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Reactions of bis[dichloro(pentamethylcyclopentadienyl)rhodium(III) and -iridium(III)] with aromatic phosphine bearing a methoxy group at an ortho-position: double insertion of 1-alkynes into a Rh–O bond

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Abstract

Reactions of $[Cp^*MCl_2]_2$ (**1a**: M = Rh, **1b**: M = Ir; $Cp^* = C_5Me_5$) with 2-methoxyphenylphosphines at room temperature gave the corresponding $^1\eta$-P coordination complexes, $[Cp^*MCl_2(PPh_{3-n}R_n)]$ (**2**: $n = 1$; **4**: $n = 2$; **6b**: $n = 3$ for $R = C_6H_4$-2-MeO). Reaction of **1** with (2-methoxyphenyl)diphenylphosphine at reflux in diglyme underwent demethylation to afford Cp*MCl(MMMPP-*P*,*O*) (**3**) (M = Rh, Ir; MMMPP-*P*,*O* = *P*$Ph_2(C_6H_4$-2-*O*)) with a (*P*,*O*) chelating ligand. In the reaction with bis(2-methoxyphenyl)phenylphosphine, Cp*MCl(BMMPP-*P*,*O*) (**5**) (M = Rh, Ir; BMMPP-*P*,*O* = *P*Ph(C_6H_4-2-MeO)(C_6H_4-2-*O*)) was generated at reflux in a mixture of diglyme and MeOH. Tris(2-methoxyphenyl)phosphine reacted with **1a** at reflux in MeOH to give Cp*RhCl(TMMPP-*P*,*O*) (**7a**) (TMMPP-*P*,*O* = *P*$(C_6H_4$-2-MeO$)_2(C_6H_4$-2-*O*)), whereas the reaction with **1b** at reflux in EtOH generated Cp*Ir(TMMPP-*P*,*O*,*O′*) (**8b**) (TMMPP-*P*,*O*,*O′* = *P*(C_6H_4-2-MeO)$(C_6H_4$-2-*O*$)_2$) with a (*P*,*O*,*O′*) tridentate ligand. Crystal structural analyses of **3a**, **5a** and **8b** were carried out. Complex **3a** underwent a double insertion of alkyne into a Rh–O bond on treatment with phenylacetylene or *p*-tolylacetylene in the presence of KPF_6, giving [Cp*Rh{*P*$Ph_2(C_6H_4$-*O*-CR=CH–CH=*C*R}](PF_6) (**9a**: R = *p*-MeC_6H_4; **9b**: R = Ph) with a (*P*,*O*,*C*) tridentate ligand, in which X-ray crystal analysis of **9a** was performed.

Keywords: 2-Methoxyphenylphosphines; Bis[dichloro(pentamethylcyclopentadienyl)rhodium(III) and -iridium(III)]; P–O chelating ligand; Double insertion of alkyne

1. Introduction

We have reported that one or two of the *ortho*-methoxy groups in (2,6-dimethoxyphenyl)diphenylphosphine, bis(2,6-dimethoxyphenyl)phenylphosphine, and tris(2,6-dimethoxyphenyl)phosphine were demethylated in the reactions with bis[dichloro(η^6-arene)ruthenium(II)] [1] or bis[dichloro(η^5-pentamethylcyclopentadienyl)rhodium(III) or -iridium(III)] [2,3], giving (η^6-arene)RuCl(MDMPP-*P*,*O*), (η^6-arene)RuCl(TDMPP-*P*,*O*) (arene = *p*-cymene, 1,2,3-$Me_3C_6H_3$, 1,3,5-$Me_3C_6H_3$, and C_6Me_6; MDMPP-*P*,*O* = *P*$Ph_2(C_6H_3$-2-*O*-6-MeO), TDMPP-*P*,*O* = *P*{C_6H_3-2,6-(MeO$)_2$}$_2$(C_6H_3-2-*O*-6-MeO)), Cp*MCl(MDMPP-*P*,*O*), Cp*MCl(BDMPP-*P*,*O*) and Cp*M(TDMPP-*P*,*O*,*O′*) (M = Rh and Ir; $Cp^* = \eta^5$-C_5Me_5; BDMPP-*P*,*O* = *P*Ph{C_6H_3-2,6-(MeO$)_2$} (C_6H_3-2-*O*-6-MeO), TDMPP-*P*,*O*,*O′* = *P*{C_6H_3-2,6-(MeO$)_2$} (C_6H_3-2-*O*-6-MeO$)_2$) with bidentate (η^2-*P*,*O*) or tridentate (η^3-*P*,*O*,*O′*) chelating phosphines, respectively.

Recently, we reported that these (η^2-*P*,*O*) and (η^3-*P*,*O*,*O′*) chelating complexes of rhodium(III) and iridium(III) reacted readily with strongly electron-deficient olefin such as tetracyanoethylene and 7,7,8,8-tetracyano-*p*-quinodimethane, which inserted into weakly activated C–H bonds on the phenyl ring of the phosphine ligand [4]. In the reactions of alkynes with (η^2-*P*,*O*) chelating rhodium complexes in the presence of KPF_6, they underwent the single- or double insertion of alkyne into a Rh–O bond to generate five-, six- and seven-membered metallacycles, the transannular addition of alkyne between metal atom or *ipso*-carbon atom of the phosphine, and the insertion of alkyne into a

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metal–P bond, depending on the nature of the alkyne, the metal atom and the chelating phosphine ligand [5–7].

We were interested in chemistry of less bulky 2-methoxyphenylphosphines in comparison with 2,6-dimethoxyphenylphosphines. 2-Methoxyphenylphosphines are known to lead to O- or C-metallation with various metal complexes. Thus, 2-methoxyphenyl-di-t-butylphosphine, $PBu^t_2(C_6H_4OMe\text{-}2)$, in the reactions with platinum(II) complexes is metallated much more readily than $PPh_2(C_6H_4OMe\text{-}2)$, and $PMe_2(C_6H_4OMe\text{-}2)$ could not be metallated [8,9]. These metallations are promoted by steric effects.

