ELSEVIER

Journal of Organometallic Chemistry 561 (1998) 157–165

Journal of Organometallic Chemistry

# ($\eta^5$-Pentamethylcyclopentadienyl)rhodium(III) complexes bearing $\eta^1$-P and $\eta^2$-phosphino-phenoxide coordinations derived from (2,6-dimethoxyphenyl)diphenylphosphine: their preparation and reactions with Lewis bases

Xiao-Hong Han, Yasuhiro Yamamoto *

*Department of Chemistry, Faculty of Science, Toho University, Miyama 2-2-1, Funabashi, Chiba 274, Japan*

Received 24 December 1997; received in revised form 25 February 1998

**Abstract**

Reaction of $[Cp^*RhCl_2]_2$ with (2,6-dimethoxyphenyl)diphenylphosphine (MDMPP) gave $Cp^*RhCl_2$(MDMPP-*P*) **2** and $Cp^*RhCl$(MDMPP-*P*,*O*) **5**, depending on the reaction conditions. Treatment of **2** with $NaPF_6$ formed the O-coordination complex, [Cp*RhCl(MDMPP-*P*,*O*Me)]($PF_6$) **3**. Complex **3** was reconverted to **2** by treatment with $[N(CH_2Ph)Et_3]Cl$. Reactions of **3** with isocyanide, carbon monoxide or $P(OCH_2)_3CMe$ eliminated the O-coordination to give the corresponding complexes [Cp*RhCl(MDMPP-*P*)(L)]($PF_6$) **4** (L = CO (**a**), 2,6-$Me_2C_6H_3NC$ (**b**), *p*-$TosCH_2NC$ (**c**), and $P(OCH_2)_3CMe$) (**d**). Complex **5** reacted with Lewis bases (L) in the presence of $NaPF_6$ to produce [Cp*Rh(MDMPP-*P*,*O*)(L)]($PF_6$) **6** and could be also obtained from **3** and MDMPP. The CO ligand of **4a** or **6a** was labile and was replaced with isocyanide or phosphine to produce the corresponding complexes, whereas its reverse reaction did not occur. Conversion of **4d** to **6d** was also observed, but conversion from **4** to **6** did not occur in other complexes. X-ray analyses of **2**, **4a**, **5** and **6a**·$C_6H_6$ were performed and showed that the complexes have the piano-stool structure; **2**: triclinic, P1 (no. 2), $a = 10.639(3)$, $b = 15.965(3)$, $c = 8.800(3)$ Å, $\alpha = 94.43(2)$, $\beta = 103.75(3)$, $\gamma = 88.62(2)°$, $V = 1447.4(7)$ Å$^3$, $Z = 2$, $R = 0.039$, $R_w = 0.042$; **4c** (L = *p*-$TosCH_2NC$): orthorhombic, $Pna2_1$ (no. 33), $a = 26.817(4)$, $b = 17.662(5)$, $c = 8.673(4)$ Å, $V = 4108(1)$ Å$^3$, $Z = 4$, $R = 0.040$, $R_w = 0.042$; **5**: orthorhombic, *Pbca* (no. 61), $a = 8.212(8)$, $b = 17.808(10)$, $c = 35.96(1)$ Å, $V = 5259(4)$ Å$^3$, $Z = 8$, $R = 0.040$, $R_w = 0.042$; **6a**·$C_6H_6$ (L = CO): monoclinic, $C2/c$ (no. 15), $a = 33.29(2)$, $b = 8.567(5)$, $c = 29.26(3)$ Å, $\beta = 124.51(3)°$, $V = 6877(7)$ Å$^3$, $Z = 8$, $R = 0.040$, $R_w = 0.042$. 

*Keywords:* (2,6-Dimethoxyphenyl)diphenylphosphine; Bis[dichloro(pentamethylcyclopentadienyl) rhodium(II); Crystal structures; P–O chelating ligand

## 1. Introduction

The introduction of ether–phosphine species, instead of classical phosphines, plays an important role as an anchor to prepare intramolecular solvent complexes which are much more stable than simple solvent molecules [1]. A weak metal–oxygen bond provides as a condition of valuable precursors in catalytically-operating process. Aromatic phosphines containing the alkoxy groups at the 2- and 6-positions are one of the categories in the ether–phosphine species. Tris(2,4,6-trimethoxyphenyl)phosphine (TMPP) has produced the complexes containing a variety of coordination modes such as ($\eta^1$-*P*), ($\eta^2$-*P*,*O*Me), ($\eta^2$-*P*,*O*), and ($\eta^3$-*P*,*O*,*O*Me) [2], because of its high basicity and large cone angle [3]. Tris(2,6-dimethoxyphenyl)phosphine (TDMPP) and its related phosphines such as bis(2,6-dimethoxyphenyl)phenylphosphine (BDMPP) and (2,6-dimethoxyphenyl)diphenylphosphine (MDMPP) also showed interesting chemical behavior. Recently we have

* Corresponding author. Fax: +81 474 751855.

0022-328X/98/$19.00 
*PII* S0022-328X(98)00523-3

carried out the systematic reactions of bis[dichloro($\eta^6$-arene)ruthenium(II)] with these phosphines (TDMPP, BDMPP, and MDMPP) [4]. We reported that the reaction with TDMPP gave the complexes ($\eta^6$-arene)Ru[P(2-O-6-$MeOC_6H_3$)$_2$(2,6-$(MeO)_2C_6H_3$)] having new type of trihapto-(*P*,*O*,*O*) coordination and that the reaction with BDMPP or MDMPP formed the dihapto-(*P*,*O*) complex, ($\eta^6$-arene)RuCl[P(2-O-6-$MeOC_6H_3$)(2,6-$(MeO)_2C_6H_3$)Ph] and the monohapto-(*P*) one, ($\eta^6$-arene)$RuCl_2$[$PPh_2$(2,6-$(MeO)_2C_6H_3$)], respectively. Complexes prepared in these reactions have been obtained as a result of the direct formation.

Our research was extended to bis[dichloro($\eta^5$-pentamethylcyclopentadienyl)rhodium(III)] [Cp*$RhCl_2$]$_2$ **1**, which has an isoelectronic structure. In the reactions of **1** with MDMPP, we could isolate the ($\eta^1$-*P*), ($\eta^2$-*P*,*O*Me) and ($\eta^2$-*P*,*O*) coordinated complexes of ($\eta^5$-pentamethylcyclopentadienyl)rhodium(III). We found that the stepwise conversion from the ($\eta^1$-*P*) to the phosphino–phenoxido complexes occurred and these complexes showed versatile reactivities to Lewis bases. Here we wish to report the preparations and reactions of monohapto-($\eta^1$-*P*) and dihapto-(*P*,*O*Me) and (*P*,*O*) chelated complexes derived from a MDMPP ligand.

## 2. Experimental

All reactions were carried out under nitrogen atmosphere. Complex **1** [5], MDMPP [3], P$(OCH_2)_3$CMe [6], and xylyl isocyanide [7] were prepared according to the literature. *p*-$TosCH_2NC$ (*p*-Tos = *p*-$MeC_6H_4SO_2$) and (*p*-tolyl)$_3$P (*p*-tolyl = *p*-$MeC_6H_4$) were available commercially. Toluene, $CH_2Cl_2$ and other solvents were distilled over $CaH_2$. The IR 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 at 100 MHz using 85% $H_3PO_4$ as an external reference.

