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Reactions of (η^6-C_6Me_6)RuCl(MDMPP-*P*,*O*) and (η^6-C_6Me_6)RuCl(BDMPP-*P*,*O*,*O*) complexes with Lewis bases or alkynes, where MDMPP-*P*,*O*=P(2-O-6-MeOC_6H_3)Ph_2 and BDMPP-*P*,*O*,*O*=P(2-O-6-MeOC_6H_3)$_2${2,6-(MeO)$_2C_6H_3$}[1]

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Abstract

Reaction of [(η^6-C_6Me_6)RuCl(MDMPP-*P*,*O*)] **1** (MDMPP-*P*,*O*=P(2-O-6-MeOC_6H_3)Ph_2] with CO under high pressure at 95° gave RuCl$(CO)_3$(MDMPP-*P*,*O*) **2**. [(η^6-*p*-cymene)Ru(TDMPP-*P*,*O*,*O*)] (TDMPP-*P*,*O*,*O*=P(2-O-6-MeOC_6H_3)$_2${2,6-(MeO)$_2C_6H_3$}) reacted with CO or CO/2,6-xylyl isocyanide under high pressure to form Ru$(CO)_3$(TDMPP-*P*,*O*,*O*) **4** or Ru$(CO)_2$(XylNC)(TDMPP-*P*,*O*,*O*) **5** (Xyl = 2,6-$Me_2C_6H_3$), respectively. Reactions of **1** with Lewis bases in the presence of NH_4PF_6 gave [(η^6-C_6Me_6)RuL(MDMPP-*P*,*O*)](PF_6) **6** (L = CO, XylNC). Complex **1** reacted with mono-substituted acetylenes in acetone in the presence of bases to form the metal alkynyl complexes [(η^6-C_6Me_6)Ru(C≡CR)(MDMPP-*P*,*O*)] **7**. Similar reaction of **1** with PhC≡CH in the presence of $NaPF_6$ in acetone or MeOH gave a vinylidene **8a** (R = C=CHPh) and a carbene complex **9a** (R = CCH_2Ph(OMe)) [(η^6-C_6Me_6)Ru(=R)(MDMPP-*P*,*O*)](PF_6), respectively. A reaction of **1** with HC≡CMe_2OH and $NaPF_6$ in MeOH gave a metallabutadiene complex **10c** [(η^6-C_6Me_6) Ru{=C(OMe)CH=CMe_2}(MDMPP-*P*,*O*)]. X-ray analyses of **6b** (L = XylNC), **7a** (R = Ph) and **7e** (R = CH_2OH) were carried out to confirm the structures; **6b**, monoclinic, space group $P2_1/c$ (No. 14), $a = 9.910(8)$ Å, $b = 25.370(7)$ Å, $c = 16.020(7)$ Å, $\beta = 105.29(5)°$, $V = 3885(7)$ Å^3, $Z = 4$, $R = 0.050$, $R_w = 0.053$ for 4064 reflections ($I > 3.0\sigma(I)$); **7a**, orthorhombic, space group *Pbca*, $a = 17.222(4)$ Å, $b = 23.772(8)$ Å, $c = 16.003(8)$ Å, $V = 6552(7)$ Å^3, $Z = 8$, $R = 0.052$, $R_w = 0.052$ for 1836 reflections ($I > 3.0\sigma(I)$); **7e**, triclinic, space group P_1 (No. 2), $a = 10.639(4)$ Å, $b = 14.778(3)$ Å, $c = 10.214(3)$ Å, $\alpha = 97.05(2)°$, $\beta = 113.01(2)°$, $\gamma = 79.12(2)°$, $V = 1449(2)$ Å^3, $Z = 2$, $R = 0.041$, $R_w = 0.040$ for 3270 reflections ($I > 3.0\sigma(I)$). © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Bis[dichloro(η^6-arene)ruthenium(II)]; (2,6-Dimethoxyphenyl)diphenylphosphine; Ruthenium alkyne complexes

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1. Introduction

Tertiary aromatic phosphines bearing methoxy groups at 2- and 6-positions such as P[2,6(MeO)$_2C_6H_3$]$_3$, P[2,4,6-(MeO)$_3C_6H_2$]$_3$, and their related phosphines have provided characteristic reactivity because of the high basicity and steric bulkiness [1,2]. These phosphines are functionalized phosphines which have the potential to form hemilable chelates in a similar manner to phosphinoethers [3]. We have shown previously that complexes with various coordination modes such as *P*, (*P*,*O*), or (*P*,*O*,*O*′) chelation were obtained in the coordination chemistry of P[2,6(MeO)$_2C_6H_3$]$_3$ (TDMPP), PPh[2,6-(MeO)$_2C_6H_3$]$_2$ (BDMPP), and PPh_2[2,6-(MeO)$_2C_6H_3$] (MDMPP) with bis[dichloro(η^6-arene)ruthenium(II)], depending on arenes and phosphines [4]. Reaction of MDMPP with bis[dichloro(η^6-arene)ruthenium] led to an elimination

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[1] Dedicated to Professor Akira Nakamura on the occassion of his retirement from Osaka University.

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of MeCl to give [(η^6-arene)RuCl(MDMPP-*P*,*O*)] **1** (MDMPP-*P*,*O*=P(2-O-6-MeOC_6H_3)Ph_2] bearing the *P*,*O* chelation as a bidentate ligand, whereas the reaction with TDMPP eliminated two molecules of MeCl to yield (η^6-arene)Ru(TDMPP-*P*,*O*,*O′*) **3** (TDMPP-*P*,*O*,*O′*=[P(2-O-6-MeOC_6H_3)$_2${2,6-(MeO)$_2$ C_6H_3}] bearing the *P*,*O*,*O′* chelation as a tridentate ligand. In some attempts to examine the stability of the *P*,*O*-chelation and their reactivities to various small molecules, we carried out the reactions of these complexes **1** and **3** with Lewis base and acetylenes.