We have now investigated the reactions of 2-methoxyphenylphosphines with bis[dichloro(pentamethylcyclopentadienyl)rhodium(III) or -iridium(III)], compared with 2,6-dimethoxyphenylphosphines, and performed the reaction of the resulting metallated complex with alkyne.

2. Experimental

All complexes were carried out under nitrogen atmosphere. Dichloromethane was distilled over CaH_2 and Et_2O was distilled over $LiAlH_4$. 2-Methoxyphenylphosphines [10] and $[Cp^*MCl_2]_2$ (M = Rh [11], Ir [7]; Cp* = C_5Me_5) were prepared according to the literature. The IR and electronic absorption spectra were measured on FT/IR-5300 and U-best 30 instruments, respectively. NMR spectroscopy was carried out on a Bruker AC250. The ^1H NMR spectra were measured at 250 MHz, and $^{31}P\{^1H\}$ NMR spectra were measured at 100 MHz using 85% H_3PO_4 as an external reference.

2.1. Reaction of **1a** with (2-methoxyphenyl)diphenylphosphine

2.1.1. At room temperature

A mixture of **1a** (0.300 g, 0.485 mmol) and (2-methoxyphenyl)diphenylphosphine (0.350 g, 1.20 mmol) was stirred in CH_2Cl_2 (30 ml) for 5 h. The solvent was removed in vacuo and the residue was washed with Et_2O. The solid was recrystallized from CH_2Cl_2 and Et_2O to give yellow crystals of $[Cp^*RhCl_2\{PPh_2(C_6H_4\text{-}2\text{-}MeO)\}]$ (**2a**) (0.375 g, 64.3%). UV–Vis (CH_2Cl_2): λ_{max} 408, 274 nm. ^1H NMR ($CDCl_3$): δ 1.32 (d, $J_{PH} = 4.0$ Hz, Cp*, 15H), 3.27 (s, MeO, 3H), 6.7–8.2 (m, ArH, 14H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 29.1 (d, $J_{RhP} = 142$ Hz). *Anal*. Calc. for $C_{29}H_{32}Cl_2OPRh$: C, 57.92; H, 5.36. Found: C, 58.16; H, 5.44%.

Complex **2b** (66.3%) was obtained according to a procedure similar to **1a**. UV–Vis (CH_2Cl_2): λ_{max} 350, 289 nm. ^1H NMR ($CDCl_3$): δ 1.32 (d, $J_{PH} = 2.0$ Hz, Cp*, 15H), 3.27 (s, MeO, 3H), 6.7–8.0 (m, ArH, 14H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 0.56 (s). *Anal*. Calc. for $C_{29}H_{32}Cl_2IrOP$: C, 50.43; H, 4.67. Found: C, 50.06; H, 4.55%.

2.1.2. At reflux

A mixture of **1a** (1.0 g, 1.62 mmol) and (2-methoxyphenyl)diphenylphosphine (1.04 g, 3.56 mmol) in diglyme (40 ml) was refluxed for 10 h. The solvent was removed in vacuo and the residue was washed with Et_2O. The solid was recrystallized from CH_2Cl_2 and Et_2O to give brown crystals of $[Cp^*RhCl\{PPh_2(C_6H_4\text{-}2\text{-}O)\}]$ (**3a**) (1.34 g, 74.9%). UV–Vis (CH_2Cl_2): λ_{max} 400 (sh), 334, 255 nm. ^1H NMR ($CDCl_3$): δ 1.50 (d, $J_{PH} = 3.0$ Hz, Cp*, 15H), 6.9–7.6 (m, ArH, 14H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 49.3 (d, $J_{RhP} = 142$ Hz). *Anal*. Calc. for $C_{28}H_{29}ClOPRh$: C, 61.05; H, 5.31. Found: C, 60.76; H, 5.40%. Complex **3b** (orange, 91.8%): UV–Vis (CH_2Cl_2): λ_{max} 330 nm. ^1H NMR ($CDCl_3$): δ 1.53 (d, $J_{PH} = 2.0$ Hz, Cp*, 15H), 6.5–8.0 (m, ArH, 14H). ^{31}P NMR ($CDCl_3$): δ 26.7 (s). *Anal*. Calc. for $C_{28}H_{29}ClIrOP$: C, 52.53; H, 4.57. Found: C, 52.23; H, 4.62%.

2.2. Reactions of **1a** or **1b** with bis(2-methoxyphenyl)phenylphosphine

2.2.1. At room temperature

A mixture of **1a** (0.30 g, 0.486 mmol) and bis(2-methoxyphenyl)phenylphosphine (0.356 mg, 1.10 mmol) in CH_2Cl_2 (15 ml) was stirred for 5 h at room temperature (r.t.) and the solvent was removed. The residue was chromatographed on alumina (containing 10% water) using CH_2Cl_2 as an eluent after washing of the residue with Et_2O. The eluate was concentrated and Et_2O was added to form orange–brown crystals of **4a** (0.486 g, 74.2%) contained CH_2Cl_2. UV–Vis (CH_2Cl_2): λ_{max} 408, 278 nm. ^1H NMR ($CDCl_3$): δ 1.35 (d, $J_{PH} = 2.5$ Hz, Cp*, 15H), 3.40 (b, MeO, 6H), 6.8–8.0 (m, ArH, 13H). ^{31}P NMR ($CDCl_3$): δ 26.0 (d, $J_{RhP} = 146$ Hz). *Anal*. Calc. for $C_{30}H_{34}Cl_2O_2PRh \cdot 0.5CH_2Cl_2$: C, 54.36; H, 5.24. Found: C, 54.02; H, 5.30%. Complex **4b** (64.3%) was prepared according to a procedure similar to **4a**. UV–Vis (CH_2Cl_2): λ_{max} 322, 287 nm. ^1H NMR ($CDCl_3$): δ 1.32 (d, $J_{PH} = 2.0$ Hz, Cp*, 15H), 3.38 (b, MeO, 6H), 6.8–7.9 (m, ArH, 13H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −1.50 (s). *Anal*. Calc. for $C_{30}H_{34}Cl_2IrO_2P$: C, 50.00; H, 4.76. Found: C, 50.02; H, 5.00%.

