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Reactions of [(η^6-arene)RuCl$_2$]$_2$ with Aromatic Phosphines Containing Methoxy Groups in 2,6-Positions

Yasuhiro Yamamoto,* Ryoichi Sato, Fumiko Matsuo, Chihiro Sudoh, and Toshiaki Igoshi

Department of Chemistry, Faculty of Science, Toho University, Funabashi, Chiba, 274 Japan

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Reactions of [(η^6-arene)RuCl$_2$]$_2$ **1** (arene = *p*-cymene (**a**), 1,2,3,4-$Me_4C_6H_2$ (**b**), 1,2,3-$Me_3C_6H_2$ (**c**)) with tris(2,6-dimethoxyphenyl)phosphine (TDMPP) led to loss of two molecules of CH_3Cl to give (η^6-arene)Ru[{2-O-C_6H_3-6-OMe}$_2${$C_6H_3(OMe)_2$-2,6}], **2a−c**, which contains a trihapto ligand (η^3-P,O,O) derived from TDMPP, whereas the 1,3,5-$Me_3C_6H_3$ (**1d**), 1,2,3,5-$Me_4C_6H_2$ (**1e**), and C_6Me_6 (**1f**) complexes did not react with TDMPP. The structures of **2a** and **2b** were confirmed by X-ray analyses: for **2a**, $a = 11.691(2)$ Å, $b = 15.228(2)$ Å, $c = 10.320(1)$ Å, $\alpha = 95.93(1)°$, $\beta = 113.783(9)°$, $\gamma = 83.86(1)°$, triclinic, $P\bar{1}$, $Z = 2$, $R = 0.051$; for **2b**, $a = 17.79(2)$ Å, $b = 15.43(1)$ Å, $c = 20.93(1)$ Å, $\beta = 91.25(8)°$, monoclinic, $P2_1/n$, $Z = 8$, $R = 0.056$. Bis(2,6-dimethoxyphenyl)phenylphosphine (BDMPP) reacted with **1a**, **1b**, and **1d** at room temperature to give (η^6-arene)RuCl[PPh(2-O-C_6H_3-6-OMe){$C_6H_3(OMe)_2$-2,6}], **3a**,**b**,**d**, which contains a dihapto (η^2-P,O) ligand derived from BDMPP by an X-ray analysis of **3a**: $a = 12.33(1)$ Å, $b = 14.246(8)$ Å, $c = 11.236(9)$ Å, $\alpha = 91.47(8)°$, $\beta = 117.28(6)°$, $\gamma = 111.70(6)°$, triclinic, $P\bar{1}$, $Z = 2$, $R = 0.040$. A similar reaction with **1f** recovered the starting materials, but that in refluxing MeCN produced [(η^6-C_6Me_6)Ru[PPh(2-O-C_6H_3-6-OMe}$_2$], **4f**, containing a trihapto (η^3-P,O,O) ligand derived from BDMPP. Complex **1d** reacted with BDMPP at reflux in MeCN/CH_2Cl_2 and resulted in a loss of an arene ring to give a five-coordinate complex, Ru[η^2-*P*,*O*-PPh(2-O-C_6H_3-6-OMe){$C_6H_3(OMe)_2$-2,6}]$_2$(MeCN), **5**. Treatment of (2,6-dimethoxyphenyl)diphenylphosphine (MDMPP) with **1f** gave (η^6-C_6Me_6)RuCl[η^2-*P*,*O*-PPh_2(2-O-C_6H_3-6-OMe)], **6f**, and that with **1b** gave (η^6-1,2,3,4-$Me_4C_6H_2$)RuCl[η^2-*P*,*O*-PPh_2(2-O-C_6H_3-6-OMe}], **6b**, and (η^6-1,2,3,4-$Me_4C_6H_2$)RuCl$_2$[η^1-*P*-PPh_2{$C_6H_3(OMe)_2$-2,6}], **7b**. The phosphine ligand of **6b** acted as a bidentate ligand derived from MDMPP: $a = 8.074(4)$ Å, $b = 16.816(3)$ Å, $c = 18.916(4)$ Å, $\beta = 94.05(3)°$, monoclinic, $P2_1/n$, $Z = 4$, $R = 0.051$. Transformation of **7b** to **6b** readily occurred accompanying an elimination of MeCl. Reaction of **1a** with MDMPP eliminated an arene ring to give the octahedral compound RuCl$_2$[η^2-P,OMe-PPh_2{$C_6H_3(MeO)_2$-2,6}]$_2$, **8**. An X-ray analysis of **8** showed that two MDMPP ligands were in a *cis*-position: $a = 10.596(14)$ Å, $b = 27.586(12)$ Å, $c = 13.036(8)$ Å, $\beta = 108.17(7)°$, monoclinic, $P2_1/n$, $Z = 4$, $R = 0.035$.

The ligand tris(2,4,6-trimethoxyphenyl)phosphine (TMPP), which has the combined characteristics of high basicity (p*K*a 11.02), large cone angle (184°), and functionality,[1] shows a wide variety of geometries and hapticities in coordination and organometallic chemistry due to the presence of ortho-methoxy groups. Elimination of a methyl group from a TMPP ligand has been often observed in the reaction with transition metal complexes. The coordination chemistry of the TMPP ligand has been studied in some research groups.[2] The arrangements of the TMPP ligand are influenced by steric and electronic requirements of the metal center. Three coordination modes (a−c) for the neutral ligand and two bonding modes (d and e) for the anionic phenoxide complexes are known: (a) the usual monohapto (η^1-P), (b) dihapto (η^2-P,OMe), (c) trihapto (η^3-P, OMe, OMe), (d) dihapto (η^2-P,O), and (e) trihapto (η^3-P,O,-OMe).[2] However, the trihapto-mode (η^3-P,O,O) is unknown for phosphino−two phenoxide coordination. Coordination chemistry of tris(2,6-dimethoxyphenyl)phosphine (TDMPP), which has lower basicity (p*K*a 9.33) than that of TMPP, has been less studied than that of TMPP.[1e] We have discovered that the reaction of bis[dichloro(η^6-arene)ruthenium (II)] with TDMPP gives the complexes containing the 6th coordination mode (η^3-P,O,O). We report the chemistry of ruthenium complexes with TDMPP ligand and its related phosphines such as bis(2,6-dimethoxyphenyl)phenylphosphine (BDMPP) (p*K*a 7.28)[1e] and (2,6-dimethoxyphenyl)diphenylphosphine (MDMPP) (p*K*a 5.39).[1e] A part of the results has appeared in a communication.[3]

Experimental Section

All reactions were carried out under nitrogen atmosphere. [(η^6-arene)RuCl$_2$]$_2$ (arene = *p*-cymene (**1a**),[4] 1,2,3,4-tetramethylbenzene

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(**1b**),[5] 1,2,3-trimethylbenzene (**1c**),[5] 1,3,5-trimethylbenzene (**1d**),[5] and hexamethylbenzene (**1f**)[6]) were prepared by the literature methods. Tris(2,6-dimethoxyphenyl)phosphine (TDMPP), bis(2,6-dimethoxyphenyl)phenylphosphine (BDMPP) and (2,6-dimethoxyphenyl)diphenylphosphine (MDMPP) were prepared according to the literature.[1a] All solvents were distilled over calcium hydride. The infrared and electronic absorption spectra were measured on FT/IR-5300 and U-best 30 spectrometers, respectively. NMR spectroscopy was carried out on a Bruker AC250. ^1H NMR spectra were measured at 250 MHz using tetramethylsilane as an internal reference, and $^{31}P\{^1H\}$ NMR spectra were measured using 85% H_3PO_4 as an external reference. The FAB mass spectra were measured on a JMS-DX300 spectrometer.

Preparation of [(η^6-1,2,3,5-tetramethylbenzene)$RuCl_2$]$_2$ (1e). This complex was prepared by the modified method of ref 5. [(*p*-cymene)-$RuCl_2$]$_2$, **1a** (2.0 g, 3.3 mmol), was heated at 180 °C in excess 1,2,3,5-tetramethylbenzene (10 mL) for 24 h. The solution was cooled, and a reddish orange solid was collected on a frit and washed with hexane and dried to yield 1.9 g (92%) of **1e**. ^1H NMR ($CDCl_3$): δ 1.98 (s, Me), 2.11 (s, 2Me), 2.13(s, Me), 5.13 (s, 2H) ppm.

