is an extremely attractive reagent in transition-metal-catalyzed organic reactions; for example, hydration of alkynes,[1−3] dienes[4] and nitriles[5] and, in particular, anti-Markovnikov hydration of terminal alkynes[6,7] and alkenes.[8] With respect to one activation reaction of water by transition metals, the first step would be the coordination of H_2O to a metal center and then the oxidative addition to afford a hydrido hydroxo complex. A number of examples of transition-metal aqua complexes[9−11] and hydrido hydroxo complexes[12−16] have been found. As for ruthenium complexes, although many examples for divalent or trivalent complexes having H_2O ligands have been reported,[7,9,10] *zerovalent* ruthenium aqua complexes have been investigated by only two groups. Sustmann et al. showed the formation of Ru(MA)$_2$(PPh$_3$)$_2$(H_2O) (**1**; MA = methyl acrylate) by the reaction of the coordinatively unsaturated ruthenium(0) complex Ru(MA)$_2$(PPh$_3$)$_2$ with H_2O (eq 1).[11a] The structure of **1**

$$\mathrm{Ru(MA)_2(PPh_3)_2 + H_2O \rightarrow \underset{\textbf{1}}{Ru(MA)_2(PPh_3)_2(H_2O)}} \tag{1}$$

was confirmed by X-ray analysis. Ogasawara et al. synthesized the ruthenium(0) aqua nitrosyl complex [Ru(CO)(NO)(P^{t}Bu$_2$Me)$_2$(H_2O)][BAr$_4$] (**2**; Ar = C_6H_3-3,5-(CF_3)$_2$) from [Ru(CO)(NO)(P^{t}Bu$_2$Me)$_2$][BAr$_4$] and H_2O (eq 2).[11b] Although both complexes are claimed to be

$$\mathrm{[Ru(CO)(NO)(P^tBu_2Me)_2][BAr_4] + H_2O \rightarrow \underset{\textbf{2}}{[Ru(CO)(NO)(P^tBu_2Me)_2(H_2O)][BAr_4]}} \tag{2}$$

formed in high yields *in solution* on the basis of their NMR spectra, neither the procedure of the isolation of the products nor the isolated yields have been reported.

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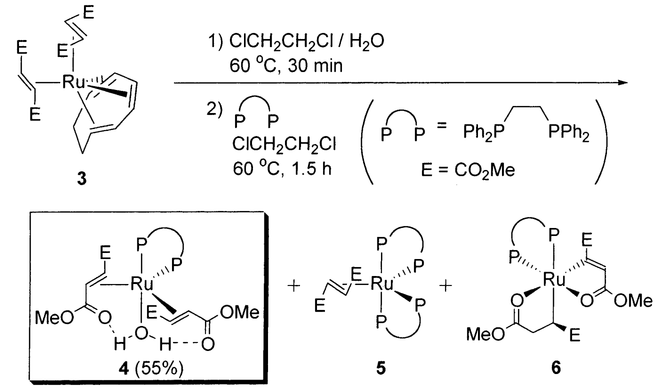
Scheme 1. Synthesis of a Ruthenium Aqua Complex, Ru(dmfm)$_2$(dppe)(H$_2$O) (4)



These zerovalent ruthenium complexes are apparently unstable, and they do not tolerate the isolation procedures. It was claimed that an attempt to isolate **2** in pure form under vacuum gave [Ru(CO)(NO)(P^{t}Bu$_2$Me)$_2$][BAr$_4$] via dissociation of the H$_2$O ligand.

We report here the synthesis and characterization of a rare example of a novel, stable, and isolable zerovalent ruthenium aqua complex.