2.2.2. At reflux

A mixture of **1b** (0.610 g, 0.766 mmol) and bis(2-methoxyphenyl)phenylphosphine (0.538 mg, 1.699 mmol) was refluxed in diglyme (10 ml) and MeOH (30 ml) for 10 h. The solvent was removed in vacuo and the residue was washed with Et_2O. The solid was chromatographed on alumina (10% water), using CH_2Cl_2–MeOH (16:1) as an eluant. Yellow eluate was concentrated to give yellow solid of **5b** (0.683 mg, 66.5%). The solid was recrystallized from CH_2Cl_2 and Et_2O for purification. ^1H NMR ($CDCl_3$): δ 1.53 (d, $J_{PH} = 2.5$ Hz, Cp*, 15H), 3.78 (s, MeO, 3H), 6.4–7.9 (m, ArH, 13H). ^{31}P NMR ($CDCl_3$): δ 35.0 (s). *Anal*. Calc. for $C_{29}H_{31}ClIrO_2P$: C, 51.97; H, 4.66. Found: C, 52.31; H, 4.59%. Reddish–brown complex of **5a** (68.3%) were obtained as well as **5b**. UV–Vis (CH_2Cl_2): λ_{max} 338, 260 nm. ^1H NMR ($CDCl_3$): δ 1.52 (d, $J_{PH} = 3.0$ Hz, Cp*, 15H), 3.81 (s, MeO, 1H), 6.4–8.0 (m, ArH, 13H). ^{31}P NMR ($CDCl_3$): δ 48.7 (d, $J_{RhP} = 141$ Hz). *Anal*. Calc. for $C_{29}H_{31}ClO_2PRh$: C, 59.96; H, 5.38. Found: C, 60.02; H, 5.31%.

2.3. *Reaction of **1a** with tris(2-methoxyphenyl)phosphine*

A mixture of **1a** (0.150 g, 0.243 mmol) and tris(2-methoxyphenyl)phosphine (0.250 mg, 0.71 mmol) was stirred for 4 h at reflux in MeOH (20 ml). The solvent was removed in vacuo and the residue was washed with Et_2O. The solid was chromatographed on alumina (10% water), using CH_2Cl_2 as an eluant. Brown eluate was concentrated to give brown solid of [Cp*RhCl{*P*(C_6H_4-2-MeO)$_2$(C_6H_4-2-*O*)}] (**7a**) (0.683 g, 66.5%). UV–Vis (CH_2Cl_2): λ_{max} ca. 410 (sh), 366, 253 nm. ^1H NMR ($CDCl_3$): δ 1.53 (d, $J_{PH} = 2.5$ Hz, Cp*, 15H), 3.20 (bs, OMe, 6H), 3.72 (bs, OMe, 3H), 6.5–8.0 (m, ArH, 14H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 40.9 (d, $J_{RhP} = 155$ Hz). *Anal*. Calc. for $C_{30}H_{33}ClO_3PRh \cdot 0.25CH_2Cl_2$: C, 57.43; H, 5.37. Found: C, 57.98; H, 5.46%.

2.4. *Reaction of **1b** with tris(2-methoxyphenyl)phosphine*

2.4.1. *At room temperature*

A mixture of **1b** (0.230 g, 0.289 mmol) and tris(2-methoxyphenyl)phosphine (0.250 mg, 0.710 mmol) was stirred for 3 h at r.t. in CH_2Cl_2 (15 ml). The solvent was removed in vacuo and the residue was washed with Et_2O. The residue was recrystallized from CH_2Cl_2 and Et_2O, giving yellow crystals of **6b** (0.325 mg, 75%). UV–Vis (CH_2Cl_2): λ_{max} ca. 360 (sh), ca. 310, 287 nm. *Anal*. Calc. for $C_{31}H_{36}Cl_2IrO_3P$: C, 49.60; H, 4.83. Found: C, 49.62; H, 4.99%.

2.4.2. *At reflux*

A mixture of **1b** (0.150 g, 0.188 mmol) and tris(2-methoxyphenyl)phosphine (0.250 mg, 0.710 mmol) was stirred for 4 h at reflux in MeOH (20 ml). The solvent was removed in vacuo and the residue was washed with Et_2O. The solid was chromatographed on alumina (10% water), using CH_2Cl_2 as an eluant. Brown eluate was concentrated to give brown solid of [Cp*IrCl{*P*(C_6H_4-2-MeO)$_2$(C_6H_4-2-*O*)}] (**7b**) (0.149 mg, 56.6%). UV–Vis (CH_2Cl_2): λ_{max} 328, 289 nm. ^1H NMR ($CDCl_3$): δ 1.55 (d, $J_{PH} = 2.0$ Hz, Cp*, 15H), 3.21 (s, OMe, 6H), 3.73 (s, OMe, 3H), 6.4–7.5 (m, ArH, 14H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 34.5 (s). *Anal*. Calc. for $C_{30}H_{33}ClIrO_3P$: C, 51.46; H, 4.75. Found: C, 51.47; H, 4.80%.