Reaction of [(*p*-cymene)$RuCl_2$]$_2$, 1a, with TDMPP. To a solution of [(*p*-cymene)$RuCl_2$]$_2$ **1a** (0.20 g, 0.33 mmol) in CH_2Cl_2 (20 mL) was added TDMPP (0.44 g, 1.0 mmol) at room temperature, and the mixture was stirred for 2 h. The solvent was removed *in vacuo*, and the residue was chromatographed on deactivated alumina (containing 10% H_2O), benzene−CH_2Cl_2 (1:3) being used as an eluant. The solvent was removed and crystallization of the residue from CH_2Cl_2−hexane gave yellow crystals (η^6-*p*-cymene)Ru[P(2-O-C_6H_3-6-OMe)$_2$\{$C_6H_3(OMe)_2$-2,6\}] **2a** (containing a solvated CH_2Cl_2) (0.38 g, 51.9% based on **1a**). IR (Nujol): 1581, 1547 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.89 (d, J_{HH} = 7.0 Hz, CH*Me₂*, 6H), 1.89 (s, C_6*Me*, 3H), 2.41 (sept J_{HH} = 7.0 Hz, C*H*Me_2, 1H), 3.47, 3.51 (s, *Me*O, 6H), 5.27 (s, CH_2Cl_2, 2H) and 5.6−7.5 (m, *Ph*). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 50.2. UV−vis (CH_2Cl_2): λ_{max} 322 sh (log ϵ 3.89), 374 sh (3.15), 445 sh (2.56). Anal. Calcd for $C_{33}H_{37}O_6Cl_2Ru$: C, 54.10; H, 5.15. Found: C, 54.01; H, 5.09.

Similar reactions with the 1,2,3,4-tetramethylbenzene (**1b**) and 1,2,3-trimethylbenzene (**1c**) ruthenium complexes gave the corresponding compounds, (η^6-arene)Ru[P(2-O-C_6H_3-6-OMe)$_2$\{$C_6H_3(OMe)_2$-2,6\}] (**2b**, arene = 1,2,3,4-$Me_4C_6H_2$; **2c**, arene = 1,2,3-$Me_3C_6H_3$). Data for **2b** follow (yellow, 51% based on **1b**). IR (Nujol): 1582, 1549 cm^{-1}. ^1H NMR ($CDCl_3$): δ (ppm) 1.72 (s, C_6Me_2, 6H), 2.26 (d, J_{PH} = 1.5 Hz, C_6Me_2, 6H), 3.46, 3.49 (s, *Me*O, 12H), 4.30 (d, J_{PH} = 3.2 Hz, $C_6Me_4H_2$, 2H) and 5.6−7.6 (m, *Ph*). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ (ppm) 48.3. Anal. Calcd for $C_{32}H_{35}O_6PRu$: C, 59.34; H, 5.45. Found: C, 58.77; H, 5.48. Data for **2c** follow (yellow, 62% based on **1c**). IR (Nujol): 1578, 1549 cm^{-1}. ^1H NMR ($CDCl_3$): δ(ppm) 1.99 (s, 3H, 2−*Me*C_6), 2.04 (s, 6H, 1,3−Me_2C_6), 3.47, 3.49 (s, 12H, *Me*O), 4.47 (t−d, J_{HH} = 5.0 Hz, J_{PH} = 3.2 Hz, 4,6-C_6H_2), 4.59 (d−d, J_{HH} = 5.9 Hz, J_{PH} = 1.5 Hz, 5-C_6H), and 5.6−7.6 (m, P-*Ph*). $^{31}P\{^1H\}$ NMR($CDCl_3$): δ (ppm) 47.8. UV−vis (CH_2Cl_2): λ_{max} 325 nm. Anal. Calcd for $C_{31}H_{33}O_6PRu$: C, 58.76; H, 5.25. Found: C, 58.65; H, 5.29.

Reaction of [(η^6-1,2,3,4-$Me_4C_6H_2$)$RuCl_2$]$_2$, 1b, with BDMPP. To a solution of **1b** (0.15 g, 0.25 mmol) in CH_2Cl_2 (20 mL) was added BDMPP (0.187 g, 0.50 mmol) at room temperature, and the mixture was kept stirring for 3 h. The solvent was removed *in vacuo* and the residue was chromatographed on alumina with CH_2Cl_2. An orange band was collected. The solvent was removed and the residue was crystallized from CH_2Cl_2−diethyl ether to give (η^6-1,2,3,4-$Me_4C_6H_2$)-RuCl[PPh(2-O-C_6H_3-6-OMe)\{$C_6H_3(OMe)_2$-2,6\}], **3b**, as orange crystals (0.207 g, 65% based on **1b**). IR (Nujol): 1581, 1550 cm^{-1}. ^1H NMR ($CDCl_3$, diastereomers A and A′): A, δ (ppm) 1.58, 2.04 (s, C_6Me_2), 2.18, 2.19 (d, J_{PH} = 1.8 Hz, C_6Me_2), 3.27(s, 2*Me*O), 3.38 (s, *Me*O); A′, δ (ppm) 1.68, 1.93 (s, C_6Me_2), 2.11, 2.30 (d, J_{PH} = 2.4 Hz), 3.05 (s, *Me*O), 3.22 (s, 2*Me*O), 3.78 (s, *Me*O); A + A′, δ (ppm) 4.5−8.1 (m, *Ph*). $^{31}P\{^1H\}$ NMR ($CDCl_3$): A, δ (ppm) 39.6; A′, δ (ppm) 36.9. Anal. Calcd for $C_{31}H_{34}O_4PClRu$: C, 58.35; H, 5.37. Found: C, 58.56; H, 5.57.

Similar complexes (**3a** and **3d**) were obtained from reactions with the *p*-cymene (**1a**) and 1,3,5-$Me_3C_6H_3$ complexes (**1d**). Data for **3a** follow (orange, 66% based on **1a**). IR (Nujol): 1584, 1551 cm^{-1}. ^1H NMR ($CDCl_3$, diastereomers A and A′): A, δ (ppm) 1.12, 1.15 (d, J_{HH} = 7.2 Hz, C_6Me_4), 1.94 (s, *Me*), 3.09, 3.27, 3.35 (s, *Me*O); A′, δ (ppm) 1.05, 1.06 (d, J_{HH} = 6.9 Hz, C_6Me_4), 1.97 (s, *Me*), 3.26, 3.32, 3.76 (s, *Me*O); A + A′, δ (ppm) 2.75 (m,C*H*Me_2), 5.27 (s, CH_2Cl_2), 4.6−8.3 (m, *Ph*). $^{31}P\{^1H\}$ NMR($CDCl_3$): δ (ppm) A, 39.00, A′, 31.56; UV−vis (CH_2Cl_2): λ_{max} 291 sh (3.88), 319 sh (3.70), 466 sh (2.52) nm. Anal. Calcd for $C_{32}H_{36}O_4PCl_3Ru$: C, 52.15; H, 5.02. Found: C, 52.20; H, 4.93. Data for **3d**·0.5CH_2Cl_2 follow (orange, 15% based on **1d**). IR (Nujol): 1577, 1547 cm^{-1}. ^1H NMR ($CDCl_3$, diastereomers A and A′): A, δ (ppm) 1.98 (s, C_6Me_3), 3.10, 3.12, 3.34 (s, O*Me*), 4.85 (s, C_6H_3); A′, δ (ppm) 1.88 (s, C_6Me_3), 3.04, 3.16, 3.80 (s, O*Me*), 4.77 (s, C_6H_3); A+A′, δ 5.27 (s, CH_2Cl_2), 5.6−8.0 (m, *Ph*). $^{31}P\{^1H\}$ NMR($CDCl_3$): A, δ (ppm) 48.4; A′, δ 38.7. Anal. Calcd for $C_{30}H_{32}O_4PClRu\cdot 0.5CH_2Cl_2$: C, 55.15; H, 5.13. Found: C, 54.96; H, 4.99.

Reaction of 1b with BDMPP at Reflux. A mixture of **1b** (76.5 mg, 0.125 mmol) and BDMPP (0.10 g, 0.262 mmol) in CH_2Cl_2 (30 mL) was stirred at room temperature for 3 h and was then refluxed for 1.5 h. The solvent was removed *in vacuo* and the residue was extracted with benzene/CH_2Cl_2 (1:1). The solution was chromatographed on alumina, using CH_2Cl_2 as an eluant. The solvent was removed from an orange solution and the residue was recrystallized from benzene/hexane to give **3b** (0.099 g, 62.5% based on **1b**) as orange crystals.