2. Experimental

All reactions were carried out under nitrogen atmosphere. Arene ruthenium complexes [4], (η^6-C_6Me_6)RuCl(MDMPP-*P*,*O*) **1**, (η^6-*p*-cymene)Ru(TDMPP-*P*,*O*,*O′*) **3**, and xylyl isocyanide [5] were prepared according to the literature. MeCN and CH_2Cl_2 were distilled over CaH_2 and other reagents were used as commercially available. 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. ^{1}H-NMR spectra were measured at 250 MHz using tetramethylsilane as an internal reference and ^{31}P{^{1}H}-NMR spectra were measured using 85% H_3PO_4 as an external reference. The FAB mass spectra were measured on a JMS-Dx300 spectrometer.

2.1. Reactions of complexes **1** and **3**

2.1.1. Reaction of **1** with CO

A mixture of **1** (50 mg, 0.08 mmol) and 45 kg cm^{-2} of CO in CH_3CN (3 ml) and toluene (4 ml) was charged in a 100 ml-stainless steel autoclave and heated at 95°C for 4.5 h. A solution color changed from yellow to pale yellow. The solvent was removed under reduced pressure, and the residue was recrystallized from CH_2Cl_2 and diethyl ether to give pale yellow crystals (25 mg, 59%) of RuCl[P(2-O-6-MeOC_6H_3)Ph_2](CO)$_3$ **2**. IR(Nujol): 2058, 1986, 1946 ($C\equiv O$) cm^{-1}. Anal. Calc. for $C_{22}H_{13}NO_5Cl$ PRu: C, 50.06; H, 3.06. Found: C, 50.02; H, 3.37.

2.1.2. Reaction of **3** with CO

A mixture of **3** (57 mg, 0.078 mmol) and 45 kg cm^{-2} of CO in CH_3CN (3 ml) and toluene (4 ml) in a 100 ml-stainless steel autoclave was heated at 95°C for 4.5 h. A solution color changed from yellow to very pale yellow. The solvent was removed under reduced pressure, and the residue was recrystallized from CH_2Cl_2 and diethyl ether to give colorless crystals (23 mg, 46.1%) of Ru(TDMPP-*P*,*O*,*O*)(CO)$_3\cdot\frac{1}{2}CH_2Cl_2$ **4**$\cdot\frac{1}{2}CH_2Cl_2$. IR(Nujol): 2042, 1956, 1932 ($C\equiv O$) cm^{-1}. UV-vis (CH_2Cl_2): λ_{max} 301(4.06), 262(sh) nm. Anal. Calc. for $C_{25.5}H_{22}O_9ClPRu$: C, 47.86; H, 3.47. Found: C, 48.33; H, 3.70.

2.1.3. Reaction of **3** with CO and xylyl isocyanide

A mixture of **3** (57 mg, 0.078 mmol), xylyl isocyanide (39 mg, 0.298 mmol) and 45 kg cm^{-2} of CO in CH_3CN (3 ml) and toluene (4 ml) in a 100 ml-stainless steel autoclave was heated at 95°C for 3.5 h. A solution color changed from yellow to very pale yellow. The solvent was removed under reduced pressure, and the residue was recrystallized from CH_2Cl_2 and diethyl ether to give colorless crystals (47.8 mg, 87.4%) of Ru(TDMPP-*P*,*O*,*O*)(CO)$_2$(XylNC) **5**. FAB mass (*m*/*z*): 701 (M$^+$), 645 (M–2CO$^+$), 514 (M–2CO–RNC$^+$). UV-vis (CH_2Cl_2): λ ca. 300 (sh) nm. IR(Nujol): 2176 ($N\equiv C$), 2031, 1970 ($C\equiv O$), 1582, 1549 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 2.60 (s, *o*-Me), 5.51, 3.57 (s, MeO), 5.9–7.5 (c, Ph) ppm.

2.1.4. Reaction of **1** with CO in the presence of NH_4PF_6

Carbon monoxide was bubbled through a solution of **1** (100 mg, 0.16 mmol) in CH_2Cl_2 (10 ml) at room temperature, and NH_4PF_6 (140 mg, 0.83 mmol) in acetone (5 ml) was added to the solution. The mixture was stirred for 4 h, in which CO was bubbled each hour. The solvent was removed under reduced pressure and the residue was extracted with CH_2Cl_2, followed by filtration of the extract through a glass filter (G4). Removal of the solvent and crystallization of the residue from CH_2Cl_2 and diethyl ether gave yellow crystals of [(η^6-C_6Me_6)Ru(CO)(MDMPP-*P*,*O*)](PF_6) **6a** (35 mg, 30%). IR(Nujol): 2004 ($C\equiv O$), 1587, 1552, 835 (PF_6) cm^{-1}. UV-vis (CH_2Cl_2): λ_{max} 333 (sh), 285 (sh) nm. ^{1}H-MR($CDCl_3$): δ 2.04 (s, C_6*Me*$_6$), 3.39 (s, *Me*O), 6.1–7.6 (m, *Ph*). ^{31}P{^{1}H}-NMR ($CDCl_3$): δ 52.0 (s), -114.7 (sep. PF_6, $J_{PF}=708$ Hz). Anal. Calc. for $C_{32}H_{34}O_3F_6P_2Ru$: C, 51.54; H, 4.60. Found: C, 51.49; H, 4.68.

2.1.5. Reaction of **1** with xylyl isocyanide in the presence of NH_4PF_6

To a mixture of **1** (100 mg, 0.16 mmol) and xylyl isocyanide (44 mg, 0.33 mmol) in CH_2Cl_2 (10 ml) was added NH_4PF_6 (140 mg, 0.83 mmol) in acetone (5 ml). After the mixture was stirred for 2 h at room temperature, the solvent was removed under reduced pressure and the residue was extracted with CH_2Cl_2, followed by filtration of the extract through a glass filter (G4). Removal of the solvent and crystallization of the residue from CH_2Cl_2 and diethyl ether gave yellow crystals of [(η^6-C_6Me_6)Ru(XylNC)(MDMPP-*P*,*O*)]

(PF_6) (78 mg, 60%). IR(Nujol): 2135 (N≡C), 1581, 1548, 844 (PF_6) cm^{-1}. UV-vis (CH_2Cl_2): 330 (sh), 274 (sh) nm. ^{1}H-NMR$(CDCl_3)$: δ 1.84 (s, *o-Me*), 2.05 (s, C_6Me_6), 3.33 (s, *Me*O), 6.0–7.6 (m, *Ph*) ppm. $^{31}P\{^1H\}$-NMR $(CDCl_3)$: δ 53.6 (s), -114.7 (sep. $J_{PF} = 709$ Hz, PF_6) ppm. Anal. Calc. for $C_{40}H_{43}NO_2F_6P_2Ru$: C, 56.60; H, 5.11; N, 1.65. Found: C, 56.64; H, 5.13; N, 1.85.