Results and Discussion

Ru(η^6-cot)(dmfm)$_2$ (**3**;[17] cot = 1,3,5-cyclooctatriene, dmfm = dimethyl fumarate) in 1,2-dichloroethane/H$_2$O was treated with dppe at 60 °C. From the reaction solution, a novel ruthenium(0) aqua complex, Ru(dmfm)$_2$(dppe)(H$_2$O) (**4**), was isolated in 55% yield as a pale yellow, relatively air-stable powder (Scheme 1). Simultaneously, two known complexes, **5** and **6**,[18] were also obtained as byproducts. The reaction of **3** with other phosphine ligands such as 1,2-bis(diethylphosphino)ethane, bis(diphenylphosphino)methane, 1,3-bis(diphenylphosphino)propane, 1,4-bis(diphenylphosphino)butane, and triphenylphosphine did not give an analogue of **4**.

As mentioned in the Introduction, there have been only two reports on the synthesis of ruthenium(0) aqua complexes; however, their isolated yields have not been reported. Thus, the complex **4** is the first example of a ruthenium(0) aqua complex suitable for large-scale synthesis and further investigation of the reactivity.

The ^{1}H, ^{13}C, and ^{31}P NMR spectra of **4** at room temperature showed very broad peaks, which suggests that complex **4** is fluxional in solution. At −20 °C, all signals were sharpened, and the results are summarized in Table 1. In the ^{1}H NMR spectrum, the four singlet signals (3.90, 3.38, 3.00, and 2.82 ppm) for the methyl groups of dmfm were observed, showing that neither the mirror plane nor the symmetry axis exists in the complex **4**; in other words, both of the dmfm ligands coordinate with the same enantioface, not with a combination of (*re*, *re*) and (*si*, *si*) faces. In contrast to this result, Sustmann's complex **1**, Ru(MA)$_2$(PPh$_3$)$_2$(H$_2$O), has a mirror plane; two methyl acrylates coordinate to the ruthenium center with a combination of *re* and *si* faces. Although it was revealed that **1** in solution isomerizes into two isomeric complexes in the geometry around ruthenium, the complex **4** was revealed to be a single isomer on the basis of variable-temperature ^{1}H and ^{31}P NMR spectroscopy (−55 to 50 °C).

Table 1. ^{1}H, ^{13}C, and ^{31}P NMR Spectra of 4 (δ)^a

^{1}H		^{13}C	
	Dimethyl Fumarate		
=CH	3.82 (m)	=CH	53.95
	2.74 (d, 10.6)		51.16
	2.41 (dd, 9.6, 4.4)		47.12
	3.21 (d, 9.6)		45.87
Me	3.90 (s)	Me	51.78 (2C)
	3.38 (s)		50.85
	3.00 (s)		50.30
	2.82 (s)	C═O	182.59
			182.43
			176.84
			179.26
		dppe	
Ph	7.93−6.83 (m)	Ph	139.24−127.11
PCH$_2$	3.00 (br)	PCH$_2$	29.20 (dd, 136.8, 87.6)
	2.81 (br)		18.26 (d, 78.8)
	2.30 (br d, 7.6)		
	1.91 (br)		
H$_2$O	4.72 (br s)		

^{31}P	
dppe	73.9 (d, 12.2)
	42.7 (d, 12.2)

^{a} Measured in CDCl$_3$ solution at −20 °C. Legend: s = singlet, d = doublet, m = multiplet, br = broad. Values in parentheses are the coupling constants *J* (Hz).