Reaction of [(η^6-C_6Me_6)$RuCl_2$]$_2$, 1f, with BDMPP at Reflux. A mixture of [(η^6-C_6Me_6)$RuCl_2$]$_2$, **1f**, (0.10 g, 0.15 mmol), and BDMPP (228 mg, 0.60 mmol) was refluxed in CH_3CN (15 mL). After 1.5 h, the solvent was removed and the residue was chromatographed on alumina, using CH_2Cl_2 as an eluant. After drying up, crystallization of the residue from CH_2Cl_2−ether gave compound (η^6-C_6Me_6)Ru[PPh-(2-O-C_6H_3-6-OMe)$_2$], **4f** (0.108 g, 59% based on **1f**), as orange crystals. IR (Nujol): 1581, 1550 cm^{-1}. ^1H NMR ($CDCl_3$): δ (ppm) 1.80 (s, C_6Me_6), 3.48 (s, O*Me*), 5.77−7.65 (m, *Ph*). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ (ppm) 58.79. Anal. Calcd for $C_{32}H_{35}O_4PRu$: C, 62.43; H, 5.73. Found: C, 62.51; H, 5.77.

Reaction of [(η^6-1,3,5-$Me_3C_6H_3$)$RuCl_2$]$_2$, 1d, with BDMPP. A mixture of **1d** (0.10 g, 0.17 mmol) and BDMPP (0.20 g, 0.52 mmol) was refluxed in MeCN (20 mL) and CH_2Cl_2 (5 mL). The color of the solution changed from orange to blue. After 1.5 h, the solvent was removed and the residue was chromatographed on alumina, using CH_2Cl_2 as an eluent. Workup of the blue band gave the blue complex Ru[PPh(2-O-C_6H_3-6-OMe)\{C_6H_3-2,6-$(MeO)_2$\}]$_2$(MeCN), **5** (0.053 g, 35.6% based on **1d**) (recrystallized from CH_2Cl_2 and hexane). FAB mass: *m/z* 877 (876.8). IR (Nujol): 2220, 1582, 1555 cm^{-1}. ^1H NMR-($CDCl_3$): δ (ppm) 2.53 (s, *Me*CN, 3H), 3.30 (s, O*Me*, 2Me), 3.37 (s, O*Me*, 4Me), 6.4−7.7 (m, *Ph*). Anal. Calcd for $C_{44}H_{43}NO_8P_2Ru$: C, 60.27; H, 4.94; N, 1.60. Found: C, 60.55; H, 4.76; N, 1.58.

Reaction of 1a with BDMPP at Reflux. A mixture of **1a** (0.050 g, 0.08 mmol) and BDMPP (0.15 g, 0.40 mmol) in MeCN (15 mL) was refluxed for 3 h and the solvent was removed in *vacuo*. The residue was chromatographed on alumina, using CH_2Cl_2 as an eluent. The blue band was collected, and the solvent was removed to ca. 3 mL and hexane added to yield the blue compund **5** (0.073 g, 71% based on **1d**).

Reaction of 1b with MDMPP. To a solution of **1b** (0.10 g, 0.16 mmol) in CH_2Cl_2 (15 mL) was added MDMPP (0.13 g, 0.40 mmol) in CH_2Cl_2 (15 mL) at 0 °C. After 30 min, the solvent was removed and the residue was chromatographed on alumina, using benzene-CH_2Cl_2 (2:1) and CH_2Cl_2 as eluents. Workup of the first orange band and crystallization from CH_2Cl_2−diethyl ether gave (η^6-1,2,3,4-$Me_4C_6H_2$)-RuCl[PPh_2\{2-O-C_6H_3-6-OMe\}], **6b** (14% based on **1b**), as orange crystals. From the second band complex (η^6-1,2,3,4-$Me_4C_6H_2$)$RuCl_2$-[PPh_2\{$C_6H_3(OMe)_2$-2,6\}], **7b** (19% based on **1b**), was isolated as orange crystals. Data for **6b** follow IR (Nujol): 1583, 1539 cm^{-1}. ^1H NMR-($CDCl_3$): δ (ppm) 1.65, 1.98 (s, C_6*Me*), 2.14 (d, J_{PH} = 2.0 Hz, C_6*Me*), 2.19 (d, J_{PH} = 1.5 Hz, C_6*Me*), 3.40 (s, O*Me*), 3.56 (d−d, J_{HH} = 5.0 Hz, J_{PH} = 3.0 Hz, C_6H), 4.74 (d−d, J_{HH} = 5.0 Hz, J_{PH} = 2.7 Hz, C_6H), 5.8−8.0 (m, *Ph*). $^{31}P\{^1H\}$ NMR($CDCl_3$): δ (ppm) 55.4. Anal. Calcd for $C_{29}H_{30}O_2PClRu$: C, 60.25; H, 5.23. Found: C, 59.79; H, 5.22. Data for **7b** follow IR (Nujol): 1577 cm^{-1}. ^1H NMR ($CDCl_3$):

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Table 1. Crystal Data for **2a**, **2b**, **3a**, **6b**, and **8**

	2a	**2b**	**3a**	**6b**	**8**
formula	$C_{33}H_{37}O_6PCl_2Ru$	$C_{32}H_{35}O_6PRu$	$C_{32}H_{36}O_4Cl_3PRu$	$C_{92}H_{30}O_2ClPRu$	$C_{40}H_{38}O_4Cl_2P_2Ru$
mol wt	732.6	647.7	723.0	578.1	816.7
color	orange	reddish orange	reddish orange	orange	red
cryst syst	triclinic	monoclinic	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)
lattice params					
a, Å	11.691(2)	17.79(2)	12.33(1)	8.074(4)	10.596(14)
b, Å	15.228(2)	15.43(1)	14.246(8)	16.816(3)	27.586(12)
c, Å	10.320(1)	20.93(1)	11.236(9)	18.916(4)	13.036(8)
α, deg	95.93(1)	90.0	91.47(8)	90.0	90.0
β, deg	113.783(9)	91.25(8)	117.28(6)	94.05(3)	108.17(7)
γ, deg	83.86(1)	90.0	111.70(6)	90.0	90.0
V, Å^3	1667.8(4)	5748(1)	1584(2)	2562(1)	3621(6)
Z	2	8	2	4	4
D_{calcd}, g/cm^3	1.459	1.506	1.516	1.499	1.498
μ, cm^{-1}	7.09	6.31	8.24	7.90	6.99
no. of unique data	5861(6179)	13607	5619	4681	6540
no. of observns	3453 ($I > 3.0\sigma(I)$)	6835 ($I > 3.0\sigma(I)$)	4517 ($I > 3.0\sigma(I)$)	3223 ($I > 3.0\sigma(I)$)	4534 ($I > 3.0\sigma(I)$)
no. of variables	389	721	406	307	442
$F(000)$	752	2704	740	1184	1672
R; R_w[a]	0.051; 0.039	0.056; 0.069	0.040; 0.047	0.032; 0.040	0.035; 0.047
GOF	1.58	2.56	1.61	1.47	1.47

[a] $R = \sum||F_o| - |F_c||/|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$ $(w = 1/\sigma^2(F_o))$.

δ (ppm) 1.89 (s, C_6Me_2), 2.08 (d, $J_{PH} = 2.3$ Hz, C_6Me_2), 3.29 (s, O*Me*), 4.5−8.0 (m, *Ph*). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ (ppm) 19.7. Anal. Calcd for $C_{30}H_{33}O_2PCl_2Ru{\cdot}0.5CH_2Cl_2$: C, 54.68; H, 4.81. Found: C, 55.11; H, 5.05. Compund **6f** (orange, 61% based on **1f**) was isolated by the reaction of **1f** with MDMPP at room temperature. IR (Nujol): 1583, 1541 cm^{-1}. ^1H NMR ($CDCl_3$): δ (ppm) 1.82 (d, $J_{PH} = 0.5$ Hz, C_6Me_6), 3.35 (s, O*Me*), 5.8−8.0 (m, *Ph*). $^{31}P\{^1H\}$ NMR($CDCl_3$): δ (ppm) 54.4. Anal. Calcd for $C_{31}H_{34}O_2PClRu$: C, 61.43; H, 5.65. Found: C, 61.58; H, 5.57.