### 2.1. Reaction of *1* with MDMPP

To a solution of **1** (82.8 mg, 0.134 mmol) in $CH_2Cl_2$ (15 ml) was added MDMPP (108.2 mg, 0.334 mmol) at room temperature (r.t.). After the mixture was stirred for 2 h, the solvent was removed to ca. 3 ml under reduced pressure and hexane was added to the solution to give dark red crystals of [Cp*$RhCl_2$(MDMPP-*P*)] **2** (150.4 mg, 89%). IR (nujol): 1575 $cm^{-1}$. UV–vis ($CH_2Cl_2$): $\lambda_{max}$ 404 (log $\varepsilon$ 3.94), 278 (log $\varepsilon$ 4.46) nm. $^1$H-NMR ($CDCl_3$): $\delta$ 1.15 (d, $J_{PH}$ = 3.5 Hz, $C_5Me_5$), 3.28 (s, O*Me*), 6.4–7.7 (m, *Ph*) ppm. $^{31}$P{$^1$H}-NMR ($CDCl_3$): $\delta$ 23.6 (d, $J_{RhP}$ = 150.9 Hz) ppm. Anal. Calc. for $C_{30}H_{34}O_2Cl_2PRh$: C, 57.07; H, 5.43. Found: C, 56.65; H, 5.12%.

### 2.2. Reaction of *2* with $NaPF_6$

To a solution of **2** (125 mg, 0.198 mmol) in $CH_2Cl_2$ (10 ml)/acetone (5 ml) was added $NaPF_6$ (60 mg, 0.357 mmol) at r.t. After 4 h, the solvent was removed and the residue was extracted with $CH_2Cl_2$. The solvent was removed to ca. 3 ml and hexane was added to give red crystals of [Cp*RhCl(MDMPP-*P*,*O*Me)]($PF_6$) **3** (132 mg, 86%). IR (nujol): 1585, 1537, 835 ($PF_6$) $cm^{-1}$. UV–vis ($CH_2Cl_2$): $\lambda_{max}$ 365, 285 nm. $^1$H-NMR ($CDCl_3$): $\delta$ 1.50 (d, $J_{PH}$ = 3.0 Hz, $C_5Me_5$), 3.88 (s, O*Me*), 6.7–7.7 (m, *Ph*) ppm. $^{31}$P{$^1$H}-NMR ($CDCl_3$): $\delta$ 37.8 (d, $J_{RhP}$ = 146.5 Hz), −143.9 (sep, $J_{PF}$ = 708.8 Hz) ppm. Anal. Calc. for $C_{30}H_{34}O_2ClF_6P_2Rh$: C, 48.63; H, 4.63. Found: C, 48.62; H, 4.32%.

This complex was also prepared from the stoichiometric reaction of **1** with MDMPP in the presence of $NaPF_6$.

### 2.3. Reaction of *3* with [(PhCH$_2$)Et$_3$N]Cl

A solution of **3** (16 mg, 0.022 mmol) and benzyltriethylammonium chloride (4.6 mg, 0.025 mmol) in $CH_2Cl_2$ (10 ml) was stirred at r.t. for 3 h. The precipitate was filtered off and the solvent was removed to ca. 3 ml from the filtrate and ether was added to give **2** (6.42 mg, 78%).

### 2.4. Reaction of *3* with CO

Carbon monoxide was bubbled for 3 min through a solution of **3** (61.5 mg, 0.083 mmol) in $CH_2Cl_2$ (10 ml) at r.t. After the mixture had been stirred for 2 h, the solvent was removed under reduced pressure, and the residue was recrystallized from $CH_2Cl_2$ and hexane to give orange crystals (44.3 mg, 86%) of [Cp*RhCl(MDMPP-*P*)(CO)]($PF_6$)·0.5$CH_2Cl_2$ **4a**·0.5$CH_2Cl_2$. IR (nujol): 2071 (C≡O), 1583, 835 ($PF_6$) $cm^{-1}$. UV–vis ($CH_2Cl_2$): $\lambda_{max}$ 366, 286 nm. $^1$H-NMR ($CDCl_3$): $\delta$ 1.50 (d, $J_{PH}$ = 3.0 Hz, $C_5Me_5$), 3.88 (s, O*Me*), 5.27 (s, C$H_2Cl_2$), 6.7–7.7 (m, *Ph*) ppm. $^{31}$P{$^1$H}-NMR ($CDCl_3$): $\delta$ 20.2 (d, $J_{RhP}$ = 121.8 Hz), −144.0 (sep, $J_{PF}$ = 708.8 Hz) ppm. Anal. Calc. for $C_{31.5}H_{35}O_3ClF_6P_2Ru$: C, 48.76; H, 4.55. Found: C, 48.85; H, 4.39%.

### 2.5. Reaction of *3* with xylyl isocyanide

Xylyl isocyanide (18.2 mg, 0.138 mmol) was added to a solution of **3** (54.3 mg, 0.086 mmol) in $CH_2Cl_2$ (10 ml) at r.t. After the mixture had been stirred for 2 h, the solvent was removed to ca. 3 ml in vacuo and diethyl ether was added to give orange crystals (75.4

mg, 98%) of [Cp*RhCl(MDMPP-*P*)(XylNC)](PF$_6$) **4b**. UV–vis ($CH_2Cl_2$): $\lambda_{max}$ 340 nm. IR (nujol): 2168 (N≡C), 1581, 839 (PF$_6$) cm$^{-1}$. $^1$H-NMR ($CDCl_3$): $\delta$ 1.69 (d, $J_{PH}$ = 3.75 Hz, $C_5Me_5$), 2.11 (s, *o*-*Me*), 3.37 (s, O*Me*), 6.7–7.8 (c, *Ph*) ppm. $^{31}$P{$^1$H}-NMR ($CDCl_3$): $\delta$ 21.7 (d, $J_{RhP}$ = 130.5 Hz), −144.0 (sep, $J_{PF}$ = 708.8 Hz) ppm. Anal. Calc. for $C_{39}H_{43}O_2NF_6ClP_2Rh$: C, 53.71; H, 4.94; N, 1.61. Found: C, 53.72; H, 4.95; N, 1.64%.

Complex **4c** (20.5 mg, 65%) was prepared from the reaction of **3** (25.3 mg, 0.034 mmol) with *p*-Tos$CH_2$NC (9.4 mg, 0.045 mmol). UV–vis ($CH_2Cl_2$): $\lambda_{max}$ 337 nm. IR (nujol): 2214 (NaC), 1581, 850 (PF$_6$) cm$^{-1}$. $^1$H-NMR ($CDCl_3$): $\delta$ 1.63 (d, $J_{PH}$ = 3.75 Hz, $C_5Me_5$), 2.51 (s, *p*-*Me*), 3.33 (s, O*Me*), 4.68 (a center value of a AB type, $J_{AB}$ = 13.9 Hz, $v_{AB}$ = 4.7 Hz), 6.6–8.1 (c, *Ph*) ppm. $^{31}$P{$^1$H}-NMR ($CDCl_3$): $\delta$ 22.0 (d, $J_{RhP}$ = 126.9 Hz), −144.0 (sep, $J_{PF}$ = 708.8 Hz) ppm. Anal. Calc. for $C_{39}H_{43}O_4NSClF_6P_2Rh$: C, 50.04; H, 4.63; N, 1.49. Found: C, 49.98; H, 4.58; N, 1.37%.