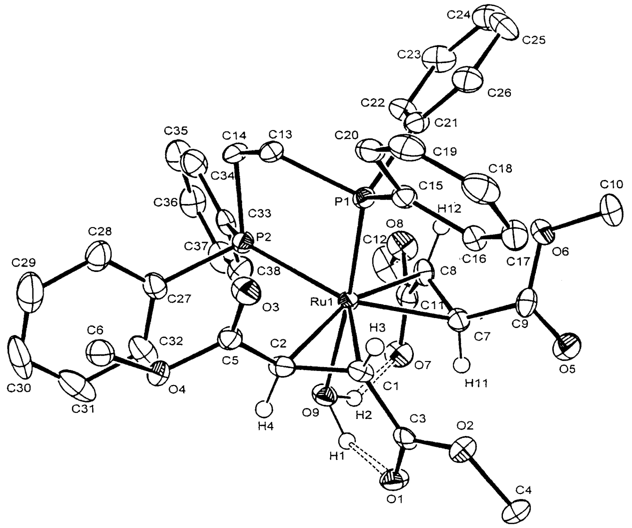


Figure 1. Structure of **4**·C$_6$H$_5$Cl. Some hydrogen atoms and C$_6$H$_5$Cl molecules are omitted for clarity. Ellipsoids are given at the 50% probability level. Selected bond lengths (Å): Ru(1)−P(1) = 2.269(2), Ru(1)−P(2) = 2.389(2), Ru(1)−O(9) = 2.241(5), Ru(1)−C(1) = 2.147(6), Ru(1)−C(2) = 2.177(6), Ru(1)−C(7) = 2.158(6), Ru(1)−C(8) = 2.203(6).

The solid-state structure of **4** was confirmed by X-ray analysis, and the result is shown in Figure 1. Single crystals of **4**·C$_6$H$_5$Cl for X-ray analysis were obtained by recrystallization from C$_6$H$_5$Cl/pentane. The crystal data and the details are given in Table 2. The structure of **4** can be rationalized as a distorted trigonal bipyramid in which one of the phosphorus atoms of dppe and H$_2$O

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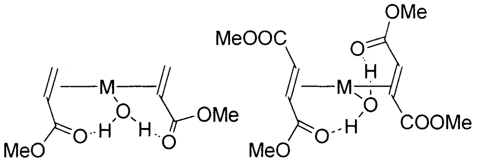
Table 2. Crystal Data of 4·C_6H_5Cl and 7-dppm

	4·C_6H_5Cl	**7-dppm**
empirical formula	$C_{38}H_{42}O_9P_2Ru·C_6H_5Cl$	$C_{39}H_{40}O_4P_2Ru$
fw	918.32	735.76
cryst syst	orthorhombic	monoclinic
space group	$P2_12_12_1$ (No. 19)	$P2_1/n$ (No. 14)
a (Å)	8.9235(1)	11.810(3)
b (Å)	12.7964(3)	15.917(3)
c (Å)	36.6115(7)	18.031(2)
β (deg)	90	99.43(1)
V (Å^3)	4180.6(1)	3343.8(1)
D_{calcd} (g/cm^3)	1.459	1.461
Z	4	4
F_{000}	1896.00	1520.00
μ(Mo Kα) (cm^{-1})	5.71	6.06
T (°C)	−130	23.0
$2\theta_{max}$ (deg)	55.0	55.0
no. of rflns measd	19 557	8353
no. of unique rflns	4947 (R_{int} = 0.056)	7689 (R_{int} = 0.058)
residuals: R; R_w	0.040; 0.051	0.040; 0.041
GOF	1.05	0.60

Chart 1. Partial Structures of 1 and 4



1 **4**

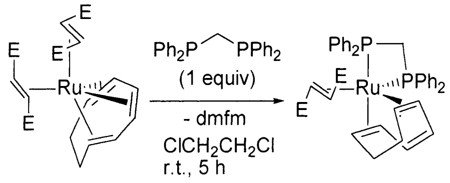
occupy two axial positions and two dimethyl fumarate molecules and the other phosphine moiety of dppe hold equatorial positions. The X-ray analysis reveals that both dmfm ligands coordinate to the ruthenium center with the same enantioface, which coincides with the results of the NMR spectra (vide supra). The structure showed that the water molecule was fixed by two hydrogen bonds to the carbonyl oxygen atoms of each dmfm ligand. In complex **1**, $Ru(MA)_2(PPh_3)_2(H_2O)$, the H_2O molecule is also held by two hydrogen bonds with the carbonyl oxygen atoms of methyl acrylate. However, the orientations of the two hydrogen bonds are somewhat different. In complex **1**, since the two methoxy carbonyl groups are oriented to the same side, the hydrogen bonds are formed with the adjacent carbonyl groups. On the other hand, in complex **4**, hydrogen bonds are formed between distant carbonyl groups (Chart 1). In solution complex **2**, $[Ru(CO)(NO)(P^tBu_2Me)_2(H_2O)][BAr_4]$, is stable, but the H_2O ligand, having no hydrogen bond, is only weakly coordinated. Removal of the solvent in vacuo gives the starting unsaturated ruthenium(0) complex.[11b] Thus, the hydrogen bonds in **4** and the stronger π-acid, dimethyl fumarate, would stabilize the coordination of H_2O to form an isolable zerovalent ruthenium complex.