Reaction of 1a with MDMPP. To a solution of **1a** (0.15 g, 0.25 mmol) in CH_2Cl_2 (15 mL) was added MDMPP (0.33 g, 0.75 mmol) in CH_2Cl_2 (15 mL) at room temperature. After 5 h, the solvent was removed and the residue was chromatographed on alumina with CH_2Cl_2. Workingup of the orange band and crystallization of the residue from CH_2Cl_2 and diethyl ether gave red crystals $RuCl_2[PPh_2\{C_6H_3\text{-}(OMe)_2\text{-}2,6\}]$, **8** (0.118 g, 55% based on **1a**) (containing $0.5CH_2Cl_2$ of solvation). IR (Nujol): 1583, 1574 cm^{-1}. ^1H NMR($CDCl_3$): δ (ppm) 3.17, 4.53 (s, *Me*O), 5.27 (s, CH_2Cl_2), 6.5−7.5 (m, *Ph*). $^{31}P\{H\}$ NMR ($CDCl_3$): δ (ppm) 61.1; UV−vis (CH_2Cl_2): $\lambda_{\max}$ 279 sh (3.88), 320 (3.43), 516 (2.74) nm. Anal. Calcd for $C_{40.5}H_{39}O_4P_2Cl_3Ru$: C, 56.62; H, 4.58. Found: C, 56.83; H, 4.72.

Data Collection. Complexes **2a**, **2b**, **3a**, **6b**, and **8** were recrystallized from CH_2Cl_2/hexane or CH_2Cl_2/ether. Cell constants were determined on a Rigaku AFC5S four-circle automated diffractometer from the setting angles of 20−25 reflections. The crystal parameters along with data collection details are summarized in Table 1. Data collection was carried out on a Rigaku AFC5S diffractometer. Intensities were measured by the 2θ-ω scan method using Mo Kα radiation ($\lambda = 0.710\,69$ Å). A scan rate of 16° min^{-1} was used. Throughout the data collection the intensities of the three standard reflections were measured every 150 reflections as a check of the stability of the crystals and no decay was observed. A total 5861 independent intensities ($2\theta < 50°$) was measured for **2a**, 13607 ($2\theta < 55°$) for **2b**, 5619 ($2\theta < 50°$) for **3a**, 4681 ($2\theta < 50°$) for **6b** and 6540 ($2\theta < 50°$) for **8.** Of these, there are respectively 3453, 6835, 4517, 3223, and 4534 unique reflections with $I > 3.0\sigma(I)$ which were used in the solutions and refinements of the structures. Intensities were corrected for Lorentz and polarization effects and for absorption. Atomic scattering factors and anomalous dispersion effects were taken from the usual tabulation.[7] All calculations were performed on a Digital VAX Station 3100 M38 computer using the TEXSAN-TEXRAY Program System.

Determination of the Structures. The structures were solved by direct methods with MITHRIL except for **2b** and **8**, which were solved by Patterson methods. The ruthenium atom was located in the initial *E* map, and subsequent Fourier syntheses gave the positions of other non-hydrogen atoms. Hydrogen atoms were calculated at the ideal positions with a C−H distance of 0.95 Å and were not refined. The non-hydrogen atoms were refined with anisotropic thermal parameters by using full-matrix least-squares methods. The final refinement converged to $R = 0.051$ and $R_w = 0.039$ for **2a**, 0.056 and 0.069 for **2b**, 0.041 and 0.040 for **3a**, 0.032 and 0.039 for **6b**, and 0.035 and 0.047 for **8**, respectively. Final difference Fourier syntheses showed peaks at heights up to 0.34−1.89 e A^{-3}. The positional parameters for complexes **2a**, **2b**, **3a**, **6b**, and **8** are listed in the Supporting Information.

Results and Discussion

Overall reactions of bis[dichloro(η^6-arene)ruthenium(II)] with TDMPP, BDMPP, and MDMPP are depicted in Scheme 1.

Reactions with TDMPP. Reaction of bis[dichloro(η^6-arene)-ruthenium(II)], **1** (for arene: *p*-cymene (**a**); 1,2,3,4-$Me_4C_6H_2$ (**b**); 1,2,3-$Me_3C_6H_3$ (**c**)), with TDMPP in CH_2Cl_2 at room temperature gave yellow compound **2**, formulated as (η^6-arene)-$Ru[P(2\text{-}O\text{-}C_6H_3\text{-}6\text{-}OMe)_2\{C_6H_3(OMe)_2\text{-}2,6\}]$. In the ^1H NMR spectra of **2**, the two kinds of *O*-methyl protons appeared at ca. δ 3.50 (s) ppm in a 6:6 intensity ratio. In the ^1H NMR spectrum of **2b**, the methyl protons on the benzene ring appeared at δ 1.72 ppm as a singlet and δ 2.26 ppm as a doublet. The latter signal has a coupling constant of $J_{PH} = 1.6$ Hz. Protons on the benzene ring in the 5- and 6-positions were also observed as a doublet ($J_{PH} = 3.2$ Hz). In the attempts to elucidate the detailed structure, X-ray analyses of **2a** and **2b** were carried out. The molecules consist of a piano stool structure and the Ru atom is coordinated to an arene group, a P atom, and two σ-bonded oxygen atoms (Figures 1 and 2).

The arene complexes **1** (arene = 1,3,5-trimethylbenzene (**1d**), 1,2,3,5-tetramethylbenzene (**1e**), and hexamethylbenzene (**1f**)) did not react with TDMPP and the corresponding starting materials were recovered almost quantitatively. The reactivities of arene complexes for TDMPP do not necessarily depend on the number of the methyl groups on the benzene ring, but appear to depend on the partial crowding in the benzene ring as judged from reactivity difference between 1,2,3,4- and 1,2,3,5-$Me_4C_6H_2$ complexes and between 1,2,3-$Me_3C_6H_2$ and 1,3,5-$Me_3C_6H_2$ complexes. Some attempts to isolate O-coordination products of the MeO groups assumed as intermediates were unsuccessful, and the only isolated complex was **2**. In an attempt to

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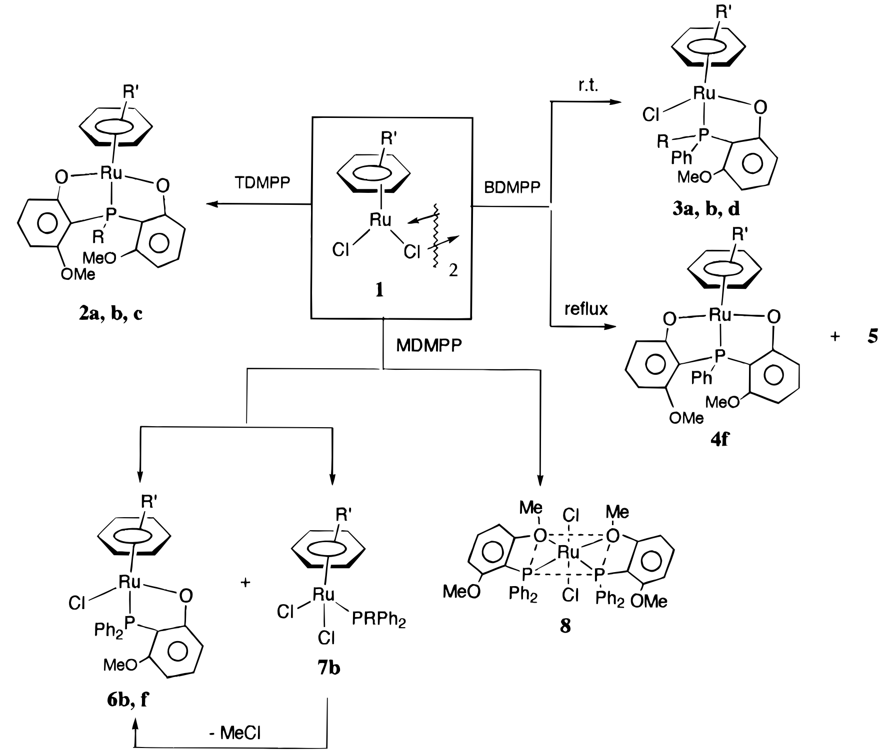
(7) Cromer, D. T.; Waber, J. T. International Tables for X-ray Crystallography; Kynoch Press: Birmingham, England, 1974; Vol. IV.