Complex **4d**·0.75$CH_2Cl_2$ (24.9 mg, 73%) was prepared from the reaction of **3** (28 mg, 0.038 mmol) with P(O$CH_2$)$_3$CMe (10.7 mg, 0.079 mmol). UV–vis ($CH_2Cl_2$): $\lambda_{max}$ 339, 233 nm. IR (nujol): 2110 (N≡C), 1583, 837 (PF$_6$) cm$^{-1}$. $^1$H-NMR ($CDCl_3$): $\delta$ 0.75 (s, C*Me*), 1.55 (dd, $J_{PH}$ = 3.5 Hz, $J_{PH}$ = 6.0 Hz $C_5Me_5$), 3.34 (s, *o*-*Me*), 4.15 (c, O$CH_2$), 5.27 (s, $CH_2Cl_2$), 6.6–7.6 (m, *Ph*) ppm. $^{31}$P{$^1$H}-NMR ($CDCl_3$): $\delta$ 19.02 (dd, $J_{RhP}$ = 135.7 Hz, $J_{PP}$ = 89.0 Hz), 114.0 (dd, $J_{RhP}$ = 223.5 Hz, $J_{PP}$ = 89.0 Hz) ppm. Anal. Calc. for $C_{34.75}H_{44.5}O_5Cl_{2.5}F_6P_3Rh$: C, 44.37; H, 4.77. Found: C,44.76;H, 4.55%.

### 2.6. Reaction of *3* with MDMPP

A solution of **3** (10.8 mg, 0.015 mmol) and MDMPP (7.1 mg, 0.021 mmol) in $CH_2Cl_2$ (15 ml) was stirred at r.t. After 2 h, the solvent was removed to dryness and the residue was crystallized from $CH_2Cl_2$/hexane to yield reddish orange crystals of Cp*RhCl(MDMPP-*P*,*O*) **5** (7.1 mg, 84%). IR (nujol): 1585, 1537 cm$^{-1}$. UV–vis ($CH_2Cl_2$): $\lambda_{max}$ 331, 400(sh) nm. $^1$H-NMR ($CDCl_3$): $\delta$ 1.48 (d, $J_{PH}$ = 3.0 Hz, $C_5Me_5$), 3.34 (s, O*Me*), 5.8–7.9 (m, *Ph*) ppm. $^{31}$P{$^1$H}-NMR ($CDCl_3$): $\delta$ 50.4 (d, $J_{RhP}$ = 139.6 Hz) ppm. Anal. Calc. for $C_{29}H_{31}O_2ClPRh$: C, 59.95; H, 5.38. Found: C 59.65; H, 5.15%.

Complex **3** (26.2 mg, 0.041 mmol) in EtOH (10 ml) was heated for 3 h in a sealed tube, and the solvent was removed to dryness and the residue was crystallized from $CH_2Cl_2$/hexane to yield **5** (11 mg, 42%).

### 2.7. Heating of *4a* in $CH_2Cl_2$

A solution of **4a** (30 mg, 0.041 mmol) in $CH_2Cl_2$ (10 ml) was refluxed for 2 h. The work-up of the mixture and recrystallization from $CH_2Cl_2$ and diethyl ether gave **3** (24.5 mg, 81%).

### 2.8. Reactions of *4a* with xylyl isocyanide or $P(OCH_2)_3CMe$

A $CH_2Cl_2$ solution of **4a** and xylyl isocyanide or P(O$CH_2$)3CMe was stirred for 2 h at r.t. The work-up of the mixture gave the corresponding **4b** or **4d**.

### 2.9. Reaction of *5* with CO

Carbon monoxide was bubbled through a mixture of **5** (171.7 mg, 0.237 mmol) and excess $NaPF_6$ in $CH_2Cl_2$ (10 ml) and acetone (5 ml) for 3 min at r.t. and the mixture was kept stirring for 2 h. The solvent was removed in vacuo, the residue was extracted with $CH_2Cl_2$. The solvent was removed to ca. 3 ml and diethyl ether was added to yield red crystals of [Cp*Rh(MDMPP-*P*,*O*)(CO)](PF$_6$)·0.75$CH_2Cl_2$ **6a**·0.75$CH_2Cl_2$ (131.2 mg, 78%). $\lambda_{max}$ 366, 286. IR (nujol): 2089 (C≡O), 1583, 1545, 839 (PF$_6$) cm$^{-1}$. $^1$H-NMR ($CDCl_3$): $\delta$ 1.68 (d, $J_{PH}$ = 4.0 Hz, $C_5Me_5$), 3.39 (s, *Me*O), 6.7–7.9 (m, *Ph*) ppm. $^{31}$P{$^1$H}-NMR ($CDCl_3$): $\delta$ 46.8 (d, $J_{RhP}$ = 111.9 Hz), −140.0 (sep *P*F$_6$, $J_{PF}$ = 708.8 Hz) ppm. Anal. Calc. for $C_{30.75}H_{32.5}O_3Cl_{1.5}F_6P_2Rh$: C, 47.22; H, 4.15. Found: C, 47.83; H, 3.91%.

### 2.10. Reaction of *5* with $P(OCH_2)_3CMe$

A sample of P(O$CH_2$)$_3$CMe (11 mg, 0.081 mmol) was added to a solution of 5 (25 mg, 0.046 mmol) and an excess of $NaPF_6$ in $CH_2Cl_2$ (10 ml) and acetone (5 ml) at r.t. After 2 h, the solvent was removed to dryness and the residue was extracted with $CH_2Cl_2$. The solvent was removed to ca. 3 ml and diethyl ether was added to yield orange crystals of [Cp*Rh(MDMPP-*P*,*O*){P(O$CH_2$)$_3$CMe}](PF$_6$) **6d** (18.7 mg, 51%). UV–vis ($CH_2Cl_2$): $\lambda_{max}$ 309 nm. IR (nujol): 1583, 1548, 839 (PF$_6$) cm$^{-1}$. $^1$H-NMR ($CDCl_3$): $\delta$ 0.60 (s, C*Me*), 1.53 (dd, $J_{PH}$ = 3.0 Hz, $J_{PH}$ = 5.0 Hz, $C_5Me_5$), 3.32 (s, *Me*O), 3.82 (m, $CH_2$), 6.0–7.6 (m, *Ph*). $^{31}$P{$^1$H}-NMR ($CDCl_3$): $\delta$ 47.4 (dd, $J_{RhP}$ = 121.5 Hz, $J_{PP}$ = 85.0 Hz, MDMPP-*P*), 115.4 [dd, $J_{RhP}$ = 230.7 Hz, $J_{PP}$ = 85.0 Hz, (*p*-tol)$_3$P], −143.8 (sep PF$_6$, $J_{PF}$ = 708.8 Hz). Anal. Calc. for $C_{33}H_{40}O_5F_6P_3Rh$: C, 47.96; H, 4.88. Found: C, 47.70; H, 4.62%.