Preparation of $Ru(dmfm)_2(dppe)(D_2O)$ (**4-*d*₂**) was attempted. Unfortunately, the isolation of pure **4-*d*₂** was unsuccessful. Formation of **4-*d*₂** was confirmed in the reaction of **3** with D_2O and dppe; however, ligand exchange between the coordinated D_2O and the adsorbed H_2O on alumina occurred during the isolation procedure of chromatography on alumina. When 1 drop of D_2O was added to **4** in $CDCl_3$, the intensity of the ^1H NMR signal for H_2O decreased to 1/10, which means that **4-*d*₂** was formed in situ. Another synthesis of **4-*d*₂** was attempted as follows. Complex **4** was treated with D_2O in dichloromethane. After the biphasic solution was stirred for 15 min at room temperature, the solvent and D_2O were evaporated under reduced pressure. These procedures were repeated three times, and then the residue was dissolved in $CDCl_3$ and the ^1H NMR spectrum revealed that up to 69% of the water hydrogens were exchanged with D.

Complex **4** was reacted with another molecule of dppe in 1,2-dichloroethane at 60 °C for 2 h to give **5**. The reaction of **5** with water did not give the aqua complex **4**. While the interconversion from **6** to **4** was not observed, the transformation of **4** into **6** occurred by heating **4** in solution with a drying reagent, molecular sieves 3A (see the Experimental Section).

A plausible mechanism of the formation of complex **4** is as follows (Scheme 2). We already reported that one of the dmfm ligands and one of the olefinic moieties of the cot ligand in **3** are replaced by a bidentate nitrogen ligand in the reaction of complex **3** with 2,2′-bipyridyl or 1,10-phenanthroline.[19] Considering this ligand exchange reaction, intermediate **7** would be formed at an early stage by the reaction of **3** with a bidentate phosphine ligand, dppe. Successive replacement of the coordinated olefin moieties of cot by dmfm and H_2O will lead to the formation of **4** along with the liberation of cot. The formation of **5** would be explained by the ligand exchange of the cot moiety of **7** with dppe. In the case of the formation of **6**, sp^2 C−H bond activation of dmfm and successive insertion of another molecule of dmfm into a Ru−H bond are involved.

An analogue of the intermediate **7**, Ru(1−2-η:5−6-η-1,3,5-cyclooctatriene)(dmfm)(dppm) (**7-dppm**) in eq 3, was obtained by the reaction of **3** with bis(diphenylphosphino)methane (dppm) in 1,2-dichloroethane. Even



(3)

3 **7-dppm** (95%)

in the presence of water as a solvent, the product was not an aqua complex such as $Ru(dmfm)_2(dppm)(H_2O)$ but **7-dppm**. The structure of **7-dppm** was determined by X-ray analysis (Figure 2). The crystal data and experimental details of **7-dppm** are given in Table 2. The complex **7-dppm** seemed to be very stable, and further ligand exchange reactions did not occur.