2.1.6. Reaction of **1** with PhC≡CH in the presence of potassium hydroxide

To a solution of 1 (66.8 mg, 0.11 mmol) and phenyl acetylene (0.37 ml, 3.4 mmol) in CH_2Cl_2/methanol (10 ml/10 ml) was added 0.55 ml (0.152 mmol) of a 0.277 mmol methanol solution containing potassium hydroxide at room temperature. After stirring for 24 h, the solvent was removed under reduced pressure and the residue was extracted with CH_2Cl_2, followed by filtration through a glass filter (G4). The filtrate was chromatographed on alumina, using CH_2Cl_2 as an eluant. Removal of the yellow eluate and crystallization of the residue from ether and hexane gave orange yellow crystals $(\eta^6\text{-}C_6Me_6)Ru(C{\equiv}CPh)(MDMPP\text{-}P,O)\cdot\frac{1}{2}H_2O$ **7a**$\cdot\frac{1}{2}H_2O$ (75.7 mg, 65%). IR(Nujol): 2089 (C≡C), 1580, 1543 cm^{-1}. ^{1}H-NMR$(CDCl_3)$: δ 1.91 (s, C_6Me_6), 3.03 (s, *Me*O), 5.84–7.8 (m, *Ph*) ppm. $^{31}P\{^1H\}$-NMR $(CDCl_3)$: δ 58.1 (s) ppm. Anal. Calc. for $C_{39}H_{40}O_{2.5}PRu$: C, 68.81; H, 5.92. Found: C, 68.59; H, 5.54.

2.1.7. Reaction of 1 with HC≡CCOOMe in the presence of potassium hydroxide

To a solution of **1** (66.8 mg, 0.11 mmol) and HC≡CCOOMe (0.18ml, 2.0 mmol) in CH_2Cl_2 / methanol (10 ml/10 ml) was added 0.38 ml (0.11 mmol) of a 0.277 mmol methanol solution containing potassium hydroxide at room temperature. After stirring for 15 min, the solvent was removed under reduced pressure and the residue was extracted with CH_2Cl_2, followed by filtration through a glass filter (G4). The solution was removed to ca. 3 ml and hexane was added to give orange yellow crystals $(\eta^6\text{-}C_6Me_6)Ru(C{\equiv}CCOOMe)(MDMPP\text{-}P,O)\cdot\frac{1}{2}CH_2Cl_2$ **7b**$\cdot\frac{1}{2}CH_2Cl_2$ (37.7 mg, 49%). IR(Nujol): 2081 (C≡C), 1669 (C=O), 1580, 1543 cm^{-1}. ^{1}H-NMR$(CDCl_3)$: δ 1.88 (s, C_6Me_6), 3.27, 3.30 (s, *Me*O, COO*Me*), 5.27 (s, CH_2Cl_2), 5.84–7.8 (m, *Ph*) ppm. $^{31}P\{^1H\}$-NMR $(CDCl_3)$: δ 58.1 (s) ppm. Anal. Calc. for $C_{35.5}H_{38}O_4ClPRu$: C, 61.25; H, 5.50. Found: C, 61.09; H, 5.21.

2.1.8. Reaction of **1** with HC≡CCH$_2$OH in the presence of potassium hydroxide

To a solution of **1** (66.8 mg, 0.11 mmol) and 2-propyne-1-ol (0.22 ml, 3.78 mmol) in CH_2Cl_2 /methanol (10 ml/10 ml) was added 0.38 ml (0.11 mmol) of a 0.277 mmol methanol solution containing potassium hydroxide at room temperature. After stirring for 15 min, the solvent was removed under reduced pressure and the