According to analogous procedures orange crystals of **6e** (37 mg, 86%) were prepared from **5** (25 mg, 0.046 mol) and tris(*p*-tolyl)phosphine (13.9 mg, 0.046 mmol) in the presence of excess $NaPF_6$. IR (nujol): 1583, 1548, 839 (PF$_6$) cm$^{-1}$. UV–vis ($CH_2Cl_2$): $\lambda_{max}$ 333 nm. $^1$H-NMR ($CDCl_3$): $\delta$ 1.19 (t, $J_{PH}$ = $J_{P'H}$ = 3.3 Hz, $C_5Me_5$), 2.40 (bs, *p*-*Me*), 3.11 (s, O*Me*), 5.8–7.6 (c, *Ph*) ppm. $^{31}$P{$^1$H}-NMR ($CDCl_3$): $\delta$ 22.9 (dd, $J_{RhP}$ = 142.1 Hz, $J_{PP}$ = 41.0 Hz, MDMPP-*P*), 51.1 [dd, $J_{RhP}$ = 133.7 Hz, $J_{PP}$ = 41.0 Hz, (*p*-tolyl)$_3$P], −143.8 (sep PF$_6$, $J_{PF}$ = 708.8 Hz) ppm. Anal. Calc. for $C_{50}H_{52}O_2F_6P_3Rh$: C, 60.37; H, 5.27. Found: C, 60.09; H, 5.00%.

Table 1
Crystal data for ($\eta^5$-$C_5Me_5$)$RhCl_2$(MDMPP-*P*) **2**, [($\eta^5$-$C_5Me_5$)RhCl(MDMPP-*P*)(*p*-$TosCH_2NC$)]($PF_6$) **4c**, ($\eta^5$-$C_5Me_5$)RhCl(MDMPP-*P*,*O*) **5** and ($\eta^5$-$C_5Me_5$)Rh(MDMPP-*P*,*O*)(CO)]($PF_6$)·$C_6H_6$ **6a**·$C_6H_6$.

| Compound | **2** | **4c** | **5** | **6a**·$C_6H_6$ |
|---|---|---|---|---|
| Formula | $C_{30}H_{34}O_2PCl_2Rh$ | $C_{39}H_{43}NO_4ClSP_2F_6Rh$ | $C_{29}H_{31}O_2PClRh$ | $C_{36}H_{37}O_3P_2F_6Rh$ |
| $M_W$ | 631.38 | 936.13 | 580.90 | 896.53 |
| Color | Brown | Orange | Orange | Orange |
| Crystal dimensions (mm) | $0.50\times0.25\times0.20$ | $0.50\times0.30\times0.20$ | $0.2\times0.1\times0.4$ | $0.05\times0.05\times0.20$ |
| Crystal system | Triclinic | Orthorhombic | Orthorhombic | Monoclinic |
| Space group | *P*1 (no. 2) | $Pna2_1$ (no. 33) | *Pbca* (no. 61) | *C*2/*c* (no. 15) |
| Lattice parameters | | | | |
| *a* | 10.639(3) | 26.817(4) | 8.212(8) | 33.29(2) |
| *b* | 15.965(3) | 17.662(5) | 17.808(10) | 8.567(5) |
| *c* | 8.800(3) | 8.673(4) | 35.96(1) | 29.26(3) |
| $\alpha$ | 94.43(2) | 90.0 | 90.0 | 90.0 |
| $\beta$ | 103.75(3) | 90.0 | 90.0 | 124.51(3) |
| $\gamma$ | 88.62(2) | 90.0 | 90.0 | 90.0 |
| *V* (Å$^3$) | 1447.4(7) | 4108(1) | 5259(4) | 6877(7) |
| *Z* | 2 | 4 | 8 | 8 |
| $D_{calc.}$ (g cm$^{-3}$) | 1.449 | 1.513 | 1.467 | 1.538 |
| *F*(000) | 648 | 1912 | 2384 | 3243 |
| $\mu$ (cm$^{-1}$) | 8.53 | 6.76 | 8.34 | 6.56 |
| Scan rate (° min$^{-1}$) | 16 | 8 | 4 | 2 |
| No. of reflections ($\theta<50°$) | 7013 | 4109 | 7245 | 5143 |
| No. of unique data | 4424 [$I>3.0\sigma(I)$] | 2061 [$I>2.0\sigma(I)$] | 2673 ($I>3.0\sigma(I)$] | 1531 ($I>2.0\sigma(I)$] |
| No. of variables | 325 | 466 | 307 | 368 |
| *R*, $R_w$[a] | 0.039, 0.042 | 0.052, 0.052 | 0.047, 0.048 | 0.072, 0.073 |
| GOF[b] | 1.25 | 1.24 | 1.22 | 1.30 |

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

Complex **6b** (42.6 mg, 55%) was obtained from **5** (54.3 mg, 0.093 mol) and xylyl isocyanide (18.4 mg, 0.139 mmol) in the presence of excess $NaPF_6$. IR (nujol): 2183 (N≡C), 1583, 1545, 839 ($PF_6$) cm$^{-1}$. $^1$H-NMR ($CDCl_3$): $\delta$ 1.68 (d, $J_{PH}=3.3$ Hz, $C_5Me_5$), 1.84 (s, *o-Me*), 3.35 (s, O*Me*), 6.0–7.6 (c, *Ph*) ppm. $^{31}P\{^1H\}$-NMR ($CDCl_3$): $\delta$ 47.8 (d, $J_{RhP}=116.0$ Hz). Anal. Calc. for $C_{35}H_{40}O_2NF_6P_2Rh$: C, 55.55; H, 4.91; N, 1.70. Found: C, 55.65; H, 4.97; N, 1.64%. This complex **6b** was also obtained from the reaction of **6a** with xylyl isocyanide at r.t.

### 2.11. Heating of *4d* in EtOH

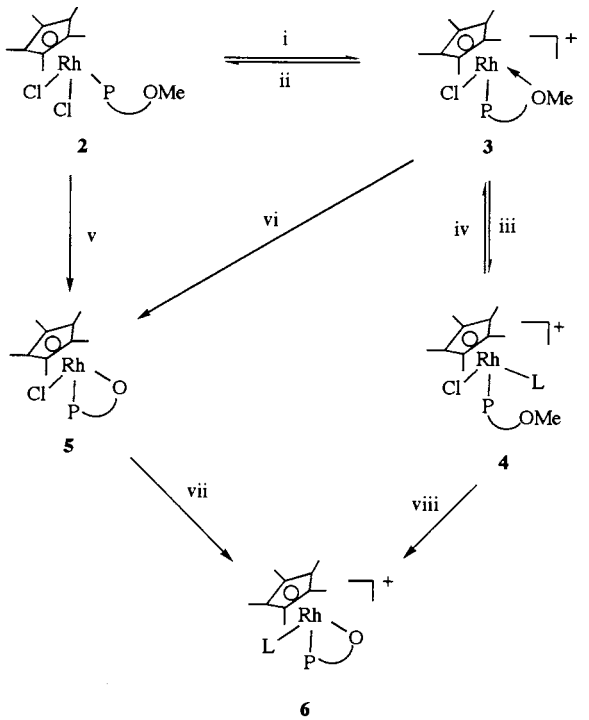
A solution of **4d** (9.5 mg, 0.011 mmol) in EtOH (10 ml) was refluxed for 4 h. The solvent was removed and the residue was crystallized from $CH_2Cl_2$ and diethyl ether to give **6d** (6.8 mg, 75%).