The reaction of **4** with carbon monoxide (1 atm) gave $Ru(CO)_2(dmfm)(dppe)$ (**8**) via the dissociation of H_2O and one of the dmfm ligands followed by the coordination of two carbon monoxide molecules (Scheme 3). The NMR spectra of **8** in solution show the fluxionality. In the ^{31}P NMR, a slightly broadened singlet signal (57.9 ppm) and a pair of doublet signals (62.9 and 60.0 ppm, J = 18.3 Hz) are observed. This result indicates the presence of two isomeric forms, **8a** and **8b**, which are different in the position of one carbon monoxide and one phosphine moiety. The singlet in the ^{31}P NMR spectrum is consistent with **8a** and the pair of doublets is in accord with **8b**. Helliwell et al. reported that an analogous complex, $Ru(CO)_2(dmfm)(PMe_2Ph)_2$,[20] shows fluxionality in solu-

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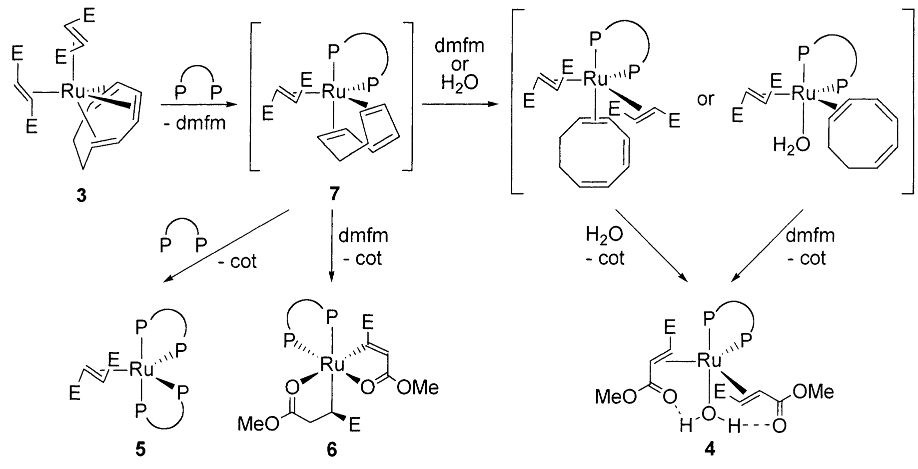
[19] Suzuki, T.; Shiotsuki, M.; Wada, K.; Kondo, T.; Mitsudo, T. *Organometallics* **1999**, *18*, 3671.

Scheme 2. Plausible Mechanism of the Formation of Complexes 4−6



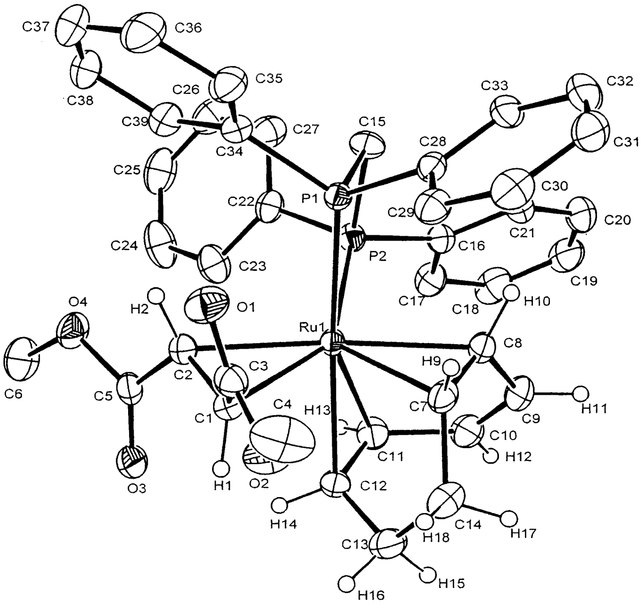
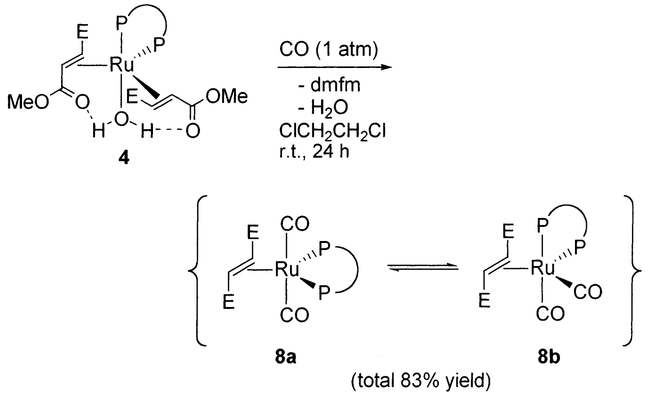