The yellow solid [Cp*Ir*P*(C_6H_4-2-MeO)(C_6H_4-2-*O*)$_2$}] (**8b**) (18.9%) was generated by refluxing in EtOH for 0.5 h, followed by chromatography on alumina (10% water), using CH_2Cl_2 and C_6H_6 (4:1) as an eluant. ^1H MNR ($CDCl_3$): δ 1.53 (d, $J_{PH} = 2.0$ Hz, Cp*, 15H), 3.20 (s, MeO, 3H), 6.4–7.8 (m, ArH, 13H). ^{31}P NMR ($CDCl_3$): δ 20.8 (s). *Anal*. Calc. for $C_{29}H_{30}IrO_3P \cdot 0.5CH_2Cl_2$: C, 51.19; H, 4.51. Found: C, 51.60; H, 4.87%.

2.5. *Reaction of **3a** with p-tolylacetylene*

A mixture of **3a** (0.050 mg, 0.091 mmol), tolylacetylene (0.10 ml, 0.91 mmol) and KPF_6 (0.167 mg, 0.91 mmol) was stirred in CH_2Cl_2 (15 ml) and C_3H_6O (10 ml) at r.t. After 48 h, the solvent was removed and the residue was extracted with CH_2Cl_2 and the solution was filtered with a glass filter. After the solvent was removed, the residue was washed with Et_2O and recrystallized from CH_2Cl_2–MeOH–Et_2O, giving reddish–brown crystals of **9a** (0.029 mg, 35.3%). FAB mass (*m*/*z*): 747 [M^+]. IR (Nujol): 1574 (C=C), 841 (PF_6) cm^{-1}. UV–Vis (CH_2Cl_2): λ_{max} 365 nm. ^1H MNR ($CDCl_3$): δ 1.39 (d, $J_{PH} = 2.5$ Hz, Cp*, 15H), 2.15 (s, *p*-Me, 3H), 2.44 (s, *p*-Me, 3H), 6.30 (d, $J_{HH} = 7.5$ Hz, 1H), 6.46 (d, $J_{HH} = 7.5$ Hz, 1H), 6.7–7.7 (m, ArH, 22H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 37.4 (d, $J_{RhP} = 158$ Hz), −140.2 (sep, $J_{PF} = 712$ Hz). *Anal*. Calc. for $C_{46}H_{45}F_6OP_2Rh \cdot 0.5CH_2Cl_2$: C, 59.72; H, 4.96. Found: C, 59.25; H, 4.95%. Analogously, reddish–brown complex **9b** was prepared by the reaction of **3a** with phenylacetylene. FAB mass (*m*/*z*): 719 [$M^+ - 1$]. IR (Nujol): 1575 (C=C), 839 (PF_6) cm^{-1}. UV–Vis (CH_2Cl_2): λ_{max} 257 nm. ^1H NMR ($CDCl_3$): δ 1.39 (d, $J_{PH} = 2.7$ Hz, Cp*, 15H), 6.31 (d, $J_{HH} = 7.5$ Hz, 1H), 6.44 (d, $J_{HH} = 7.5$ Hz, 1H), 6.8–7.7 (m, ArH, 24H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 37.3 (d, $J_{RhP} = 163$ Hz), −140.0 (sep, $J_{PF} = 712$ Hz). *Anal*. Calc. for $C_{44}H_{41}F_6OP_2Rh \cdot 0.5CH_2Cl_2$: C, 56.92; H, 4.56. Found: C, 56.94; H, 4.61%.

2.6. *Data collection*

All complexes were recrystallized from C_3H_6O/Et_2O or CH_2Cl_2/ether. Cell constants were determined from 20 reflections on Rigaku four-circle automated diffractometer AFC5S. The crystal parameters along with data collections are summarized in Table 1S (see Section 5). Data collection was carried out by a Rigaku AFC5S refractometer at 27 °C. Intensities were measured by the $2\theta-\omega$ scan method using Mo Kα radiation ($\lambda = 0.71069$ Å). Throughout the data collection the intensities of the three standard reflections were measured every 200 reflections as a check of the stability of the crystals and no decay was observed. Intensities were corrected for Lp effects. The absorption correction was made with the ψ scan methods. Atomic scattering factors were taken from the usual tabulation of Cromer and Waber [12]. Anomalous dispersion effects were included in Fcalc [13]; the values of $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley [14]. All calculations were performed using the TEXSAN crytallographic software package [15].

2.7. Determination of the structures

The structures of **3a**, **5a**, **8b** and **9a** were solved by Patterson methods (DIRDIF92 PATTY). The positions of all non-hydrogen atoms of **8b** and **9a** were refined with anisotropic thermal parameters by using full-matrix least-square methods. Heteroatoms (four atoms) and fifteen carbon atoms for **3a** and heteroatoms (five atoms) and sixteen carbon atoms for **5a** were refined anisotropically and other non-hydrogen atoms were refined isotropically. All hydrogen atoms were calculated at the ideal positions with the C–H distance of 0.95 Å. Complex **8b** consists of two independent molecules.