### 2.12. Data collection

Complexes **2**, **4c** and **5** were recrystallized from $CH_2Cl_2$/hexane or $CH_2Cl_2$/ether. Complex **6a** was recrystallized from $CH_2Cl_2$/benzene and contained a benzene molecule as a solvated molecule. Cell constants were determined from 25 reflections on Rigaku four-circle automated diffractometer AFC5S. The crystal parameters along with data collections are summarized in Table 1. Data collection was carried out by a Rigaku AFC5S refractometer at 25°C. Intensities were measured by the $2\theta-\omega$ scan method using Mo–$K_\alpha$ 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 any decay was not observed. Intensities were corrected for Lorentz and polarization effects. The absorption correction was made. Atomic scattering factors were taken from Cromer and Waber [8]. Anomalous dispersion effects were included in $F_{calc.}$ [9]; the values of $\Delta f'$ and $\Delta f''$ were from Creagh and McAuley [10]. All calculations were performed using the teXsan crystallographic software package of Molecular Structure Corporation (1985 and 1992).

### 2.13. Determination of the structures

The structures of **2** and **5** were solved by direct methods (SIR92) and **4c** and **6a**·$C_6H_6$ were solved by Patterson methods (DIRDIF92 PATTY). The rhodium atom was located in the initial *E* map, and subsequent Fourier syntheses gave the positions of other non-H atoms. Hydrogen atoms were calculated at the ideal positions with the C–H distance of 0.95 Å, and were not refined. The positions of the non-H atoms of **2**, **4c**




Scheme 1. Reactions of [Cp*RhCl$_2$(MDMPP-*P*) **2** and its related complexes. (i) $NaPF_6$. (ii) [N(PhCH$_2$)Et$_3$]Cl. (iii) L = **4a**: CO, **4b**: XylNC, **4c**: *p*-TosCH$_2$NC, **4d**: P(OCH$_2$)$_3$CMe. (iv) L = CO, refluxed in $CH_2Cl_2$. (v) Refluxed in in EtOH. (vi) MDMPP, r.t. in $CH_2Cl_2$. (vii) L = **6a**: CO, **6b**: XylNC, **6d**: P(OCH$_2$)$_3$CMe, **6e**: P(*p*-Tolyl)$_3$. (viii) **4d**, refluxed in EtOH.

and **5** were refined with anisotropic thermal parameters by using full-matrix least-squares methods. The F atoms for **4c** and the C1, C6, and F atoms and a solvated benzene atoms (C31–C36) for **6c**·$C_6H_6$ were refined isotropically and other non-H atoms were refined anisotropically by using full-matrix least-squares methods. Final difference Fourier syntheses showed peaks at heights up to 0.41–0.61 e Å$^{-3}$.

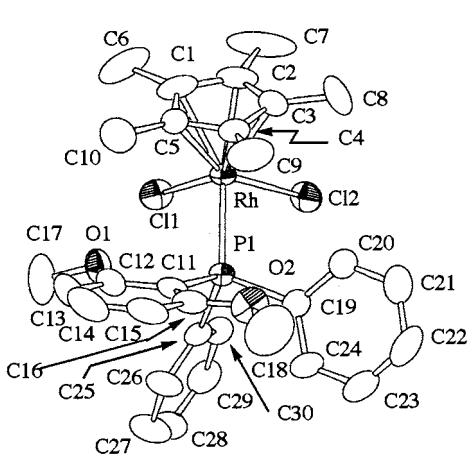



Fig. 1. Crystal structure of [Cp*RhCl$_2$(MDMPP-*P*)] **2**.

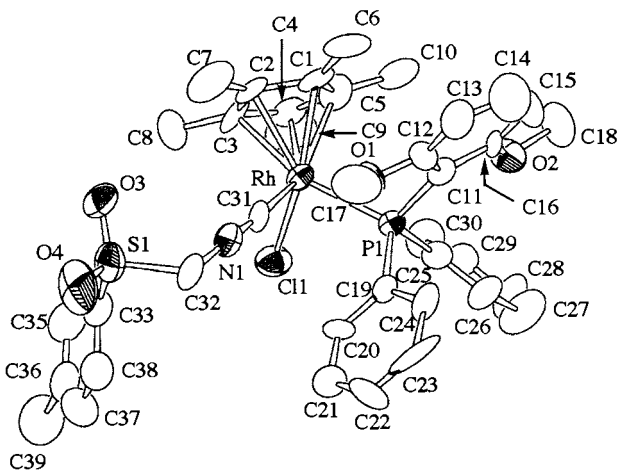



Fig. 2. Crystal structure of [Cp*RhCl(MDMPP-*P*)(*p*-TosCH$_2$-NC)](PF$_6$) **4c**. $PF_6$ is omitted for clarity.

## 3. Results and discussion

Overall reactions described here are depicted in Scheme 1. Treatment of **1** with MDMPP at r.t. gave dark red crystals **2** in a 89% yield, formulated as Cp*RhCl$_2$[PPh$_2${2,6-(MeO)$_2$C$_6$H$_3$}]. In the $^1$H-NMR spectrum the methyl protons showed a doublet at $\delta$ 1.15 ppm ($J_{PH}$ = 3.5 Hz) which was derived from a coupling with a P atom because the methyl protons on the Cp* ring of the starting complex **1** appeared as a singlet. The methoxy protons appeared at $\delta$ 3.28 ppm as a singlet. The $^{31}$P{$^1$H}-NMR spectrum showed a doublet at $\delta$ 23.5 ppm ($J_{RhP}$ = 150.9 Hz). The IR spectrum showed only one band (1575 cm$^{-1}$) in the range from 1500 to 1600 cm$^{-1}$, suggesting the presence of the $\eta^1$-P coordination [4]. It was confirmed by an X-ray analysis that the structure consists of a piano-stool in which the rhodium atom is surrounded by a phosphorus, two chloride atoms and Cp* ring (Fig. 1). The salient feature of this complex is that the in-

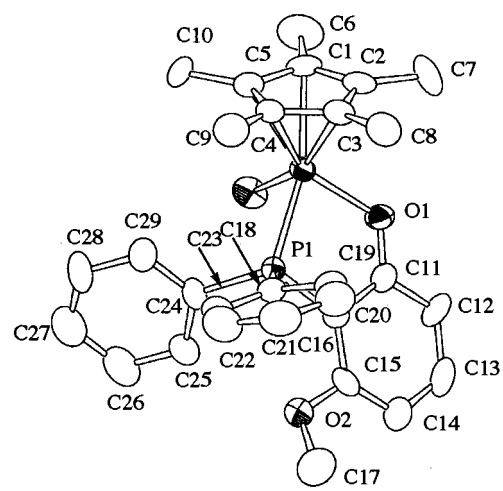



Fig. 3. Crystal structure of [Cp*RhCl(MDMPP-*P*,*O*)] **5**.

tramolecular Cl1···O1 distance is 3.247 Å and the close interaction between the methoxy group and Cl atom is expected.