Figure 2. Structure of **7-dppm**. Some hydrogen atoms are omitted for clarity. Ellipsoids are given at the 30% probability level. Selected bond lengths (Å): Ru(1)−P(1) = 2.371(1), Ru(1)−P(2) = 2.364(1), Ru(1)−C(1) = 2.174(4), Ru(1)−C(2) = 2.226(4), Ru(1)−C(7) = 2.162(4), Ru(1)−C(8) = 2.221(4), Ru(1)−C(11) = 2.325(4), Ru(1)−C(12) = 2.293(4).

Scheme 3. Reaction of 4 with Carbon Monoxide



tion on the basis of the Berry pseudorotation[21] and the rotation of the dmfm ligand. At room temperature the ratio of **8a** to **8b** was 1:1.6 on the basis of the ^{1}H NMR spectrum. As the temperature was lowered, the equilibrium inclined to the complex **8b**; actually, at −55 °C the ratio of **8a** to **8b** became 1:2.6.

In conclusion, a novel, stable, and isolable zerovalent ruthenium aqua complex has been synthesized and its reactivity revealed.

Experimental Section

Materials and Methods. All manipulations were performed under an argon atmosphere using standard Schlenk techniques. All solvents were distilled under argon over appropriate drying reagents (sodium, calcium chloride, and calcium hydride). Ru(η^6-cot)(dmfm)$_2$ (**3**) was synthesized as described in the literature.[17] 1,2-Bis(diphenylphosphino)ethane, 1,2-bis(diethylphosphino)ethane, bis(diphenylphosphino)methane, 1,3-bis(diphenylphosphino)propane, 1,4-bis(diphenylphosphino)butane, triphenylphosphine, and carbon monoxide were obtained commercially and used without further purification.

Physical and Analytical Measurements. NMR spectra were recorded on a JEOL EX-400 (FT, 400 MHz (^{1}H), 100 MHz (^{13}C), 162 MHz (^{31}P)) instrument. Chemical shifts (δ) for ^{1}H and ^{13}C are referenced to internal solvent signals and reported relative to $SiMe_4$. Chemical shifts for ^{31}P are referenced to an external $P(OMe)_3$ resonance and reported relative to H_3PO_4. IR spectra were recorded using a Nicolet Impact 410 FT-IR spectrometer. Elemental analyses were performed at the Microanalytical Center of Kyoto University.

Synthesis of Ru(dmfm)$_2$(dppe)(H$_2$O) (4). Ru(η^6-cot)(dmfm)$_2$ (**3**; 1.11 g, 2.24 mmol) in a 1,2-dichloroethane (6 mL)/H_2O (9 mL) solution was stirred at 60 °C for 30 min. Then dppe (894 mg, 2.24 mmol) in 1,2-dichloroethane (9 mL) was added dropwise and the mixture was stirred at 60 °C for 1.5 h. After the solvent and water were evaporated, the orange-yellow solid was dissolved into chloroform and then chromatographed on alumina (Merck No. 1.01097, activity II-III). Elution with chloroform gave a yellow solution, from which the solvent was evaporated. The yellow residue was recrystallized from chloroform/pentane to give **4** as pale yellow microcrystals (988 mg, 1.23 mmol, 55%). Preparation of single crystals of **4**·C_6H_5Cl will be described later.