3. Results and discussion

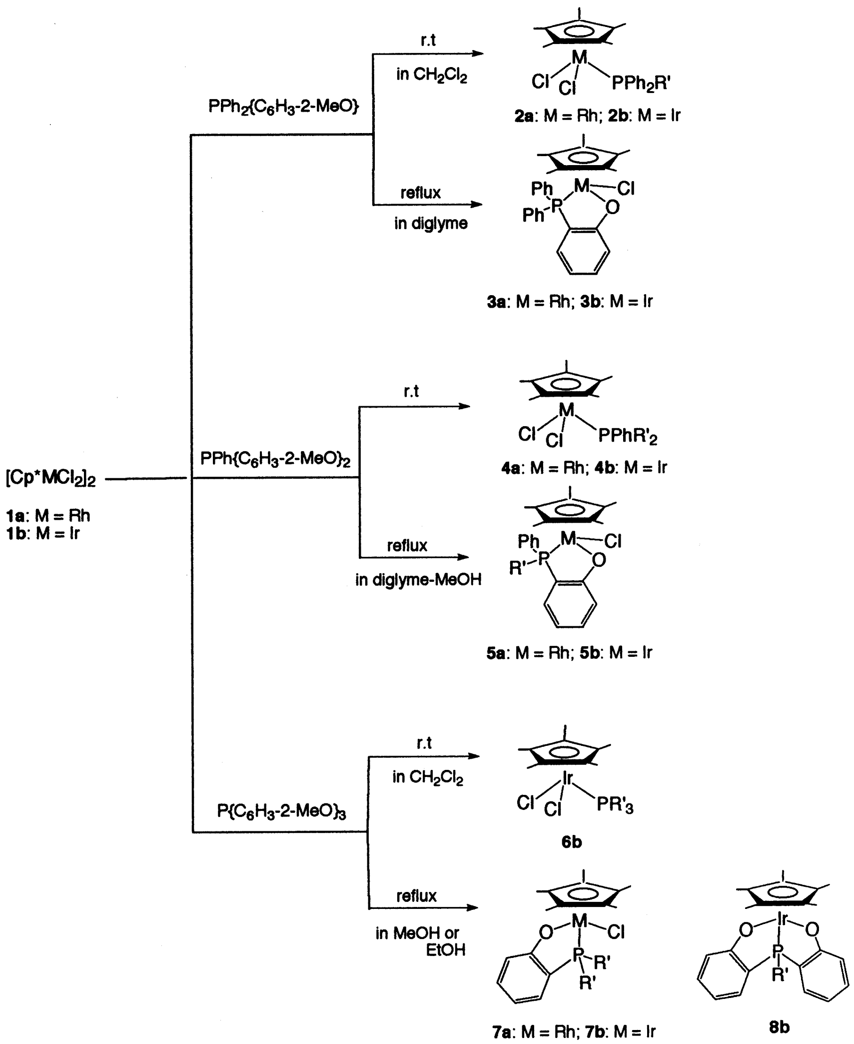
3.1. Reactions of [Cp*$MCl_2]_2$ with 2-methoxyphosphines

When **1a** and **1b** were treated with (2-methoxyphenyl)diphenylphosphine in CH_2Cl_2 at room temperature, the cleavage of bridged Cl atoms readily occurred to give yellow complexes [Cp*MCl_2\{*P*$Ph_2(C_6H_4$-2-MeO)\}] (**2a**: M = Rh; **2b**: M = Ir) in ca. 65% yield (Scheme 1). The ^1H NMR spectra showed two characteristic resonances at approximately δ 1.3 as a doublet and 3.3 as a singlet, assignable to Cp* and methoxy protons, respectively. The $^{31}P\{^1H\}$ NMR spectra showed a doublet at δ 29.1 for **2a** and a singlet at δ 0.56 for **2b**. These chemical shift values shifted to down-field by 44.9 ppm for **2a** and 16.4 ppm for **2b** from that (δ −15.8) of the parent phosphine. Similar down-field shifts have been observed in (2,6-dimethoxylphenyl)diphenylphosphine complexes [1–3]. Treatment at reflux in diglyme led to demethylation of an *ortho*-methoxy group of aromatic phosphine ligand, giving metal complexes with a (*P*,*O*)-chelating phosphine, [Cp*MCl\{*P*$Ph_2(C_6H_4$-2-*O*)\}] (**3a**: M = Rh; **3b**: M = Ir). The ^1H NMR spectra showed a characteristic signal at δ ca. 1.50, assignable to Cp* protons. The $^{31}P\{^1H\}$ NMR spectra showed a doublet at δ 49.3 for **3a** and a singlet at δ 26.7 for **3b**. The X-ray analysis of **3a** revealed that the rhodium atom is surrounded by P, Cl and O atoms in addition to Cp* moiety (Fig. 1 and Table 1). The bite P(1)–Rh(1)–O(1) angle is 79.7(6)° (Table 1). The Rh(1)–Cl(1), Rh(1)–P(1) and Rh(1)–O(1) bond lengths are 2.368(7), 2.293(6) and 2.13(2) Å, respectively.

Reaction with bulky bis(2-methoxyphenyl)phenylphosphine was carried out at room temperature, giving a η^1-P coordination complex, [Cp*MCl_2\{*P*$Ph(C_6H_4$-2-$MeO)_2$\}] (**4a**: M = Rh; **4b**: M = Ir). The reaction at reflux in dyglyme (10 ml) and MeOH (30 ml) generated a (*P*,*O*)-chelating complexes [Cp*MCl\{*P*$Ph(C_6H_4$-2-MeO)$(C_6H_4$-2-*O*)\}] (**5a**: M = Rh; **5b**: M = Ir). The ^1H NMR spectra of **4** showed two characteristic resonances at δ ca. 1.35 as a doublet and at δ ca. 3.40 as a singlet, assignable to Cp* and methoxy protons, respectively. The $^{31}P\{^1H\}$ NMR spectra showed a doublet at δ 26.0 for **4a** and a singlet at δ −1.50 for **4b**. These chemical shift values shifted to down-field by 52.9 ppm for **4a** and 25.4 ppm for **4b** from that (δ −26.9) of the parent phosphine.

Since the phosphine ligand of **5** is bidentate, binding through P and σ-bonded O atoms, the molecule has two chiral centers (metal and P atoms). The detailed structure was confirmed by X-ray analysis of **5a** (Fig. 2 and Table 2). A priority order of the ligand is aromatic ring > Cl > P > O for a metal center and Rh > 2-O-C_6H_4 > 2-$MeOC_6H_4$ > Ph for a P center. Fig. 2 showed that the molecule is a Rh_RP_R/Rh_SP_S pair. The ^1H NMR spectrum of **5a** showed the presence of only one diastereomer. The $^{31}P\{^1H\}$ NMR spectrum also supported the presence of one diastereomer, showing a doublet at δ 48.7. These NMR spectra showed that the structure in solution is similar to that in the solid state. However, we cannot rule out occurrence of rapid exchange between two diastereomers. A similar behavior was observed for the iridium complex **5b**.