When complex **2** was treated with $NaPF_6$ in an acetone/$CH_2Cl_2$ solution at r.t., an elimination of a Cl atom occurred readily to form the salt-like O-coordinated complex **3**, [Cp*RhCl(MDMPP-*P*,*O*Me)][$PF_6$]. The IR spectrum showed two bands at 1585 and 1537 $cm^{-1}$ in the range from 1500 to 1600 $cm^{-1}$, indicative of the presence of the P–O chelation [4]. The $PF_6$ group was found by a strong band at 835 $cm^{-1}$. In the $^1$H-NMR spectrum the methoxy protons appeared at $\delta$ 3.88 ppm as a broad singlet at ambient temperature, indicating a rapid exchange between free and coordinated MeO groups. The temperature-dependent NMR spectra were measured. Two sharp singlets were observed at $\delta$ 3.34 and 4.43 ppm below ca. −20°C, assignable to free and coordinated methoxy groups, respectively. Two singlets became broader with the rise of temperature and the chemical shift difference became narrower. The two broad signals coalesced at ca. −10°C, showing a rapid exchange between two methyl groups. A coalesced signal became sharper with further rise of temperature and a sharp singlet appeared at $\delta$ 3.86 ppm at 50°C. The activation energy for this intramolecular process could be evaluated using the Eyring equation as ca. 35 kJ $mol^{-1}$. For $RhCl_2$(*P*–*O*)(*P*–*O*)$_2$ [11], RhCl(*P*–*O*)(*P*–*O*) [12] and $RhCl_3$(*P*–*O*)(*P*–*O*) [13] [*P*–*O* = $R_2PCH_2CH_2OMe$ (R = $C_6H_{11}$ or Ph), $Ph_2PCH_2CH_2C(O)OEt$] the values were 50–75 kJ $mol^{-1}$, thus indicating a weaker bonding for **3**.

This weak interaction was revealed by the fact that addition of excess $NEt_3(CH_2Ph)Cl$ to **3** regenerated **2**. This labile O-coordination also led to the easy replacement with Lewis bases such as CO, XylNC (Xyl = 2,6-$Me_2C_6H_3$), *p*-$TosCH_2NC$ or $P(OCH_2)_3CMe$. When CO was bubbled into a $CH_2Cl_2$ solution of **3** at r.t., compound **4a**, formulated as [Cp*RhCl(MDMPP-*P*)(CO)][$PF_6$], was formed by an elimination of an O-coordinated methoxy group and the subsequent coordination of an incoming CO molecule. The similar complexes **4** (**b**: L = XylNC; **c** = *p*-$TosCH_2NC$; **d**: L = $P(OCH_2)_3CMe$) were isolated from **3** and the corresponding Lewis bases. However the reaction with tris(*p*-tolyl)phosphine recovered the starting material, due to steric hindrance from the greater cone angle (145°) of *p*-tolyl groups than that (101°) of $P(OCH_2)_3CMe$ [14].

The absence of the P–O chelation was confirmed by observation of only one band in the range 1500–1600 $cm^{-1}$ in the IR spectrum of each complex. The characteristic bands of these complexes (**4a–c**) appeared at 2071 $cm^{-1}$ for **4a**, 2168 $cm^{-1}$ for **4b** and 2214 $cm^{-1}$ for **4c**; the former is assigned to a CO group and the others to an NC group.

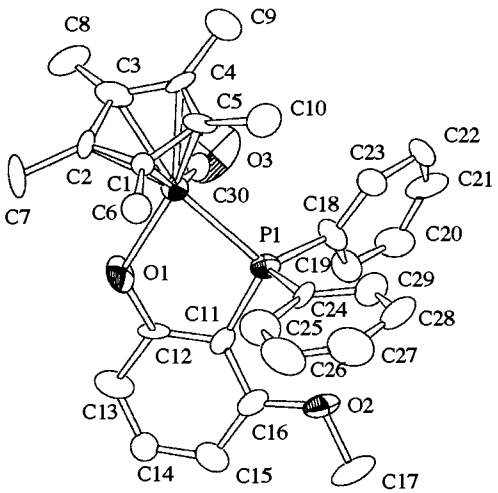



Fig. 4. Crystal structure of [Cp*Rh(MDMPP-*P*,*O*)(CO)][$PF_6$)]·$C_6H_6$ **6a**·$C_6H_6$. $PF_6$ is omitted for clarity.

In the $^1$H-NMR spectrum of **4c** the methylene protons showed an AB quartet centered at $\delta$ 4.68 ppm arising from chemical inequivalence caused by the presence of the chiral center. The $^{31}P\{^1H\}$-NMR spectrum showed a doublet at $\delta$ 22.0 ($J_{RhP}$ = 126.9 Hz) ppm for the phosphine ligand. In the $^1$H-NMR spectrum of **4d**, the Cp* protons appeared as a double doublet, with separations of 3.5 and 6.0 Hz, the larger separation being associated with the entering $P(OCH_2)_3CMe$ ligand. The methoxy and methylene protons appeared at $\delta$ 3.34 and 4.15 ppm as a singlet and complex band, respectively. In the $^{31}P\{^1H\}$-NMR spectrum two double doublets appeared at $\delta$ 19.0 ($J_{RhP}$ = 135.8 Hz, $J_{PP}$ = 89.0 Hz) and 114.0 ($J_{RhP}$ = 223.5 Hz, $J_{PP}$ = 89.0 Hz) ppm; the former is assignable to the MDMPP and the latter to $P(OCH_2)_3CMe$. The X-ray analysis of **4c** was carried out as the representative compound in order to determine the detailed structures of **4**, and the structure is a typical piano-stool one (Fig. 2). Reactions with small molecules also have been reported in Cp*Ru(P–O)(P⌒O)][$BPh_4$] complex (P–O = $\eta^1$-$Ph_2PCH_2CH_2OMe$, P⌒O = $\eta^2$-$Ph_2PCH_2CH_2OMe$) [15].

The CO ligand was very labile. When **4a** was refluxed in $Ch_2Cl_2$, the CO ligand was eliminated to regenerate **3**, whereas heating of **4b** in EtOH recovered the starting material quantitatively, suggesting the stability of a metal–isocyanide bond.

$$\mathbf{3} \underset{-\mathrm{CO/heat}}{\overset{\mathrm{CO}}{\rightleftharpoons}} \mathbf{4}$$

The coordinated CO ligand could be replaced readily with other Lewis bases. When **4a** was treated with isocyanides or $P(OCH_2)_3CMe$ in $CH_2Cl_2$ at r.t., the corresponding complex **4b**, **4c**, or **4d** was obtained, whereas its reverse reaction and an interconversion between **4b** and **4d** did not proceed. The difference in the ligand substitution reactions is due to the fact that

Table 2
Selected bond lengths (Å) and angles (°) for **2**

| | | | | | |
|---|---|---|---|---|---|
| Bond lengths (Å) | | | | | |
| Rh-Cl1 | 2.392(1) | Rh-C12 | 2.411(1) | Rh-P | 2.366(1) |
| O1-C12 | 1.357(5) | O1-C17 | 1.409(6) | O2-C16 | 1.347(6) |
| O2-C18 | 1.405(6) | Rh-Cp*(av) | 2.190 | | |
| Cl1···O1 | 3.226(3) | | | | |
| Bond angles (°) | | | | | |
| Cl1-Rh-C12 | 89.00(4) | Cl1-Rh-P | 93.05(4) | Cl2-Rh-P | 90.02(4) |

the rhodium atom in the high oxidation state prefers isocyanide or phosphine ligands with their strong $\sigma$-donor ability to the CO ligand.