Complex **4**: pale yellow crystals, mp 127−129 °C dec. Anal. Calcd for $C_{38}H_{42}O_9P_2Ru$: C, 56.64; H, 5.25. Found: C, 56.64; H, 5.24. IR spectrum (KBr disk): 3406, 1707, 1685, 1642 cm^{-1}.

Reaction of 4 with dppe. Complex **4** (50 mg, 0.10 mmol) and dppe (48 mg, 0.12 mmol) were reacted in 1,2-dichloroethane at 60 °C for 2 h. After the solvent was evaporated, the

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(21) Berry, R. S. *J. Chem. Phys.* **1960**, *32*, 933.

^{1}H NMR spectrum of the residue in CDCl$_3$ revealed that 40% of **4** was converted into **5**.

Attempt To Synthesize 4 from 6. Complex **6** and water (excess) were reacted in 1,2-dichloroethane at 60 °C for 2 h. After the solvent and water were evaporated, the ^{1}H NMR spectrum of the residue in CDCl$_3$ revealed the complete recovery of **6**.

Synthesis of 6 from 4. The complex **4** (22 mg, 27 μmol) was heated in 1,2-dichloroethane (3 mL) with molecular sieves 3A (230 mg) at 60 °C for 2 h. After the solvent was evaporated, the ^{1}H NMR spectrum of the residue in CDCl$_3$ was measured. The spectrum revealed the complete transformation of **4** into **6**.

Synthesis of Ru(cot)(dmfm)(dppm) (7-dppm). In a 50 mL Pyrex flask with a stirring bar, **3** (296 mg, 0.60 mmol) and dppm (229 mg, 0.60 mmol) were placed under an argon atmosphere. Then 1,2-dichloroethane (3 mL) was added and the mixture was stirred at room temperature for 5 h. The product was separated by filtration. The yellow residue was recrystallized from dichloromethane/pentane to give **7-dppm** (420 mg, 0.57 mmol, 95%). The ^{13}C NMR spectrum of **7-dppm** could not be measured because of the poor solubility.

Complex **7-dppm**: pale yellow crystals, mp 211−213 °C dec. Anal. Calcd for $C_{39}H_{40}O_4P_2Ru$: C, 63.67; H, 5.48. Found: C, 63.75; H, 5.65. IR spectrum (KBr disk): 1683, 1656, 1465, 1432, 1304, 1157 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.85−6.68 (m, 20H, Ar H), 5.10 (dd, 1H, $J = 3.6$ Hz, $J = 8.0$ Hz, olefin of cot), 4.88 (dt, 1H, $J = 10.4$ Hz, $J = 15.2$ Hz, olefin of cot), 4.48 (m, 1H, olefin of cot), 4.47 (d, 1H, $J = 10.0$ Hz, olefin of cot), 4.22 (dt, 1H, $J = 8.8$ Hz, $J = 7.4$ Hz, olefin of cot), 4.17 (m, 1H, olefin of cot), 4.02 (m, 1H, olefin of dmfm), 3.79 (m, 1H, CH$_2$ of cot), 3.69 (s, 3H, OCH$_3$ of dmfm), 3.54 (s, 3H, OCH$_3$ of dmfm), 3.53 (m, 2H, PCH$_2$), 2.97 (dd, 1H, $J = 6.8$ Hz, $J = 8.8$ Hz, olefin of dmfm), 2.59 (m, 1H, C*H*H of cot), 2.45 (m, 2H, CH$_2$ of cot), 1.85 (br, 1H, CH*H* of cot). ^{31}P NMR (162 MHz, CDCl$_3$, −20 °C): δ −0.90 (d, $J = 48.8$ Hz), −11.1 (d, $J = 48.8$ Hz).

Synthesis of Ru(CO)$_2$(dmfm)(dppe) (8). In a 50 mL Pyrex flask with a stirring bar, **4** (188 mg, 0.23 mmol) was placed under a carbon monoxide atmosphere (1 atm). 1,2-Dichloroethane (5 mL) was added, and the solution was magnetically stirred at room temperature. After 24 h, the solution was chromatographed on alumina. Elution with chloroform gave a pale yellow solution from which the solvent was evaporated to give **8** as pale yellow microcrystals (131 mg, 0.19 mmol, 83%).