When **1a** was treated with much bulky tri(2-methoxyphenyl)phosphine at reflux in MeOH, brown crystals of [Cp*RhCl\{*P*$(C_6H_4$-2-$MeO)_2(C_6H_4$-2-*O*)\}] (**7a**) were obtained. The ^1H NMR spectrum showed a doublet at δ 1.52 and two singlets at δ 3.20 and 3.72(b), assignable to Cp* and methoxy protons, respectively. The inequivalence for the methoxy protons is assumed to arise from the presence of a chiral center of the P atom, however, it cannot rule out the restricted rotation of the C_6H_3-2-OMe) ring about the P–C axis. Reaction with iridium complex **1b** at room temperature generated yellow complex of [Cp*$IrCl_2$\{*P*(2-$MeOC_6H_4)_3$\}] (**6b**), whereas reactions at reflux in MeOH or EtOH gave a (*P*,*O*)-chelating complex [Cp*IrCl\{*P*$(C_6H_4$-2-$MeO)_2(C_6H_4$-2-*O*)\}] (**7b**), and a (*P*,*O*,*O′*)-chelating one, [Cp*Ir\{*P*$(C_6H_4$-2-MeO)$(C_6H_4$-2-*O*$)_2$\}] (**8b**). The $^{31}P\{^1H\}$ NMR spectra of **7b** and **8b** showed singlets at δ 34.5 and 20.8, again shifting to down-field by 73.2 and 59.5 ppm from that (δ −38.7) of free phosphine, respectively. The structure of **8b** was confirmed by X-ray analyses (Fig. 3 and Table 3). The iridium atom is coordinated by a tridentate (*P*,*O*,*O′*)-chelating ligand.



Scheme 1. Reactions of $[Cp^*MCl_2]_2$ with 2-methoxyphenylphosphines ($R' = C_6H_3$-2-MeO).

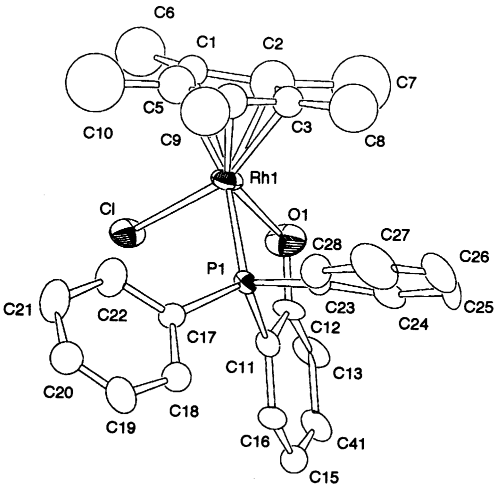


Fig. 1. Molecular structure of **3a**.

The Ir(1)–P(1), Ir(1)–O(1) and Ir(1)–O(2) bond lengths are 2.266(4), 2.10(1) and 2.09(1) Å, respectively. The Ir–Cl bond lengths are somewhat shorter than that (2.281(3) Å) found in $[Cp^*Ir\{P(C_6H_3\text{-}2,6\text{-}(MeO)_2)(C_6H_3\text{-}2\text{-}O\text{-}6\text{-}MeO)_2\}]$ bearing a similar structure [3].

In complexes **2**–**7**, the chemical shift values of Cp* protons and coordinated P atom in η^2-complexes appeared at lower fields than those of the corresponding η^1-P complexes, being a result of high electron-withdrawing ability of the phenoxide-oxygen atom. The difference of the ^{31}P chemical shift value between complex and free phosphine increased with the number of 2-methoxyphenyl substituent of the phosphine for η^1-P complexes (**2**, **4** and **6**) and (*P*,*O*)-chelating complexes (**3**, **5** and **7**), suggesting that the electron-donating ability increases with the number of the methoxy group in the phosphine. It is greater in rhodium(III) complexes than iridium(III) ones, indicating that the rhodium atom is greater in acceptability of electron pair than the iridium atom.

Table 1
Selected bond lengths (Å) and angles (°) of [Cp*RhCl{(MMMPP-*P*,*O*)] (**3a**)

Bond lengths					
Rh(1)–Cl(1)	2.368(7)	Rh(1)–P(1)	2.293(6)	Rh(1)–O(1)	2.13(2)
O(1)–C(12)	1.30(3)	C(11)–C(12)	1.44(3)	P(1)–C(11)	1.78(2)
Bond angles					
Cl(1)–Rh(1)–P(1)	89.5(2)	Cl(1)–Rh(1)–O(1)	83.3(6)	P(1)–Rh(1)–O(1)	79.7(6)
Rh(1)–O(1)–C(12)	121.0(1)	O(1)–C(12)–C(11)	118.0(2)	P(1)–C(11)–C(12)	114.0(1)
Rh(1)–P(1)–C(11)	101.0(8)				

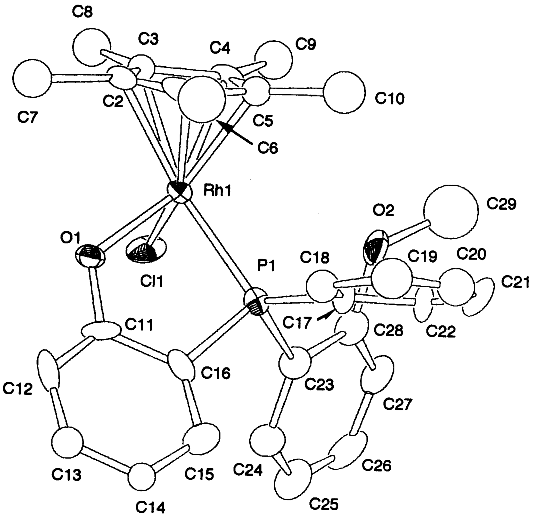


Fig. 2. Molecular structure of **5a**.