When **3** was treated with MDMPP in $CH_2Cl_2$at r.t., the phosphonium salt MDMPP·MeCl and a neutral reddish–orange phenoxido complex **5** $\eta^5$-Cp*RhCl(MDMPP-*P*,*O*) were formed. Complex **5** could be prepared also by refuxing **2** in EtOH or directly by refluxing a mixture of **1** and MDMPP in EtOH. A similar elimination reaction of MeX from a MDMPP ligand has been reported from the reaction of a square-planar $PtCl_2(MDMPP)_2$ complex with NaI under reflux in 2-methoxyethanol [16]. The IR spectrum showed the presence of the characteristic P,O-chelation at 1585 and 1537 $cm^{-1}$. The $^1$H-NMR spectrum showed a doublet at $\delta$ 1.48 ($J_{PH} = 3.0$ Hz) and a singlet at $\delta$ 3.34 ppm, assignable to methyl protons of the Cp* and methoxy groups, respectively. The X-ray analysis confirmed that the configuration around the Rh atom is not significantly different from that of ($\eta^6$-arene)RuCl(MDMPP-*P*,*O*) (Fig. 3) [4].

When a mixture of complex **5** in acetone and $CH_2Cl_2$ was treated under a CO atmosphere in the presence of $NaPF_6$ at r.t., replacement of a Cl anion occurred readily to give reddish crystals **6a** [Cp*Rh(MDMPP-*P*,*O*)(CO)]($PF_6$). Analogously, the reaction with XylNC or $P(OCH_2)_3CMe$ in the presence of $NaPF_6$ produced the corresponding orange salt-like complex **6** (**b**: L = XylNC; **d** = $P(OCH_2)_3CMe$). Compound **6d** was also prepared by heating of **4d** in EtOH, whereas heating of **4b** recovered the starting material.

Although no reaction occurred between **3** and tris(*p*-tolyl)phosphine, the complex **6e** [L = (*p*-tolyl)$_3$P] could be obtained as orange crystals from the reaction of **5** with bulky tris(*p*-tolyl)phosphine. The presence of the coordinated MeO group in **3** prevented the reaction with *tert*-phosphine, which suggests a considerable amount of steric hindrance encountered by an entering ligand.

The IR spectrum of **6a** showed a characteristic band at 2089 $cm^{-1}$ (due to a C≡O) and that of **6b**, at 2183 $cm^{-1}$ , due to a C≡N bond, appearing at higher frequency by ca. 15 $cm^{-1}$ than those of **4a** and **4b**, respectively, due to the higher electronegativity of the O atom than that of a Cl atom. The $^1$H-NMR spectrum of **6d** showed two singlets at $\delta$ 0.60 and 3.32 ppm assignable to the MeC and MeO protons and a broad signal at $\delta$ 3.82 ppm due to the $CH_2O$ groups. The Cp* protons at $\delta$ 1.53 ppm appeared as a double doublet appearing at 5.5 and 3.0 Hz, respectively; based on assignment of **4d**, the former coupling constant is responsible for the P atom of $P(OCH_2)_3CMe$ and the latter for MDMPP-*O* ligand, respectively. The $^{31}$P{$^1$H}-NMR spectrum consisted of a double doublet at $\delta$ 47.4 ppm ($J_{RhP} = 121.5$, $J_{PP} = 85.0$ Hz) due to MDMPP-*O* ligand and $\delta$ 115.4 ($J_{RhP} = 230.7$, $J_{PP} = 85.0$ Hz) ppm due to $P(OCH_2)_3CMe$ ligand. An analogous NMR behavior was also observed for **6e**. In the $^1$H-NMR spectrum of **6e**, the methyl protons of the Cp* ligand appeared at $\delta$ 1.19 ppm as a triplet, separated by $J_{PH} = J_{P'H} = 3.3$ Hz. The protons of *p*-methyl and methoxy groups appeared at $\delta$ 2.40 (bs) and 3.11 (s) ppm. The $^{31}$P{$^1$H}-NMR spectrum consisted of a dou-

Table 3
Selected bond lengths (Å) and angles (°) for **4c**

| | | | | | |
|---|---|---|---|---|---|
| Bond lengths (Å) | | | | | |
| Rh-Cl1 | 2.383(4) | Rh-P | 2.353(3) | Rh-C31 | 1.95(1) |
| C31-N1 | 1.14(1) | S1-O3 | 1.45(1) | S1-O4 | 1.44(1) |
| O1-C12 | 1.36(1) | O1-C17 | 1.43(2) | O2-C16 | 1.34(1) |
| O2-C18 | 1.46(2) | Rh-Cp*(av) | 2.22 | | |
| Bond angles (°) | | | | | |
| XCl1-Rh-P | 91.9(1) | Cl1-Rh-C31 | 88.0(4) | P1-Rh-C31 | 90.1(3) |
| Rh-C31-N1 | 172.6(10) | C31-N1-C32 | 178(1) | N1-C32-S1 | 109.1(8) |
| O3-S1-C32 | 107.5(7) | O4-S1-C32 | 107.5(7) | O3-S1-O4 | 121.5(8) |
| C32-S1-C33 | 108.3(7) | | | | |

Table 4
Selected bond lengths (Å) and angles (°) for **5**

| | | | | | |
|---|---|---|---|---|---|
| Bond lengths (Å) | | | | | |
| Rh-Cl1 | 2.404(3) | Rh-P(1) | 2.302(2) | Rh-O1 | 2.059(5) |
| O1-Cl1 | 1.284(8) | O2-C15 | 1.393(9) | O2-C17 | 1.39(1) |
| Rh-Cp*(av) | 2.177 | | | | |
| Bond angles (°) | | | | | |
| Cl1-Rh-P | 86.56(8) | Cl1-Rh-O1 | 86.6(2) | P-Rh-O1 | 82.3(1) |
| Rh-O1-Cl1 | 121.6(5) | O1-Cl1-C16 | 116.4(7) | P-Cl1-C16 | 113.7(6) |

ble doublet at $\delta$ 22.9 ($J_{RhP} = 142.1$, $J_{PP} = 41.0$ Hz) due to tris(*p*-tolyl)phosphine and 51.1 ($J_{RhP} = 133.7$, $J_{PP} = 41.0$ Hz) ppm due to the MDMPP-*O* ligand. The structure of this type of complexes was determined by an X-ray analysis of **6a** (Fig. 4).