Scheme 1. Reactions of Bis[dichloro(η^6-arene)ruthenium(II)] with Aromatic Phosphines Containing Methoxy Groups in 2,4-Positions



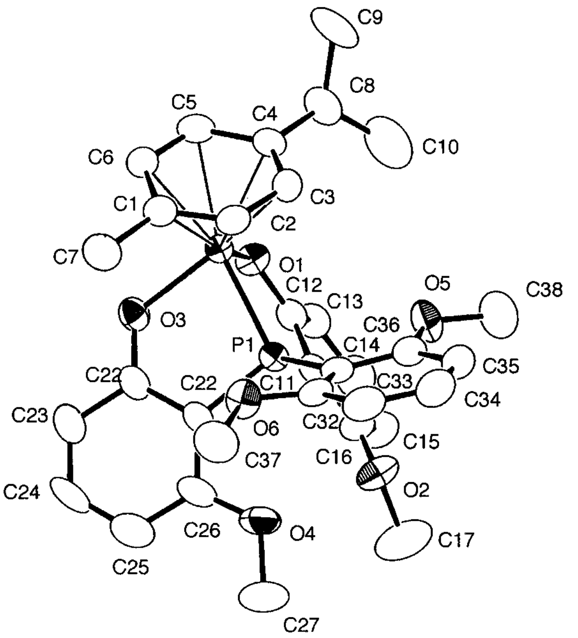


Figure 1. Molecular structure of [(η^6-*p*-cymene)Ru[P(2-O-C_6H_3-6-$OMe)_2\{C_6H_3(OMe)_2$-2,6}] (**2a**).

investigate the fate of methyl and chlorine groups, the ^{1}H NMR spectra of a reaction mixture of **1a** and TDMPP were measured and showed a doublet at δ 1.18 ppm assigned to the formation of a phosphonium ion [P{2,6-$(MeO)_2$ $C_6H_3\}_3$(Me)]Cl.

Reactions with BDMPP. Complex **1a** reacted with BDMPP to give an orange compound **3a**, (η^6-*p*-cymene)RuCl[PPh(2-O-C_6H_3-6-OMe){$C_6H_3(OMe)_2$-2,6}]. The structure was confirmed by an X-ray analysis (Figure 3). The phosphine ligand is bidentate, binding through the P and an σ-bonded O atom. The molecule has two chiral centers (Ru and P atoms). A priority order of the ligands is aromatic ring > Cl > P > O for a metal

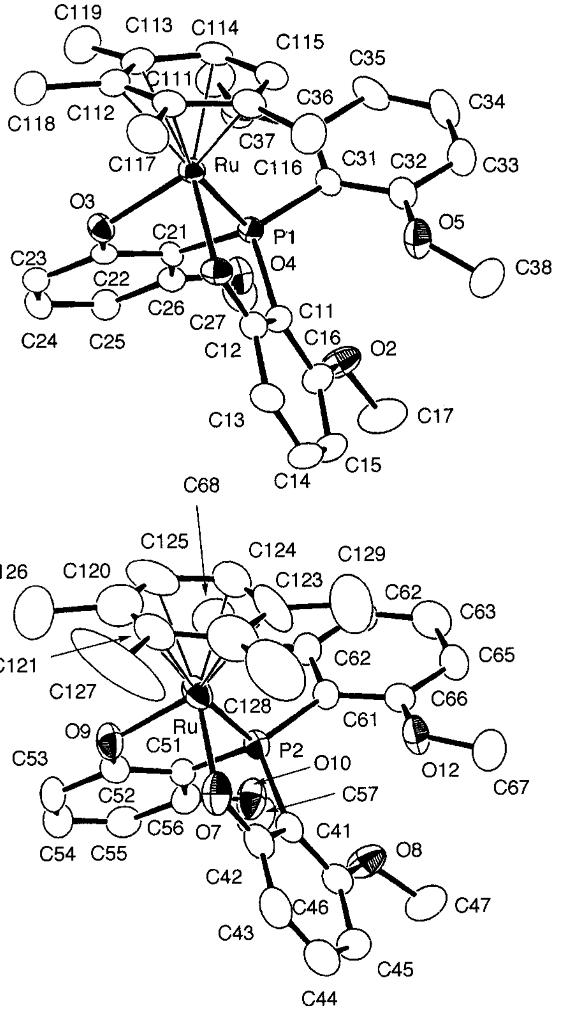


Figure 2. Molecular structures of [(η^6-1,2,3,4-$Me_4C_6H_2$)Ru[P(2-O-C_6H_3-6-$OMe)_2\{C_6H_3(OMe)_2$-2,6}] (**2bA** (top) and **2bB** (bottom)).

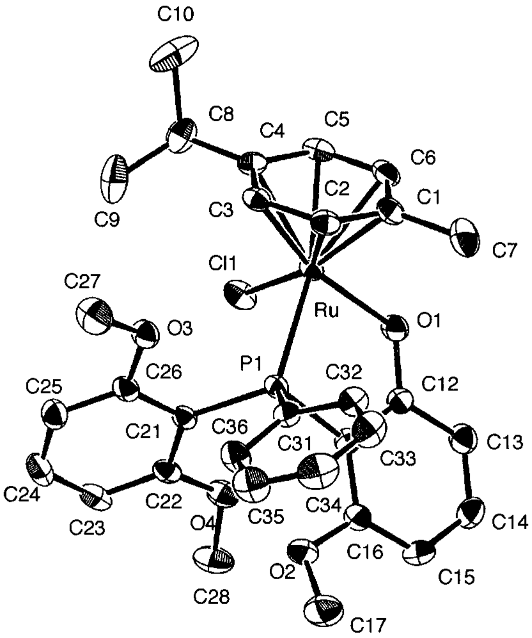
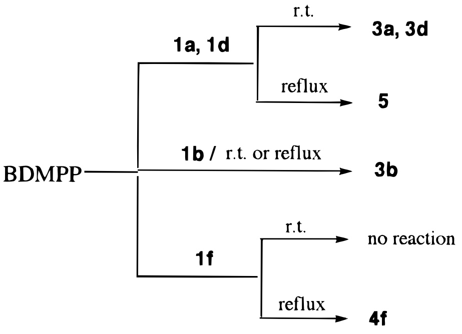


Figure 3. Molecular structure of $[(\eta^6\text{-}p\text{-cymene})Ru[PPh(2\text{-O-}C_6H_3\text{-}6\text{-OMe})\{C_6H_3(OMe)_2\text{-}2,6\}]$ (**3a**).

Scheme 2. Reactions of the (Arene)ruthenium Complexes with BDMPP



center and Ru > 2-O-6-$MeOC_6H_3$ > 2,6-$(MeO)_2C_6H_3$ > Ph for a P center.[8]

Figure 3 showed that the molecule is a Ru_RP_R/Ru_SP_S pair. The $^{31}P\{^1H\}$ NMR spectrum of the crystallized complex showed two peaks at δ 39.00 and 31.56 ppm in ca. 1:1.2 intensity ratio, suggesting the existence of two pairs of complexes (Ru_RP_R/Ru_SP_S and Ru_RP_S/Ru_SP_R) in solution. The ^1H NMR spectrum also supported the presence of the diastereomers (A and A′).[9] The methyl protons of the isopropyl and methoxy groups showed the existence of two kinds of isomers and each of them is in different environments; the former appeared at δ 1.05 (3H) and 1.06 (3H) ppm as a doublet for A and at δ 1.13 (6H) ppm as a doublet for A′, and the latter appeared at δ 3.26, 3.32, and 3.37 for A and at δ 3.09, 3.27, and 3.35 for A′.