Complex **8**: pale yellow crystals, mp 228−230 °C dec. Anal. Calcd for $C_{34}H_{32}O_6P_2Ru$: C, 58.37; H, 4.61. Found: C, 58.27; H, 4.61. IR spectrum (KBr disk): 2013, 1975, 1948, 1677, 1434 1296 cm^{-1}. For the isomer **8a**: ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.91−7.15 (Ar H), 3.67 (s, 2H, $=$CH), 3.63 (s, 6H, 2MeO), 3.09 (dd, 1H, $J = 20.8$ Hz, $J = 9.2$ Hz, PCH*H*), 2.36 (m, 1H, PC*H*H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 198.2 (m, Ru−*C*O), 178.4 (C$=$O), 138.7−125.1(C$_{Ar}$), 50.5 (OMe), 29.2 (m, $=$CH), 28.8 (t, $J = 22.1$ Hz, PCH$_2$); ^{31}P NMR (162 MHz, CDCl$_3$) δ 57.9 (s). For the isomer **8b**: ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.91−7.15 (Ar H), 3.63 (br, 1H, $=$CH), 3.53 (s, 3H, OMe), 3.29 (s, 3H, OMe), 2.76 (m, 1H, PCH*H*), 2.57 (m, 1H, PC*H*H), 2.53 (m, 1H, PCH*H*), 2.37 (br, 1H, $=$CH), 2.10 (m, 1H, PC*H*H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 201.5 (m, Ru−*C*O), 197.1 (m, Ru−*C*O), 179.2 (s, C$=$O), 178.2 (s, C$=$O), 138.7−125.1(C$_{Ar}$), 50.5 (OMe), 50.3 (OMe), 37.8 (s, $=$CH), 34.4 (dd, $J = 32.5$ Hz, $J = 20.0$ Hz, PCH$_2$), 32.2 (d, $J = 16.7$ Hz, $=$CH), 29.6 (dd, $J = 25.8$ Hz, $J = 10.8$ Hz, PCH$_2$); ^{31}P NMR (162 MHz, CDCl$_3$) δ 62.9 (d, $J = 18.3$ Hz), 60.0 (d, $J = 18.3$ Hz).

Crystallographic Study. Single crystals of complexes **4** and **7-dppm** obtained by recrystallization from chlorobenzene/pentane and dichloromethane/pentane, respectively, were subjected to X-ray crystallographic analyses. Measurements were made on a Rigaku RAXIS imaging plate area detector with graphite-monochromated Mo Kα radiation for **4** and a Rigaku AFC7R diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,69$ Å) and a rotating anode generator for **7-dppm**. The structures were solved by direct methods using SIR92[22] for **4** and **7-dppm** expanded using Fourier techniques, DIRDIF99,[23] and were refined anisotropically for non-hydrogen atoms by full-matrix least-squares calculations. Hydrogen atoms except for the H$_2$O ligand and the solvent in **4** and all hydrogen atoms in **7-dppm** were placed at their geometrically calculated positions. The hydrogen atoms of the H$_2$O ligand in **4**, H(1) and H(2), were located from Fourier maps and refined about *xyz* and B_{iso}. On the disordered solvent molecule, chlorobenzene, the hydrogen atoms were not located. The calculations were performed using the programs of Rigaku Corp. and Molecular Structure Corp. Salient crystallographic data are summarized in Table 2. Further details are given in the Supporting Information.

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Supporting Information Available: Text giving a description of the X-ray procedures, tables of X-ray data, positional and thermal parameters, and bond lengths and angles, and ORTEP diagrams for compounds **4** and **7-dppm**. This material is available free of charge via the Internet at http://pubs.acs.org.

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