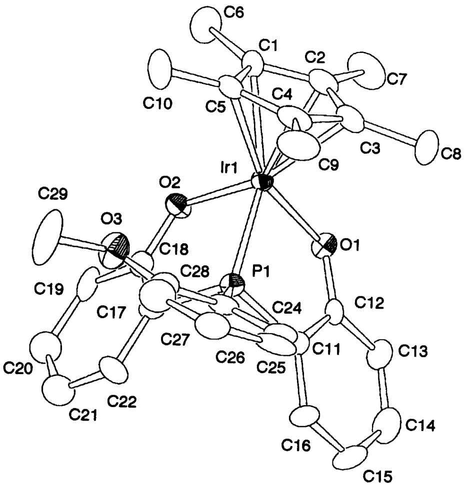


Fig. 3. Molecular structure of **8b**. (Only one molecule for clarity.)

3.2. Reaction of **3a** with 1-alkyne

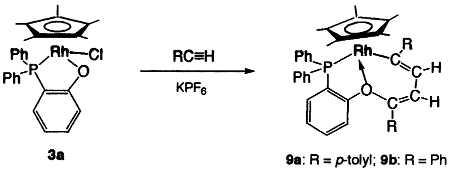
Previously, we have reported that reaction of [Cp*RhCl{PPh$_2$(C$_6$H$_3$-2-*O*-6-MeO)}] bearing a (*P*,*O*) chelating ligand with phenylacetylene in the presence of KPF$_6$ led to a head-to-head double insertion of phenylacetylene into the Rh–O σ-bond to generate the complex [Cp*Rh{*P*Ph$_2$(C$_6$H$_3$-2-(*O*–CPh=CH–CH=*C*Ph)–6-MeO)}](PF$_6$) (**10**) bearing a (*P*,*O*,*C*) tridentate ligand consisting of six- and five-membered rings sharing the rhodium atom [5,7]. A similar reaction with **3a** bearing less bulky (*P*,*O*)-chelating ligand was carried out. When **3a** was treated with *p*-tolylacetylene in the presence of KPF$_6$, reddish–brown crystals **9a** with an empirical formula as [Cp*Rh{PPh$_2$(C$_6$H$_3$-2-*O*-6-MeO)}]·(*p*-tolylC=CH)$_2$·PF$_6$ (*p*-tolyl = 4-MeC$_6$H$_4$) from elementary analysis and FAB mass spectrometry were isolated (Scheme 2). The detailed structure was determined by X-ray analysis (Fig. 4 and Table 4). A rhodium atom is surrounded by a (*P*, *O*, *C*) tridentate ligand resulting from a head-to-head double insertion of 1-alkyne into the Rh–O bond (Fig. 4). Two carbon atoms bearing a *p*-tolyl group are connected to the rhodium and oxygen atoms. The molecule contains the five- and six-membered rings through coordination of an ether-O atom. The Rh(1)–O(1) coordination bond length of 2.241(4) Å is ca. 0.11 Å longer than that of **3a**, as expected for ether coordination as opposed to a phenoxide. The Rh–P(1) and Rh–C(39) bond lengths are 2.301(2),and 2.104(6) Å, respectively, not being significantly different from the corresponding bond

Table 2
Selected bond lengths (Å) and angles (°) of [Cp*RhCl{(BMMPP-*P*,*O*)] (**5a**)

Bond lengths					
Rh(1)–Cl(1)	2.402(8)	Rh(1)–P(1)	2.315(8)	Rh(1)–O(1)	2.08(2)
O(1)–C(111)	1.35(3)	C(11)–C(16)	1.47(4)	P(1)–C(16)	1.87(3)
Bond angles					
Cl(1)–Rh(1)–P(1)	88.8(3)	Cl(1)–Ir(1)–O(1)	90.0(6)	P(1)–Rh(1)–O(1)	83.2(6)
Rh(1)–O(1)–C(111)	123.0(1)	O(1)–C(11)–C(16)	118.0(2)	C(11)–C(16)–P(1)	114.0(2)
Rh(1)–P(1)–C(16)	100.6(10)				

Table 3
Selected bond lengths (Å) and angles (°) of [Cp*Ir(TMMPP-*P*,*O*,*O′*)]·2H_2O **8b**·2H_2O

Bond lengths					
Ir(1)–P(1)	2.266(4)	Ir(1)–O(1)	2.10(1)	Ir(1)–O(2)	2.09(1)
O(1)–C(12)	1.32(2)	C(12)–C(11)	1.44(2)	P(1)–C(11)	1.80(2)
O(2)–C(18)	1.33(2)	C(18)–C(17)	1.44(2)	P(1)–C(17)	1.80(2)
Ir(2)–P(2)	2.277(5)	Ir(2)–O(4)	2.11(1)	Ir(2)–O(5)	2.11(1)
O(4)–C(41)	1.30(2)	C(40)–C(41)	1.41(2)	P(2)–C(40)	1.78(2)
O(5)–C(47)	1.33(2)	C(47)–C(46)	1.38(2)	P(2)–C(46)	1.82(2)
Bond angles					
P(1)–Ir(1)–O(1)	81.7(3)	P(1)–Ir(1)–O(2)	81.4(3)	O(1)–Ir(1)–O(2)	86.1(5)
Ir(1)–O(1)–C(12)	120.0(1)	O(1)–C(12)–C(11)	121.0(1)	C(12)–C(11)–P(1)	112.0(1)
Ir(1)–P(1)–C(11)	102.3(6)	Ir(1)–P(1)–C(17)	103.9(6)	P(1)–C(17)–C(18)	110.0(1)
O(2)–C(18)–O(17)	123.0(1)	Ir(1)–O(2)–C(18)	119.0(1)	C(11)–P(1)–C(17)	103.2(8)
P(2)–Ir(2)–O(4)	80.1(3)	P(2)–Ir(2)–O(5)	81.4(4)	O(4)–Ir(2)–O(5)	87.6(5)
Ir(2)–O(4)–C(41)	121.0(1)	O(4)–C(41)–C(40)	119.0(1)	C(41)–C(40)–P(2)	114.0(1)
Ir(2)–P(2)–C(40)	101.8(7)	Ir(2)–P(2)–C(46)	102.7(6)	P(2)–C(46)–C(47)	112.0(1)
O(5)–C(47)–O(46)	123.0(1)	Ir(2)–O(5)–C(47)	119.0(1)	C(40)–P(2)–C(46)	104.1(8)