Complex $(\eta^6\text{-}1,2,3,4\text{-}Me_4C_6H_2)RuCl[PPh(2\text{-O-}C_6H_3\text{-}6\text{-OMe})\{C_6H_3(OMe)_2\text{-}2,6\}]$, **3b**, with two chiral centers was obtained by the reaction of the 1,2,3,4-$Me_4C_6H_2$ complex, **1b**, with BDMPP at room temperature. The first crystallization from CH_2Cl_2−hexane gave two diastereomers (A:A′) in a 1:2 ratio, and the second crop from the mother liquor gave two diastereomers (A:A′) in a 2:1 ratio. When the 1,3,5-$Me_3C_6H_3$ complex **1d** was treated with BDMPP at room temperature, the reaction readily occurred, in contrast to the case of TDMPP, and the complex $(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)RuCl[PPh(2\text{-O-}C_6H_3\text{-}6\text{-OMe})\{C_6H_3(OMe)_2\text{-}2,6\}]$ **3d** was obtained. Reaction with the hexamethylbenzene complex **1f** was also carried out at room temperature and the starting materials were recovered almost quantitatively, whereas the reaction in MeCN at 80 °C for 1.5 h led to an elimination of two molecules of CH_3Cl to give $(\eta^6\text{-}C_6Me_6)Ru[PPh(2\text{-O-}C_6H_3\text{-}6\text{-OMe})_2]$, **4f**, having a trihapto (η^3-P,O,O) coordination mode without producing a dihapto (η^2-P,O) type of complex. A similar thermal reaction between BDMPP and **1b** containing a smaller tetrasubstituted arene ring was carried out to give only **3b**. These results showed that a bulky arene ring accelerated the interaction between ruthenium metal and oxygen atoms. The reactivity differences suggest a relationship with steric bulk of incoming phosphine ligands and arene rings. A similar behavior was also observed in the reaction with MDMPP (*vide infra*). When complex **1d** was refluxed with BDMPP in $MeCN/CH_2Cl_2$ for 1.5 h, the solution color changed from orange to blue, and a blue compound **5**, formulated as $Ru[PPh(2\text{-O-}C_6H_3\text{-}6\text{-OMe})\{C_6H_3(OMe)_2\text{-}2,6\}]_2(MeCN)$ on the basis of a mass spectrum and an elemental analysis, was isolated. The presence of nitrile was confirmed by the presence of a ν(C≡N) band in the infrared spectrum (2220 cm^{-1}). The ^1H NMR spectrum showed three resonances in the methyl region at δ 2.53, 3.30, and 3.37 ppm in an intensity ratio of 3:6:12; the first band is assigned to acetonitrile and the other two bands to OMe groups. It is known that the five-coordinate ruthenium complexes can be either trigonal bipyramidal or square pyramidal.[10] On the basis of spectral results, two possible structures for each geometry (A, B, C, and D) can be considered (Figure 4). An X-ray analysis clarifies its structure, but as no crystals suitable for X-ray analysis have been obtained, the precise stereochemistry remains unknown.

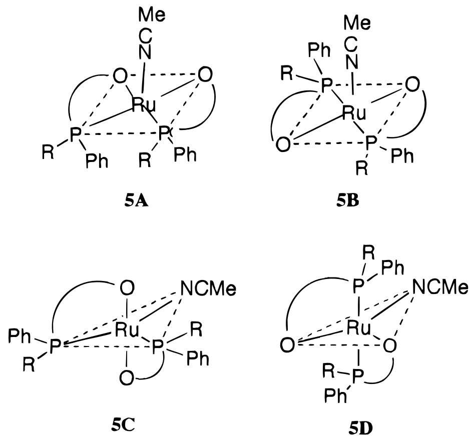


Figure 4. Possible structures of $[Ru(MeCN)\{PPh(2\text{-O-}C_6H_3\text{-}6\text{-OMe})(C_6H_3(OMe)_2\text{-}2,6\}_2]$ (**5**).

In the FAB mass spectrum of **5** the parent and base peaks appeared at *m/z* 877 (876.8) and 836 (835.8) and an easy loss of acetonitrile occurred to give a $[M - MeCN]^+$ species, from which a one-step loss of two molecules each of phenyl and 2,6-dimethoxyphenyl groups, $2[Ph\{(2,6\text{-}MeO)_2C_6H_3\}]$, was observed, suggesting high stability of the η^2-P,O chelate ring.

The same complex **5** was also obtained by refluxing a mixture of **1a** and BDMPP in MeCN. These results showed that η^6-arene rings such as *p*-cymene and 1,3,5-$Me_3C_6H_3$ are more labile than electron-rich arenes such as C_6Me_6 and 1,2,3,4-$Me_4C_6H_2$. Compound **5** is likely formed *via* **3**.

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[8] Stanley, K.; Baird, M. C. *J. Am. Chem. Soc.* **1975**, *97*, 6599.

[9] From the $^{31}P\{^1H\}$ NMR spectrum the diastereomers were tentatively assigned as A for the complex for which the chemical shift appeared in lower magnetic fields and as A′ for the other one.

[10] Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 3rd ed.; Interscience Pub.: New York, 1972, p 1001.

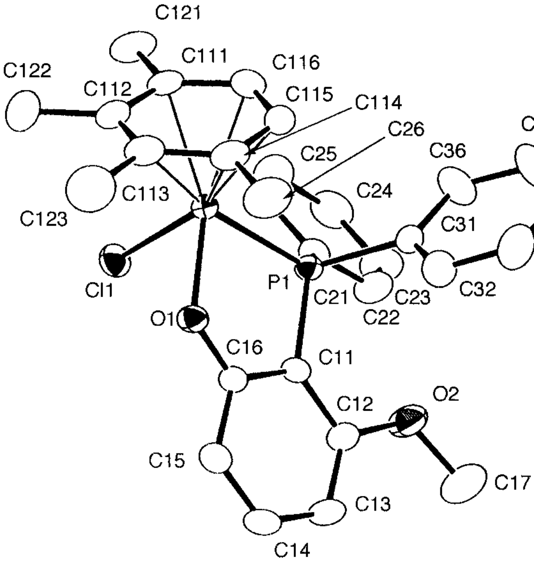
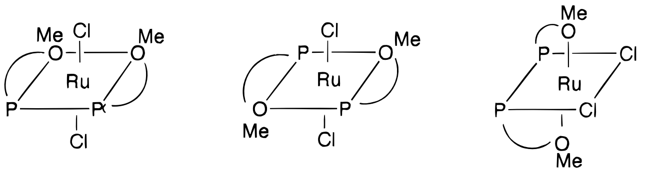


Figure 5. Molecular structure of $[(\eta^6\text{-}1,2,3,4\text{-}Me_4C_6H_2)Ru[PPh_2(2\text{-}O\text{-}C_6H_3\text{-}6\text{-}OMe)]$ (**6b**).

Reactions with MDMPP. Reaction of the hexamethylbenzene complex **1f** with MDMPP readily occurred at room temperature to give $(\eta^6\text{-}C_6Me_6)RuCl[PPh_2\{2\text{-}O\text{-}C_6H_3\text{-}6\text{-}OMe\}]$ **6f**. Refluxing of **6f** in MeCN led to recovery of the starting material with no further elimination of a CH_3Cl molecule. The ^1H NMR spectrum of **6f** showed two singlets at δ 1.86(d) and 3.39(s) ppm in a 6:1 intensity ratio assignable to methyl and methoxy groups, respectively. The $^{31}P\{^1H\}$ NMR spectrum showed a singlet at δ 54.5 ppm. The spectroscopic results showed that the MDMPP ligand acted as a bidentate ligand. When the reaction of the $1,2,3,4\text{-}Me_4C_6H_2$ complex **1b** with MDMPP was carried out at room temperature for a long time, only $(\eta^6\text{-}1,2,3,4\text{-}Me_4C_6H_2)RuCl[PPh_2\{2\text{-}O\text{-}C_6H_3\text{-}6\text{-}OMe\}]$, **6b**, was isolated, whereas the reaction at 0 °C gave compound **7b** $(\eta^6\text{-}1,2,3,4\text{-}Me_4C_6H_2)RuCl_2[PPh_2\{C_6H_3(OMe)_2\text{-}2,6\}]$ together with **6b**. The ^1H NMR spectrum of **6b** showed five resonances in equal intensity at δ 1.65 (s), 1.98 (s), 2.14 (d), 2.19 (d), and 3.40 (s) ppm for methyl protons; the last one is assigned to the OMe groups and other resonances to the methyl groups on the benzene ring. Appearance of four resonances due to the methyl groups on the benzene is due to the chiral center at the Ru atom. These NMR spectra were in good agreement with the crystal structure of **6b** (Figure 5).

The IR spectrum of **7b** showed only one peak at 1500−1600 cm^{-1}, suggesting the absence of di- and trihapto coordinations because two strong peaks are observed in the range from 1500 to 1600 cm^{-1} for the di- and trihapto complexes. The ^1H NMR spectrum showed three resonances at δ 1.89 (s), 2.08 (d), and 3.29 (s) ppm in a 6:6:6 intensity ratio for methyl groups; the last one is assigned to the OMe groups and the others to 1,4- or 2,3-methyl groups. Compound **7b** was dissolved in $CDCl_3$ and its ^1H NMR spectra were measured with time. The peaks for **7b** decreased and the peaks for **6b** increased. The spectral change showed the conversion of **7b** to **6b**, in which an elimination of CH_3Cl was confirmed by the growth of a new peak at δ 3.05 ppm. A similar spectral change was also observed in $^{31}P\{^1H\}$ NMR spectra; decrease of the peak at δ 19.7 ppm for **7b** was followed by an increase of the resonance at δ 55.4 ppm for **6b**.