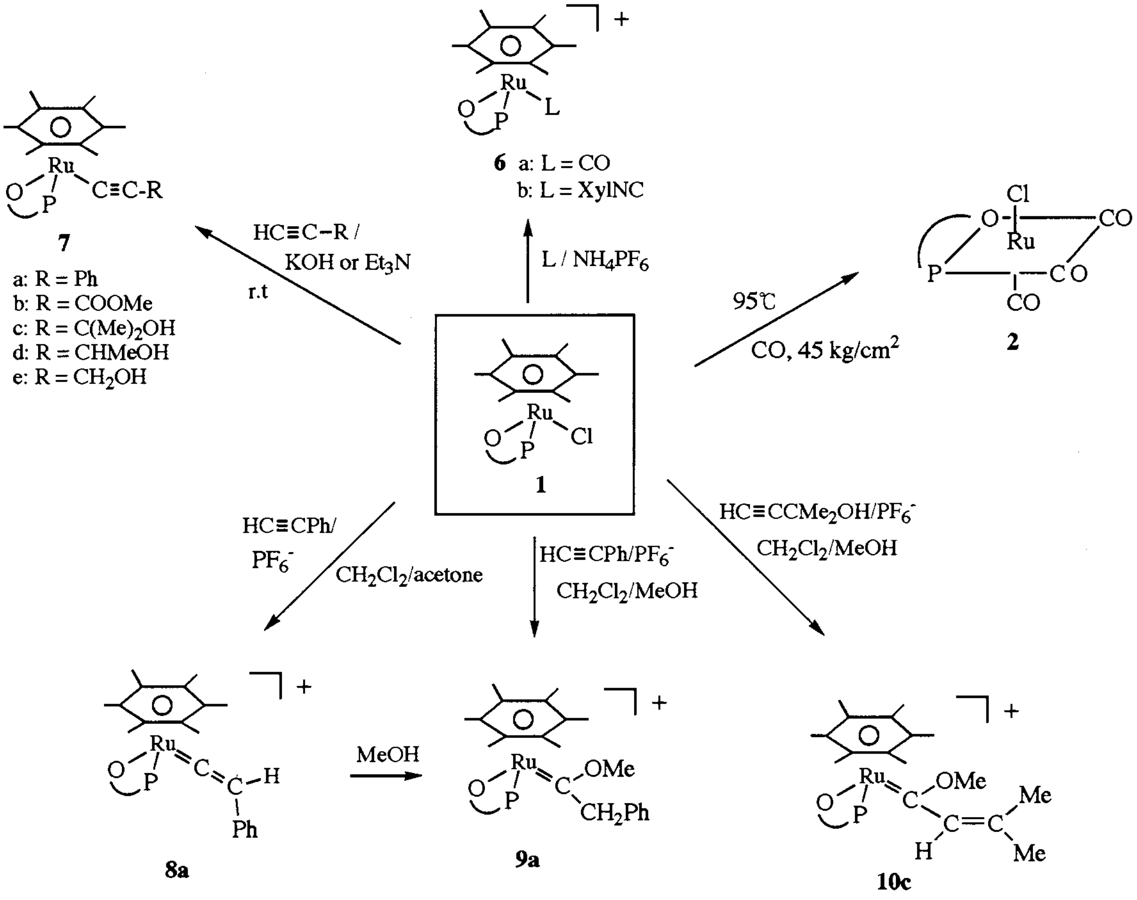
Table 1

Crystal data of $[(\eta^6\text{-}C_6Me_6)Ru(XylNC)[P(2\text{-}O\text{-}6\text{-}MeOC_6H_3)Ph_2][PF_6]$ **6b**, $(\eta^6\text{-}C_6Me_6)Ru(C{\equiv}CPh)[P(2\text{-}O\text{-}6\text{-}MeOC_6H_3)Ph_2]$ **7a** and $(\eta^6\text{-}C_6Me_6)Ru(C{\equiv}CCH_2OH)[P(2\text{-}O\text{-}6\text{-}MeOC_6H_3)Ph_2]$ **7e**.

Compound	**6b**	**7a**	**7e**
Formula	$C_{40}H_{43}NO_2F_6P_2Ru$	$C_{39}H_{39}O_2PRu$	$C_{34}H_{37}O_3PRu$
Molecular weight	846.79	671.78	625.71
Color	Yellow	Orange yellow	Yellow
Crystal dimension (mm)	0.50 × 0.50 × 0.50	0.50 × 0.50 × 0.38	0.35 × 0.22 × 0.08
Crystal system	Monoclinic	Orthorhombic	Triclinic
Space group	$P2_1/c$ (no. 14)	*Pbca* (no.)	P_1 (no. 2)
Lattice parameters			
a	9.910(8)	17.222(4)	10.639(4)
b (Å)	25.370(7)	23.772(8)	14.778(3)
c (Å)	16.020(7)	16.003(8)	10.214(3)
α (°)	90.0	90.0	97.05(2)
β (°)	105.29(5)	90.0	113.01(2)
γ (°)	90.0	90.0	79.12(2)
V (Å^3)	3885(7)	6552(7)	1449(2)
Z	4	8	2
$D_{calc.}$ (g cm^{-3})	1.447	1.362	1.434
μ cm^{-1}	5.38	5.48	6.16
$F(000)$	1736	2784	648
No. of data $(I>3.0\sigma(I))$	4064	1836	3270
No. of variables	469	388	353
R; R_w^a	0.050; 0.053	0.052; 0.052	0.041; 0.040
GOF	1.86	1.34	1.32

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

GOF, $[\Sigma w(|F_o|-|F_c|)^2/\Sigma(N_o-N_v]^{1/2}$ where N_o is the number of data; N_v is the number of variables.



Scheme 1.

residue was extracted with CH_2Cl_2, followed by filtration through a glass filter (G4). The solvent was removed under reduced pressure and the residue was recrystallized from ether/hexane to give yellow crystals of $(\eta^6\text{-}C_6Me_6)Ru(C{\equiv}CCH_2OH)(MDMPP\text{-}P,O)]\cdot\frac{1}{2}H_2O$ **7e**$\cdot\frac{1}{2}H_2O$ (49.2 mg, 71%). IR(Nujol): 2116 (C≡C), 1580, 1543 cm^{-1}. ^{1}H-NMR(CDCl$_3$): δ 1.87 (s, C_6Me_6), 2.04 (br, *O*H, 1H), 3.27 (s, *Me*O), 3.65–3.81 (m, CH_2), 5.9–7.7 (m, *Ph*) ppm. $^{31}P\{^1H\}$-NMR (CDCl$_3$): δ 57.9 (s) ppm. Anal. Calc. for $C_{34}H_{38}O_{3.5}PRu$: C, 63.44; H, 6.11. Found: C, 63.51; H, 5.73.

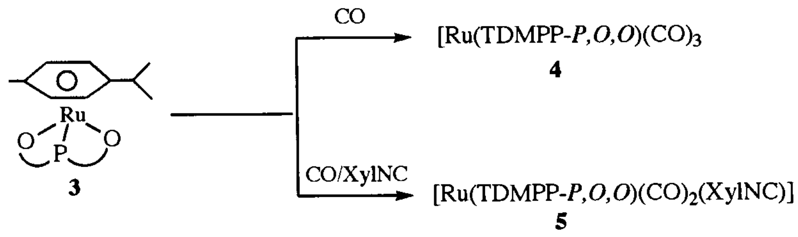
2.1.9. Reaction of **1** with HC≡CCH(Me)OH in the presence of potassium hydroxide