Scheme 2. Reaction of **3a** with alkyne.

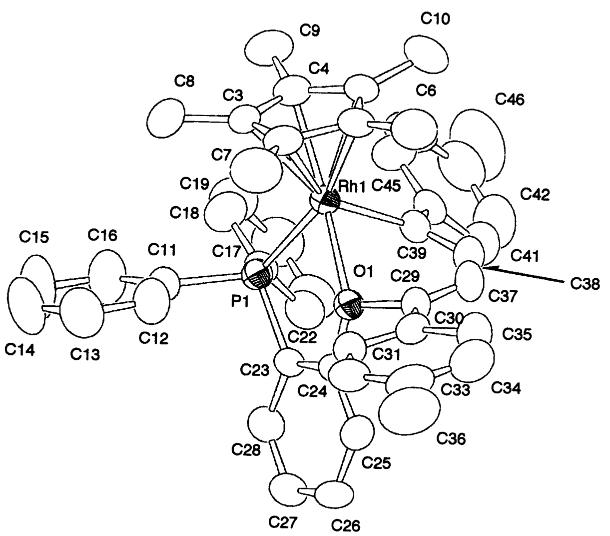


Fig. 4. Molecular structure of **9a**.

length for **10**. The P(1)–Rh(1)–O(1) bite angle of the five-membered ring were 79.5(1)°, and the O(1)–Rh(1)–C(39) bite angle of the six-membered ring are 81.4(2)°. These angles are independent of the ring-size. The P(1)–Rh(1)–C(39) bond angle of 91.0(2)° is wider by ca. 10° than those of five- and six-membered rings. Similar trend has been noted in **10**. The average length of two double bonds, C(29)–C(37) and C(38)–C(39), in the metallacyclohexadiene rings is ca. 1.34 Å, being shorter than the C(37)–C(38) single bond and in usual C–C double bonds.

The ^1H NMR spectrum showed a doublet at δ 1.39 due to Cp* protons and two singlets at δ 2.16 and 2.44, assignable to *p*-methyl protons. The CH= protons appeared at δ 6.29 and 6.46 as doublets. The $^{31}P\{^1H\}$ NMR spectra showed a doublet at δ 37.4. The PF_6 anion was confirmed by $^{31}P\{^1H\}$ NMR and IR spectrometry.

Analogously, complex [Cp*Rh{*P*Ph$_2$(C_6H_3-2-(*O*-CPh=CH–CH=*C*Ph))}](PF$_6$) (**9b**) was obtained in the reaction of **3a** with phenylacetylene.

4. Summary

2-Methoxyphenylphosphines underwent demethylation of one or two methyl groups on the phenyl rings in the reactions with [Cp*MCl$_2$]$_2$. These reactions are similar to the reactions with much more bulky 2,6-dimethylphenylphosphines, however the reactivity of 2-methyoxyphenyl phosphines are lower than that of 2,6-dimethoxyphenylphosphines. Thus, demethylation is promoted by steric effects. A double insertion of the alkyne into a Rh–O bond was found to occur in spite of the presence or absence of the 6-methoxy substituent on the phenyl rings. Reactions of small molecules for the (*P*,*O*) chelating complexes are in progress.

5. Supplementary material

A listing of atomic coordinates, thermal parameters, bond lengths, angles and torsion angles, and Table 1S, are available from the authors on request.

Table 4
Selected bond lengths (Å) and angles (°) of [Cp*Rh{PPh$_2$(C$_6$H$_4$-2-(*O*–C(*p*-tolyl)=CH–CH=C(*p*-tolyl))}](PF$_6$) (**9a**)

Bond lengths					
Rh(1)–P(1)	2.301(2)	Rh(1)–O(1)	2.241(4)	Rh(1)–C(39)	2.104(6)
O(1)–C(29)	1.452(7)	C(29)–C(37)	1.320(10)	C(37)–C(38)	1.43(1)
C(38)–C(39)	1.358(9)	P(1)–C(23)	1.819(6)	C(23)–C(24)	1.375(8)
O(1)–C(24)	1.416(7)				
Bond angles					
O(1)–Rh(1)–P(1)	79.5(1)	O(1)–Rh(1)–C(39)	81.4(2)	P(1)–Rh(1)–C(39)	91.0(2)
Rh(1)–O(1)–C(24)	119.0(3)	O(1)–C(24)–C(23)	116.9(5)	P(1)–C(23)–C(24)	118.6(4)
Rh(1)–P(1)–C(23)	102.8(2)	Rh(1)–O(1)–C(29)	112.5(3)	O(1)–C(29)–C(37)	114.5(6)
C(29)–C(37)–C(38)	128.1(7)	C(37)–C(38)–C(39)	129.5(7)	Rh(1)–C(39)–C(38)	115.6(6)

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