When **1a** was treated with MDMPP at room temperature, the arene ring was eliminated to give $RuCl_2[PPh_2\{C_6H_3(MeO)_2\text{-}2,6\}]_2$, **8**, in a moderate yield. In the ^1H NMR spectrum two peaks due to the OMe groups appeared at δ 3.17 and 4.53 ppm. The chemical shift of the P atoms appeared at δ 61.1 ppm. These



A (cct) **B** (ttt) **C** (ctc)

Figure 6. Possible structures of $RuCl_2[PPh_2\{C_6H_3(OMe)_2\text{-}2,6\}]_2$ (**8**).

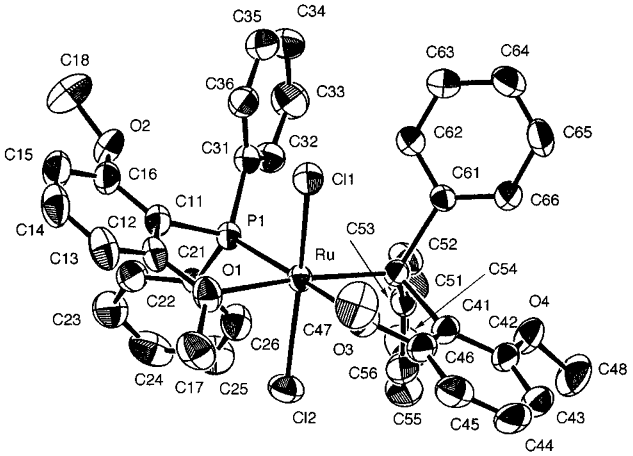


Figure 7. Molecular structure of *cct*-$RuCl_2[PPh_2\{C_6H_3(OMe)_2\text{-}2,6\}]_2$ (η^2-P, OMe) (**8**).

spectral data suggested three possible structures (A, B, C) (Figure 6). In an attempt to determine the detailed structure, an X-ray analysis was carried out. The molecule has an octahedral configuration with a *cis,cis,trans*-form (*cct*-form) (A) (Figure 7). The *cis*-configuration of the RuP_2O_2 plane has also been observed for the octahedral $[Pd\{P(C_6H_2(OMe)_3\text{-}2,4,6)_3\}_2]^{2+}$ complex **9** (η^3-P, OMe, OMe) with two strong Pd−O coordination bonds (average 2.186(7) Å) and two weak Pd···O interactions (average 2.652(7) Å).[11] On the basis of the spectral data of compounds (**2**, **3**, **4**, and **6b**), the peak at δ 3.17 ppm is assigned to free OMe groups and that at δ 4.53 ppm to coordinated OMe groups.

Crystal Structures of 2a, 2b, 3a, 6b, and 8. Molecules **2a**, **2b**, **3a**, and **6b** have the piano stool structures. The ligand derived from TDMPP acts as a trihapto-ligand and the ruthenium atom is coordinated by P and two σ-O atoms together with an arene group. This coordination mode is the first example in metal complexes of aromatic phosphines having 2,6-disubstituted methoxy groups. Selected bond distances and angles are summarized in Tables 2−5. Complex **2b** consists of two independent molecules (**2bA** and **2bB**). The average lengths of the Ru−O bonds are 2.062 Å for **2bA** and 2.050 Å for **2bB** and are in good agreement with the usual metal−σ-oxygen bond distances. This difference of bond lengths (ca 0.01 Å) is traced back to that of the Ru−P bond lengths, where the bond length (2.272(3) Å) in **2bA** is shorter than that (2.282(3) Å) in **2bB**. The Ru−O and Ru−P bond lengths of **2a** are not significantly different from those of **2b**. The P−Ru−O bite angles of **2** are in the range from 80 to 83° and are smaller than those (86−87°) of the O−Ru−O bond angles, due to a chelating effect.

In molecules of **3a** and **6b** the phosphine ligand acts as a bidentate ligand with a (η^2-P,O) coordination. The ruthenium atom is coordinated by P, σ-O, and Cl atoms along with an arene group. The average length of the Ru−P bond for **3a** and **6b** is 2.328 Å and is slightly longer than that for **2** (2.277 Å), whereas the average Ru−O bond lengths are not significantly

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(11) Dunbar, K. R.; Sun, J.-S. *J. Chem. Soc., Chem. Commun.* **1994**, 2387.

Table 2. Selected Bond Distances and Angles for **2a**

Bond Distances (Å)			
Ru1−O1	2.060(5)	Ru1−O3	2.065(5)
Ru1−P1	2.276(2)	Ru1−C1	2.169(7)
Ru1−C2	2.146(7)	Ru1−C3	2.179(7)
Ru1−C4	2.202(7)	Ru1−C5	2.280(7)
Ru1−C6	2.248(8)	O1−C12	1.328(8)
O2−C16	1.361(9)	O3−C22	1.321(8)
O4−C26	1.350(9)	O5−C36	1.361(9)
O6−C32	1.365(8)		
Bond Angles (deg)			
P1−Ru1−O1	82.2(1)	P1−Ru1−O3	80.6(2)
O1−Ru1−O3	86.6(2)	Ru1−P1−C11	102.2(2)
Ru1−P1−C21	102.0(3)	Ru1−O1−C12	120.5(4)
Ru1−O3−C22	120.4(4)	P1−C11−C12	111.9(6)
O1−C12−C11	122.6(7)	P1−C21−C22	111.0(6)
O3−C22−C21	121.6(7)		

Table 3. Selected Bond Lengths and Angles for **2b**

Bond Distances (Å)

2bA		**2bB**	
Ru1−O1	2.061(5)	Ru2−O7	2.052(6)
Ru1−O3	2.063(5)	Ru2−O8	2.047(5)
Ru1−P1	2.272(3)	Ru2−P2	2.282(3)
Ru1−C110	2.174(7)	Ru2−C120	2.24(1)
Ru1−C111	2.264(7)	Ru2−C121	2.242(8)
Ru1−C112	2.269(8)	Ru2−C122	2.159(9)
Ru1−C113	2.152(8)	Ru1−C123	2.170(8)
Ru1−C114	2.157(7)	Ru1−C124	2.169(9)
Ru1−C115	2.282(3)	Ru1−C125	2.26(1)
O1−C12	1.308(8)	O7−C42	1.326(9)
O2−C16	1.357(8)	O8−C46	1.359(8)
O3−C22	1.314(8)	O9−C52	1.320(8)
O4−C26	1.368(8)	O10−C56	1.361(8)
O5−C32	1.366(9)	O11−C62	1.356(8)
O6−C36	1.348(1)	O12−C66	1.333(8)

Bond Angles (deg)

2bA		**2bB**	
O1−Ru1−O3	87.1(2)	O7−Ru2−O9	86.4(2)
O1−Ru1−P1	82.9(2)	O8−Ru2−P2	81.3(2)
O3−Ru1−P1	80.1(2)	O9−Ru2−P2	81.8(2)
Ru1−P1−C11	101.4(2)	Ru2−P2−C41	102.0(2)
Ru1−P1−C21	101.6(2)	Ru2−P2−C51	100.6(2)
Ru1−P1−C31	119.5(2)	Ru2−P2−C61	121.2(2)
Ru1−O1−C12	119.8(4)	Ru2−O7−C42	121.2(4)
Ru1−O3−C22	120.7(4)	Ru2−O9−C52	121.2(4)
P1−C11−C12	112.5(5)	P2−C41−C42	112.5(5)
O1−C12−C11	123.3(6)	O7−C42−C41	121.6(7)
P1−C21−C22	111.0(5)	P2−C51−C52	113.5(5)
O3−C22−C21	121.8(6)	O9−C52−C51	120.9(7)

Table 4. Selected Bond Lengths and Angles for **3a**

Bond Distances (Å)			
Ru1−Cl1	2.401(4)	Ru1−P1	2.342(3)
Ru1−O1	2.069(6)	Ru1−C1	2.193(9)
Ru1−C2	2.159(8)	Ru1−C3	2.194(8)
Ru1−C4	2.228(8)	Ru1−C5	2.238(8)
Ru1−C6	2.217(8)	O1−C12	1.33(1)
O2−C16	1.37(1)	O3−C26	1.37(1)
O4−C22	1.36(1)		
Bond Angles (deg)			
Cl1−Ru1−P1	85.8(1)	Cl1−Ru1−O1	86.6(2)
P1−Ru1−O1	82.2(2)	Ru1−P1−C11	99.9(3)
Ru1−P1−C21	117.8(3)	Ru1−P1−C31	121.1(3)
Ru1−O1− C12	121.0(5)	P1−C11−C12	114.8(6)
O1−C12−C11	121.9(7)		