To a solution of **1** (66.8 mg, 0.11 mmol) and 1-butyne-3-ol (0.27 ml, 3.66 mmol) in CH_2Cl_2 /methanol (10 ml/10 ml) was added 0.38 ml (0.11 mmol) of a 0.277 mmol methanol solution containing potassium hydroxide at room temperature. After stirring for 30 min, the solvent was removed under reduced pressure and the residue was extracted with CH_2Cl_2, followed by filtration through a glass filter (G4). The solvent was removed under reduced pressure and the residue was washed with hexane to give yellow crystals of $(\eta^6\text{-}C_6Me_6)Ru(C{\equiv}CCH(Me)OH)(MDMPP\text{-}P,O)\cdot\frac{1}{4}H_2O$ **7d**$\cdot\frac{1}{4}H_2O$ (37.4 mg, 53%). IR(Nujol): 2093 (C≡C), 1580, 1545 cm^{-1}. ^{1}H-NMR(CDCl$_3$): δ 0.81*, 1.40 (dd, J_{PH} = 6.3 Hz), 1.86, 1.87* (s, C_6Me_6), 2.03 (br, *O*H,), 3.26, 3.27* (s, *Me*O), 3.98 (m, C*H*), 5.9–7.8 (m, *Ph*) ppm. $^{31}P\{^1H\}$-NMR (CDCl$_3$): δ 58.1, 58.4* (s) ppm (isomers *A** and *B*). Anal. Calc. for $C_{35}H_{39.5}O_{3.25}PRu$: C, 65.25; H, 6.18. Found: C, 65.53; H, 5.60.

According to the procedure similar to that described above, yellow complex $(\eta^6\text{-}C_6Me_6)Ru(C{\equiv}CCMe_2OH)(MDMPP\text{-}P,O)\cdot\frac{1}{4}CH_2Cl_2$ **7e**$\cdot\frac{1}{4}CH_2Cl_2$ (39.1 mg, 53%) was obtained from the reaction of **1** (66.8 mg, 0.11 mmol) with $HC{\equiv}CCMe_2OH$ (0.20 ml, 2.06 mmol). IR(-Nujol): 2098 (C≡C), 1582, 1541 cm^{-1}. ^{1}H-NMR (CDCl$_3$): δ 1.00, 1.01 (s, *Me*), 1.87 (s, C_6Me_6), 2.04 (br, O*H*), 3.27 (s, *Me*O), 5.9–7.4 (m, *Ph*) ppm. $^{31}P\{^1H\}$-NMR (CDCl$_3$): 558.1 (s) ppm. Anal. Calc. for $C_{36.25}H_{41.5}O_3Cl_{0.5}PRu$: C, 65.25; H, 6.18. Found: C, 65.53; H, 5.60.

2.1.10. Reaction of **1** with PhC≡CH in the presence of $NaPF_6$ in CH_2Cl_2/acetone

To a mixture of **1** (66.8 mg, 0.11 mmol) and PhC≡CH (0.25 ml) in CH_2Cl_2 (5 ml) and acetone (5 ml) was added $NaPF_6$ (25 mg, 0.15 mmol) at room temperature. After 15 h, the solvent was removed at reduced



Scheme 2.

pressure and the residue was recrystallized from CH_2Cl_2 and Et_2O to give **8a**·$\frac{1}{4}CH_2Cl_2$ (56.5 mg, 76.2%) as orange crystals. IR(Nujol): 1620 (C=C), 841 (PF_6) cm^{-1}. ^1H-NMR($CDCl_3$): δ 2.05 (s, $C_6\mathit{Me}_6$), 3.06 (s, *Me*O), 5.30 (s,=C*H*), 5.7–7.6 (m, *Ph*) ppm. $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ 173.6 (s), −143.8 (sep. $J_{PF} = 709$ Hz, PF_6) ppm. Anal. Calc. for $C_{36.25}H_{41.5}O_3Cl_{0.5}PRu$: C, 57.70; H, 4.22. Found: C, 56.99; H, 4.66.

*2.1.11. Reaction of **1** with PhC≡CH in the presence of $NaPF_6$ in CH_2Cl_2/MeOH*

To a mixture of **1** (62 mg, 0.102 mmol) and PhC≡CH (0.25 ml) in CH_2Cl_2 (10 ml) and MeOH (5 ml) was added $NaPF_6$ (25 mg, 0.15 mmol) at room temperature. After 15 h, the solvent was removed at reduced pressure and the residue was recrystallized from CH_2Cl_2 and Et_2O to give **9a**·$\frac{1}{2}CH_2Cl_2$ (91 mg, 46.6%) as orange crystals. IR(Nujol): 841 (PF_6) cm^{-1}. UV-vis (CH_2Cl_2): λ_{max} 476 (log ε 2.72) nm. ^1H-NMR ($CDCl_3$): δ 1.83 (s, $C_6\mathit{Me}_6$), 3.31 (s, *Me*O), 3.70 (s, *Me*O), 3.97, 4.02 (s, CH_2), 5.3–7.7 (m, *Ph*) ppm. $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ 56.0 (s), 142.9 (sep. $J_{PF} = 708$ Hz, PF6) ppm. Anal. Calc. for $C_{40.5}H_{45}O_3F_6ClP_2Ru$: C, 54.52; H, 5.08. Found: C, 54.83; H, 5.27.

*2.1.12. Reaction of **1** with $Me_2C(OH)C{\equiv}CH$ in the presence of $NaPF_6$ in CH_2Cl_2/MeOH*

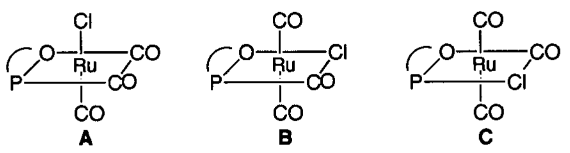
To a mixture of **1** (59.7 mg, 0.099 mmol) and $HC{\equiv}CCMe_2(OH)$ (0.25 ml) in CH_2Cl_2 (20 ml) and MeOH (10 ml) was added $NaPF_6$ (25 mg, 0.15 mmol) at room temperature. After 2.5 h, the solvent was removed at reduced pressure and the residue was recrystallized from CH_2Cl_2 and Et_2O gave **10c** (18.9 mg, 23.6%) as orange crystals. IR(Nujol): 1640 (C=C), 841 (PF_6) cm^{-1}. UV-vis (CH_2Cl_2): λ_{max} 339 nm. ^1H-NMR ($CDCl_3$): δ 1.37, 1.41 (s, =CMe_2), 1.91 (s, $C_6\mathit{Me}_6$), 3.32 (s, *Me*O), 3.68 (s, *Me*O), 4.62 (s, =C*H*), 5.9–7.6 (m, *Ph*). $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ 56.5 (s), 143.8 (sep. $J_{PF} = 708$ Hz, PF6) ppm. Anal. Calc. for $C_{37}H_{44}O_3P_2F_6Ru$: C, 53.55; H, 5.34. Found: C, 54.17; H, 5.38.

2.2. X-ray

2.2.1. Data collection

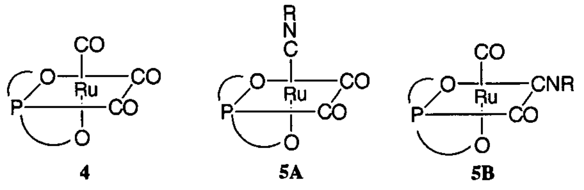
Complexes (**6b**, **7a**, and **7e**) were recrystallized from CH_2Cl_2/hexane or CH_2Cl_2/ether. Cell constants were determined on a Rigaku AFC5S four-circle automated diffractometer from the setting angles of 20–25 reflections in the range from 20.0° < 2θ < 30.0°. The crystal parameters along with data collection details are summarized in Table 1. Data collection was carried out on a Rigaku AFC5S diffractometer. Intensities were measured by the 20-co scan method using Mo–K_α radiation ($\lambda = 0.71069$ Å). Scan rates of 8° min^{-1} for **6b**, 16° min^{-1} for **7a** and 8° min^{-1} for **7e** were used, respectively. 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 of 7010 independent intensities ($2\theta < 50°$) was measured for **6b**, 5707 ($2\theta < 50°$) for **7a**, and 5116 ($2\theta < 50°$) for **7e**, respectively. Of these, there are, respectively, 4064, 1836 and 3270 ($I > 3.0\sigma(I)$) unique reflections 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 [6]. Anomalous dispersion effects were included in F_{calc} [7]; the values of Δf′ and Δf″ were from Creagh and McAuley [8]. All calculations were performed on a Digital VAX Station 3100 M38 computer using the TEXSAN-TEXRAY program system.



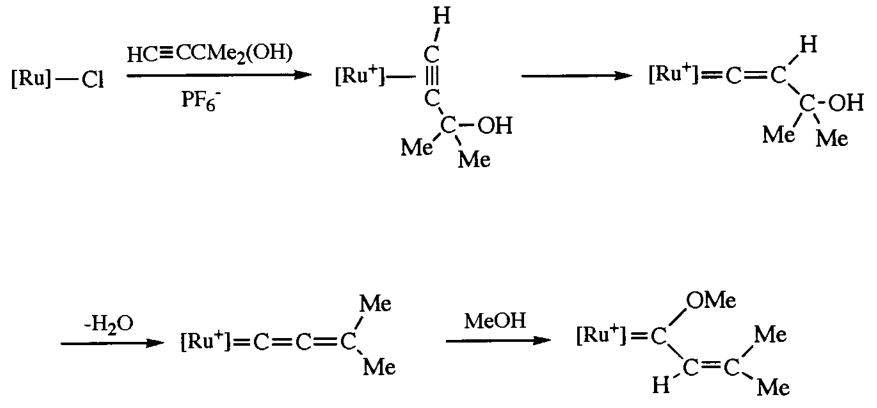
A **B** **C**

Fig. 1. Possible structure of **2**.



4 **5A** **5B**

Fig. 2. Structure of **4** and **5**.



Scheme 3.

2.2.2. *Determination of the structures*

The structures were solved by direct methods with MITHRIL for **6b** and **7a** and Patterson methods for **7e**. 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 the 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. Final difference Fourier syntheses showed peaks at heights up to 0.44–0.73 eÅ^{-3}.

3. Results and discussion

Overall reactions described here are depicted in Scheme 1 and Scheme 2.

3.1. *Reactions with Lewis bases*

It has been known that halogens of the (arene)ruthenium complexes (η^6-arene)$RuCl_2(PR_3)$ containing monophosphine ligands were substituted readily with various Lewis bases in the presence of large anions to form the [(η^6-arene)$RuCl(PR_3)(L)]^+$ complexes [9]. Analogous reactions were carried out for the P–O chelated complexes. Reaction of (η^6-C_6Me_6)RuCl-(MDMPP-*P*,*O*) **1** with carbon monoxide did not occur at room temperature, whereas on heating under a high pressure of CO the arene ring was eliminated to give [RuCl(MDMPP-*P*,*O*)$(CO)_3$] **2**. The infrared spectrum showed three peaks at 2058, 1986, and 1946 cm^{-1} due to terminal carbonyl groups. Three kinds of structures are assumed for **2**. Based on the fact that the arene ring occupies three cis-sites of an octahedral configuration, the facial structure (A) are assumed to be superior to two other meridional ones (B and C) (Fig. 1). A similar elimination of the arene ring occurred in (η^6-*p*-cymene)Ru(BDMPP-*P*,*O*,*O*) **3** to give [Ru$(CO)_3$ (TDMPP-*P*,*O*,*O*)] **4**. The infrared spectrum showed the presence of three carbonyl groups, also suggesting a facial structure as well as that of **2** (Fig. 2). When an analogous reaction was carried out in the presence of xylyl isocyanide, the complex [Ru$(CO)_2$(XylNC) (TDMPP-*P*,*O*,*O*)] **5** was obtained as an only isolated

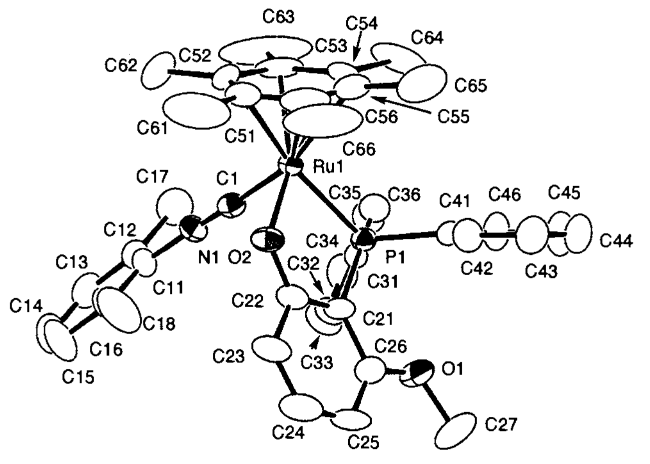


Fig. 3. Molecular structure of **6b** (PF_6 was omitted for clarity).