Table 5. Selected Bond Lengths and Angles for **6b**

Bond Distances (Å)			
Ru1−Cl1	2.408(2)	Ru1−P1	2.313(1)
Ru1−O1	2.059(3)	Ru1−C111	2.206(4)
Ru1−C112	2.265(5)	Ru1−C113	2.259(5)
Ru1−C114	2.190(5)	Ru1−C115	2.178(5)
Ru1−C116	2.186(5)	O1−C16	1.315(5)
O2−C12	1.374(6)		
Bond Angles (deg)			
Cl1−Ru1−P1	88.17(5)	Cl1−Ru1−O1	82.95(9)
P1−Ru1−O1	82.50(9)	Ru1−P1−C11	100.6(1)
Ru1−P1−C21	117.4(2)	Ru1−P1−C31	116.3(1)
Ru1−O1−C16	120.1(3)	P1−C11−C12	127.8(3)
O1−C16−C11	123.0(4)		

Table 6. Selected Bond Lengths and Angles for **8**

Bond Distances (Å)			
Ru1−Cl1	2.404(4)	Ru1−Cl2	2.384(3)
Ru1−P1	2.227(2)	Ru1−P3	2.231(2)
Ru1−O1	2.243(3)	Ru1−O3	2.240(3)
Bond Angles (deg)			
Cl1−Ru1−Cl2	167.13(5)	Cl1−Ru1−P1	90.69(7)
Cl1−Ru1−P3	96.50(8)	Cl1−Ru1−O1	86.3(1)
Cl1−Ru1−O3	86.4(1)	Cl2−Ru1−P1	96.78(7)
Cl2−Ru1−P3	91.47(8)	Cl2−Ru1−O1	84.7(1)
Cl2−Ru1−O3	85.1(1)	P1−Ru1−P3	106.27(6)
P1−Ru1−O1	79.8(1)	P1−Ru1−O3	173.69(9)
P3−Ru1−O1	173.26(9)	P3−Ru1−O3	79.7(1)
O1−Ru1−O3	94.5(1)		

different. The O−Ru−Cl and P−Ru−Cl angles of **3a** are 86.6(2) and 85.8(1)°, and those of **6b** are 82.95(9) and 88.17(5)°, respectively, minimizing repulsive interaction of P-substituents. The P−Ru−O bite angles of **3a** and **6b** are 82.2(2) and 82.50(9)°, respectively, analogous to those of **2**.

In nickel complexes containing diphosphine ligands with methylene and its related linkages, the P−Ni−P angle of five-membered ring formed by the chelating ligand is 85°.[12] The P−Ru−O angles are smaller by ca. 3° than the P−Ni−P angles. The bite angle difference between nickel and ruthenium complexes depends on covalent radii between oxygen and phosphine atoms rather than on the ionic radii of metals. The torsion angles of Cl1−Ru1−P1−C31 and Cl1−Ru1−P1−C21 bonds are −164.4(3) and −36.1(3)°, respectively. These angles showed that the 2,6-(MeO)$_2$C$_6$H$_3$ group is located toward the Cl side to minimize the repulsive interaction.

Compound **8** is octahedral, and an equatorial plane is occupied with two P and two O atoms. Two Cl atoms are located in the axial positions. The average Ru−O coordination bond distance is 2.242 Å, longer by ca. 0.18 Å than that of the Ru−O σ-bond (Table 6). The average Ru−P bond length is 2.276 Å, comparable with those of the trihapto complexes **2** and slightly shorter than that of the dihapto complexes. This is responsible for difference of coordination modes. The Cl−Ru−Cl angle is 167.13(5)° with bending toward the O-coordination, minimizing steric interaction between Cl atoms and *P*-phenyl groups. The P−M−P and P−M−O angles are not significantly different bettween **8** and **9**, where the P−M−P angle is 106.27(6)° for **8** (M = Ru) and 105.92(8)° for **9** (M = Pd), and the average P−M−O angle is 79.8° for **8** and 78.2° for **9**, whereas the O−M−O bond angle in the equatorial plane is 94.5(1)° for **8** and 99.6(2)° for **9**. This difference of the bond angles would be the result of different coordination modes (η^2- and η^3-coordination).

Possible Pathway. The possible reaction pathway is depicted in Scheme 3. The initial reaction is cleavage of Cl-bridges to

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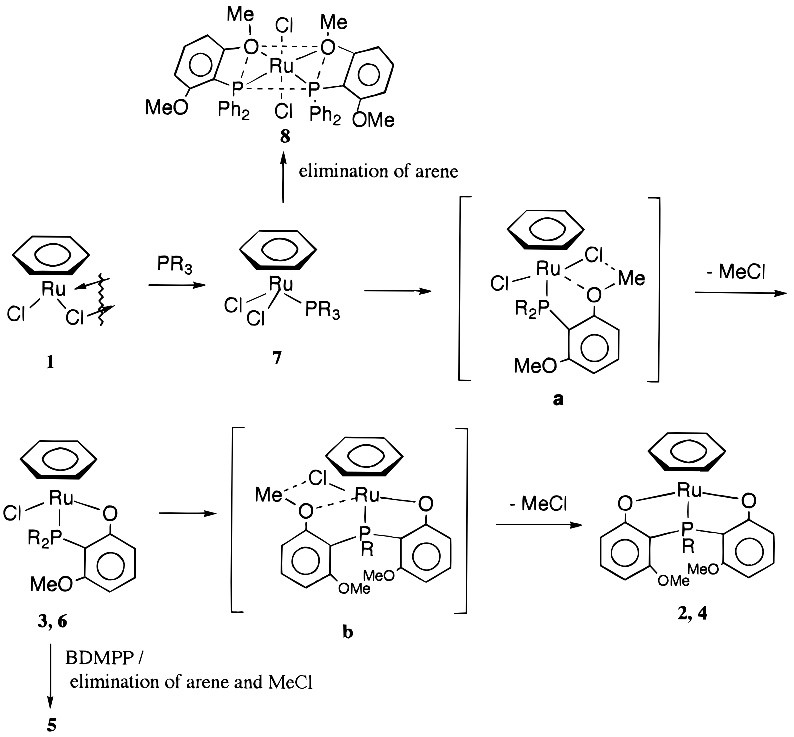
(12) Hohman, W. H.; Kountz, D. J.; Meek, D. W. *Inorg. Chem.* **1986**, *25*, 616. DiVaira, M. *J. Chem. Soc., Dalton Trans.* **1975**, 2360. Laneman, S. A.; Stanley, G. G. *Inorg. Chem.* **1987**, 26, 1177. Orlandini, A.; Sacconi, L. *Inorg. Chem.* **1976**, *15*, 78. Miedaner, A.; Haltiwanger, R. C.; DuBois, D. L. *Inorg. Chem.*, **1991**, *30*, 417.

Scheme 3. Possible Reaction Path (an Arene Group Is Shown as a Benzene Ring for Clarity)



form (η^6-arene)RuCl$_2$(PR$_3$). This type of reaction is well-known, and complex **7b** was isolated. The second process is a nucleophilic attack of oxygen on the methoxy group to the ruthenium metal, followed by an elimination of MeCl *via* a four-centered intermediate or transition state (**a**). Conversion of **7** to **3** or **6** has also been confirmed by isolation of **6b** and by NMR spectroscopy. The driving force of these reactions could be a close contact between Ru and O atoms because of the bulky phosphine. In an attempt to investigate this contact, Chem3D calculations of (η^6-*p*-cymene)RuCl[PPh(2-O-C$_6$H$_3$-6-OMe)-{C$_6$H$_3$(MeO)$_2$-2,6}], **3a**, were carried out.[13]

The closest Ru···O distance was estimated as 2.730 Å, falling in the sum of the covalent radii of ruthenium and oxygen atoms. If bulkier TDMPP instead of BDMPP was used and a dihapto intermediate derived from TDMPP was formed, the Ru···O distance would be shorter. Finally the reaction terminated by leading to formation of a trihapto-complex *via* an intermediate or transition state (**b**). Bulky arene ring also assisted formation of a four-centered intermediate. Compound **8** was formed *via* an elimination of an arene ring from **7**. The five-coordinate complex **5** was obtained through loss of both arene and MeCl groups by a further reaction of **3** with BDMPP.

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Supporting Information Available: Anisotropic thermal parameters, atomic parameters, and bond lengths and angles (68 pages). Ordering information is given on any current masthead page.

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[13] CSC Chem3D Plus Ver. 3.1.2, Cambridge Scientific Computing Inc. In the Chem3D calculations the distances and angles were set to the values which were measured by the X-ray analysis of **3a**.