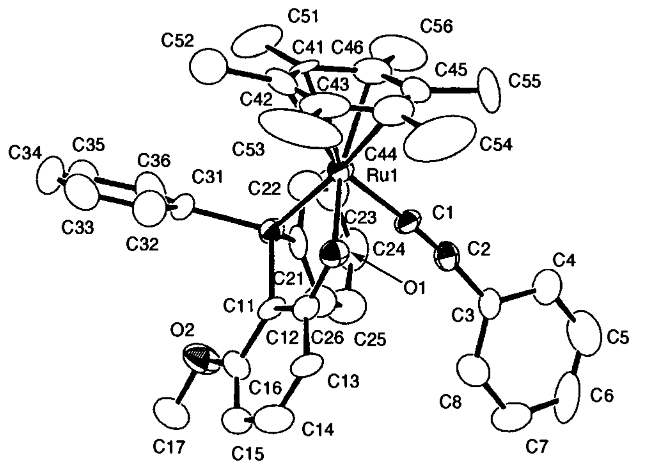


Fig. 4. Molecular structure of **7a**.

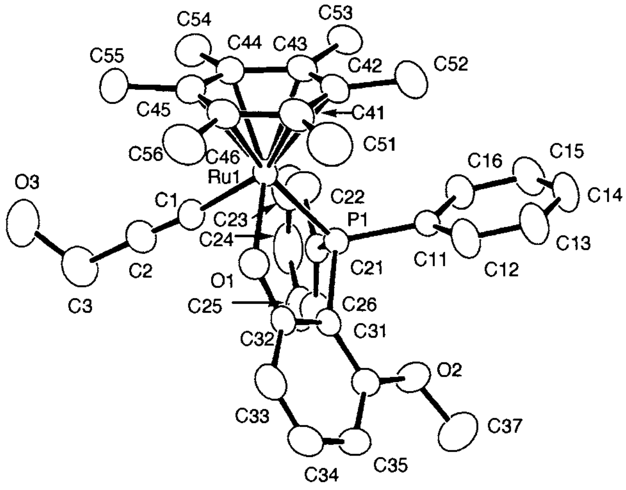


Fig. 5. Molecular structure of **7e**.

product from the mass spectrum and elemental analysis. The infrared spectrum showed three characteristic bands at 2176 (N≡C), 2031 and 1970 (C≡O) cm^{-1}. Two possible structures (A and B) are considered, but the detailed structure is kept unknown (Fig. 2). Elimination of an arene ligand has been observed in the reaction of $[(\eta^6\text{-}p\text{-cymene})RuCl_2]_2$ with MDMPP at room temperature to give $[RuCl_2(MDMPP\text{-}P,OMe)$ [4].

When **1** was treated with CO or xylyl isocyanide in the presence of NH_4PF_6 at room temperature, yellow crystals formulated as $[(\eta^6\text{-}C_6Me_6)Ru(MDMPP\text{-}P,O)(L)](PF_6)$ (**6a**: L = CO, **6b**: L = XylNC) were obtained, respectively. The infrared spectra showed a band at 2004 cm^{-1} for **6a** and at 2135 cm^{-1} for **6b** due to a ν(CO) or ν(NC) band, respectively. The $^{31}P\{^1H\}$-nmr spectrum of **6a** appeared at the lower field by δ 1.6 ppm than that (δ 52.0 ppm) of **6b**, responsible for the higher σ-donor ability of isocyanide than carbon monoxide.

3.2. Metal acetylides and their related complexes

Metal vinylidene and related unsaturated carbene species play an important role in Fisher-Tropsch chemistry [10]] and in acetylene polymerization [11]. They can be synthesized from metal aklynyl complexes [12].

When **1** in CH_2Cl_2/methanol was treated with phenyl acetylene in the presence of triethylamine or methanolic potassium hydroxide, orange yellow crystals of $[(\eta^6\text{-}C_6Me_6)Ru(C{\equiv}CPh)(MDMPP\text{-}P,O)]$ **7a** were isolated. The infrared spectrum showed a peak at 2089 cm^{-1} due to the ν(C≡C) band. The ^1H-nmr spectrum showed two singlets at δ 1.91 and 3.03 ppm assignable to the methyl and methoxy groups, respectively. The $^{31}P\{^1H\}$-NMR spectrum showed a singlet at δ 58.1 ppm. The reaction with methyl propiolate also gave the acetylide complex **7b**. The infrared spectrum showed two characteristic bands at 2081 and 1669 cm^{-1}, due to the ν(C≡C) and ν(C=O) bands, respectively. The ^1H-NMR spectrum showed three bands at δ 1.88, 3.27 and 3.30 ppm in a 6:1:1 intensity ratio, assignable to methyl, methoxy and methoxycarbonyl groups, respectively. Analogous acetylide complexes **7**, $[(\eta^6\text{-}C_6Me_6)Ru(C{\equiv}CR)(MDMPP\text{-}P,O)]$ (**c**: R = $C(Me)_2OH$; **d**: R = CH(Me)OH; **e** = CH_2OH) were obtained from the reactions with the corresponding propargyl alcohol

Table 2
Selected bond lengths (Å) and angles (°) of **6b**

Bond length					
Rul–P1	2.318(2)	Ru1–O2	2.070(4)	Rul–C1	1.940(7)
O1–C26	1.357(9)	O1–C27	1.421(9)	O2–C22	1.314(7)
Cl–N1	1.138(7)	$Ru–C^*_{av}$	2.257(8)		
Bond angle					
Pl–Ru1–O2	82.4(1)	Pl–Rul–C1	84.7(2)		
O2–Rul–C1	85.1(2)	Ru1–O2–C22	120.2(4)		
Rul–Pl–C21	99.5(2)	Rul–Cl–N1	175.2(6)		
Cl–Nl–C11	171.8(6)				

Table 3
Selected bond lengths (Å) and angles (°) of **7a**

Bond length					
Rul–P1	2.298(4)	Ru1–O1	2.095(8)	Rul–C1	1.99(l)
O1–C12	1.32(1)	O2–C16	1.38(2)	O2–C17	1.38(1)
C1–C2	1.19(2)	$Rul–C^*_{av}$	2.25(1)		
Bond angle					
Pl–Ru1–O1	82.0(3)	Pl–Rul–C1	81.8(4)		
O1–Rul–C1	84.6(5)	Ru1–O1–C12	120.6(9)		
Rul–Pl–C11	101.5(5)	Rul–Cl–C2	177(1)		
C1–C2–C3	174(2)				

Table 4
Selected bond lengths (Å) and angles (°) of **7e**

Bond length					
Rul–P1	2.296(2)	Ru1–O1	2.090(4)	Rul–C1	2.009(6)
O2–C32	1.317(6)	O2–C36	1.366(6)	O2–C37	1.390(7)
O3–C3	1.396(8)	C1–C2	1.192(7)	Ru–C^*_{av}	2.249(5)
Bond angle					
Pl–Ru1–O1	82.1(1)	Pl–Rul–C1	84.6(2)		
O1–Rul–C1	82.7(2)	Rul–Pl–C31	101.6(2)		
Ru1–O1–C32	120.0(3)	Rul–Cl–C2	170.8(5)		
C1–C2–C3	177.8(7)				

derivatives. The structures of these complexes were confirmed by an X-ray analysis of **7e** (vice infra). The $^{31}P\{^1H\}$-NMR spectrum of **7d** showed two singlets at δ 58.1 and 58.4* ppm consisting of an intensity ratio 45: 55, suggesting the diastereomers derived from two chiral centers. The ^1H-NMR spectrum also supported the presence of two isomers. It consists of a well-defined pair for each of the methyl protons of the arene, acetylide and mehthoxy groups; each pair is δ 1.86 (s) and 1.87 (s)* ppm, 0.81* (d, $J_{HH} = 6.3$ Hz) and 1.40 (d, $J_{HH} = 6.3$ Hz) ppm, and 3.26 (s) and 3.27 (s)* ppm, respectively.

When **1** was treated with phenylacetylene in CH_2Cl_2/acetone in the presence of $NaPF_6$, the orange complex formulated as $[(\eta^6\text{-}C_6Me_6)Ru(MDMPP\text{-}P,O)({=}C{=}CH\text{-}Ph)](PF_6)$ **8a** was isolated. The infrared spectrum showed a C=C double bond at 1620 cm^{-1}. The ^1H-NMR spectrum showed three singlets at δ 2.05, 3.06 and 5.30 ppm, assignable to methyl, methoxy and vinylidene protons. The $^{31}P\{^1H\}$-NMR spectrum showed a singlet at δ 173.6 ppm. When the reaction was carried out in MeOH, a carbene complex $[(\eta^6\text{-}C_6Me_6)Ru(MDMPP\text{-}P,O)\{{=}C(OMe)(CH_2Ph)\}](PF_6)$ **9a** was isolated. The ^1H-NMR spectrum showed three singlets at δ 1.83, 3.32 and 3.70 ppm, due to one methyl and two methoxy protons. The reaction of **1** with $Me_2C(OH)C{\equiv}CH$ in the presence of $NaPF_6$ in MeOH gave orange crystals **10c** formulated as $[(\eta^6\text{-}C_6Me_6)Ru(MDMPP\text{-}P,O)\ \{{=}C(OMe)CH{=}CMe_2\}](PF_6)$ in 24% yield. In the infrared spectrum the peak due to the double bond appeared at 1640 cm^{-1} and the presence of the *P–O* chelation was confirmed by two peaks at 1582 and 1547 cm^{-1}]. The spectral pattern of the ^1H-NMR spectrum is similar to that of the metallabutadiene complex $[(\eta^6\text{-}1,2,3,4\text{-}Me_4C_6H_2)RuCl(PMe_3)\{{=}C(OMe)CH{=}CMe_2\}](PF_6)$ obtained from the reaction of $(\eta^6\text{-}1,2,3,4\text{-}Me_4C_6H_2)RuCl_2(PMe_3)$ with $Me_2C(OH)\text{-}C{\equiv}CH$ in the presence of $NaPF_6$ in MeOH [13]. Thus, the ^1H-NMR spectrum showed six singlets at δ 1.37, 1.41, 1.91, 3.32, 3.68, and 4.62 ppm consisting of an intensity ratio of 3:3:6:3:3:1; the first three peaks are due to two vinylic methyl and methyl groups of the arene ring, the last one to a vinyl proton, the others to methoxy group of phosphine and α-substituted methoxy one, respectively.

The reaction consists of an initial formation of an acetylene complex, followed by rearrangement of a proton to form a vinylidene complex and by the formation of an allenylidene intermediate via a subsequent elimination of H_2O [13]. The final metallabutadiene complex is completed by the 1,2-addition of MeOH to the intermediate (Scheme 3).

3.3. Structures of *6b*, *7a*, and *7e*

All complexes display a piano-stool structure which a Ru atom was coordinated by phosphorus, oxygen and carbon atoms and an arene ring (Figs. 3–5). The selected bond lengths and angles were shown in Table 2, Table 3 and Table 4. The Ru–P bond length of **6b** is somewhat longer than those found in the alkynyl complexes **7**. This difference of bond length (ca. 0.02 Å) is traced back to that of the Ru–O bond lengths, where the bond length (2.070(4) Å) in **6b** is shorter by 0.02 Å than those in **7**. The Ru–C bond length (1.940(7) Å) of **6b** is shorter than those of **7a** and **7e**, responsible for the difference of chemical bonding mode and the difference of back-bonding ability between **6** and **7**. The Ru–C–C, Ru–C–N, C–C–C and C–N–C bond angles are not sign)ficantly different from linearity. The N≡C triple bond length of 1.19(2) Å is shorter than those of the C≡C triple bond, depending on the covalent radii. The bite angles of three complexes are ca. 82°, not different from those of the starting and related complexes [4].

4. Supplementary materials

Tables of atomic positional parameters, anisotropic temperature factors, and bond lengths and angles, and a listing of observed and calculated structure factors are available from Y.Y. on request.

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