The CO ligand of **6a** could be eliminated readily, as well as that of **4a**. When **6a** was treated with xylyl isocyanide or $P(OCH_2)_3CMe$ in $CH_2Cl_2$ at r.t., the corresponding complex **6b** or **6d** was isolated in high yield, respectively, but the reverse reactions did not occur. An interconversion between **6b** and **6d** also did not proceed.

### 3.1. Molecular structures

The molecular structures of **2**, **4c**, **5**, and **6a**·$C_6H_6$ are depicted in Figs. 1–4. The selected bond lengths and angles are shown in Tables 2–5. All complexes have piano-stool structures. Average bond angles (A–Rh–B) among three ligands except the Cp* ring are ca. 90° for **2** and **4c**, but ca. 86° for **5** and **6a**·$C_6H_6$. The bond angles of the complexes bearing the P–O chelation are narrower than those of non-chelated complexes. Such difference was also observed in the Rh–P bond lengths; non-chelated complexes **2** and **4c** are slightly longer than the chelated complexes **5** and **6a**·$C_6H_6$, minimizing the steric influence of *tert*-phosphine. The Rh–O bond lengths in **5** and **6a**·$C_6H_6$ are 2.059(5) and 2.08(1) Å, respectively, being not different significantly.

The salient feature in **2** is an intramolecular interaction of 3.226(3) Å between Cl1 and O1 atoms, being close to a sum (3.20 Å) of the van der Waals' radii of the two atoms. This value suggested the presence of some interaction between a Cl atom and a methyl group, which is likely a driving force of an elimination of MeCl. The Rh–C31 (isocyanide) length of 1.939(10) Å in **4c** is not significantly different from the Rh–C30 (carbon monoxide) one of 1.96(2) Å. The C≡O and C≡N bond lengths fall in the range of the usual triple bond distances. The Rh–C31–N1 and C31–N1–C32 bond angles in **4c** are 172.6(10) and 177(1)°, respectively. These values are not unusual. The Rh–C30–O3 angle in **6a**·$C_6H_6$ is bent and measures 164(1)°.

## 4. Conclusion

Complexes **2**, **3** and **5** showed versatile reactivities for Lewis bases such as CO, isocyanide and phosphines. Some of the complexes are interconvertible and the route from **2** to **6** proceeded stepwise. These complexes can act as starting materials for chemistry of the rhodium complexes bearing the P–O coordination. The diversity of chemical reaction is expected for other small molecules, such as acetylenes and olefins and studies of these such molecules are currently in progress.

## 5. Supplementary material

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

Table 5
Selected bond lengths (Å) and angles (°) for **6a**·$C_6H_6$

| | | | | | |
|---|---|---|---|---|---|
| Bond length (Å) | | | | | |
| Rh-P | 2.334(5) | Rh-O1 | 2.08(1) | Rh-C30 | 1.96(2) |
| O1-C12 | 1.35(2) | O2-C16 | 1.38(2) | O2-C17 | 1.43(2) |
| O3-C30 | 1.04(2) | Rh-Cp*(av) | 2.208 | | |
| Bond angle (°) | | | | | |
| P1-Rh-O1 | 82.1(4) | P1-Rh-C30 | 87.8(6) | O1-Rh-C30 | 86.8(6) |
| Rh-C30-O3 | 164(1) | Rh-P1-Cl1 | 99.7(6) | Rh-O1-C12 | 118(1) |

## Acknowledgements

The authors would like to thank Professor Sigetoshi Takahashi and Fumie Takei in Osaka University for measurement of FAB mass spectroscopy.

## References

[1] A. Bader, E. Lindner, Coord. Chem. Rev. 108 (1991) 27.
[2] (a) S.C. Haefner, K.R. Dunbar, C. Bender, J. Am. Chem. Soc. 13 (1991) 9540 and therein. (b) S.C. Haefner, K. Dunbar, Organometallics 11 (1992) 1431 and therein. (c) K.R. Dunbar, J.H. Matonic, V.P. Saharan, Inorg. Chem. 33 (1994) 25. (d) L.-J. Baker, G.A. Bowmaker, D. Camp, P.C. Healy, H. Schmidbaur, O. Steigelmann, A.H. White, J. Inorg. Chem. 31 (1992) 3656. (e) L.-J. Baker, G.A. Bowmaker, B.W. Skelton, A.H. White, J. Chem. Soc. Dalton Trans. (1993) 3235. (f) K.R. Dunbar, S.C. Haefner, C.E. Uzelmeier, A. Howard, Inorg. Chim. Acta 240 (1995) 527. (g) L.-J. Baker, R.C. Bott, G.A. Bowmaker, P.C. Healy, B.W. Skelton, P. Schwerdtfeger, A.H. White, J. Chem. Soc. Dalton Trans. (1995) 1341 and therein.
[3] (a) M. Wada, S. Higashizaki, A. Tsuboi, J. Chem. Soc. Synop. (1985) 38; J. Chem. Res. Miniprint 1985, 0467. (b) M. Wada, A. Tsuboi,J. Chem. Soc. Perkin Trans. 1 (1987) 151. (c) Y. Yamashoji, T. Matsushita, M. Wada, T. Shono, Chem. Lett. (1988) 43.
[4] (a) Y. Yamamoto, R. Sato, M. Ohshima, F. Matsuo, J. Organomet. Chem. 489 (1995) C68. (b) Y. Yamamoto, R. Sato, F. Matsuo, C. Sudoh, T. Igoshi, Inorg. Chem. 35 (1996) 2329.
[5] J.W. Kang, K. Moseley, M. Maitlis, J. Am. Chem. Soc. 91 (1969) 5971.
[6] W.S. Wadsworth, W.D. Emmons, J. Am. Chem. Soc. 84 (1962) 610.
[7] H.M. Walborsky, G.E. Niznik, J. Org. Chem. 37 (1972) 187.
[8] D.T. Cromer, J.T. Waber, International Tables for X-ray Crystallography, vol. IV, Kynoch Press, Birmingham, UK, Table 2.2A, 1974.
[9] J.A. Ibers, W.C. Hamilton, Acta. Crystallogr. 17 (1964) 781.
[10] D.C. Creagh, W.J. McAuley, in: A.J.C. Wilson, (Ed.), International Tables for Crystallography, vol. C, Kluwer Academic, Boston, Table 4.2.6.8, 1992, pp. 219–222.
[11] (a) P. Braunstein, Y. Chauvin, J. Nahring, Y. Dusausoy, D. Bayeul, A. Tiripicchio, F. Ugozzoli, J. Chem. Soc. Dalton Trans. (1995) 851. (b) J.-B. Ballif, P. Braunstein, A.D. Burrows, R.D. Adams, W. Wu, J. Cluster Sci. 5 (1994) 443. (c) J. Andrieu, P. Braunstein, A.D. Burrows, J. Chem. Res. S (1993) 380. (d) P. Braunstein, D. Matt, Y. Dusausoy, Inorg. Chem. 22 (1983) 2043. (e) E. Lindner, B. Karle, Z. Natureforsch. Teil B 45 (1990) 1108.
[12] (a) P. Braunstein, D. Matt, Y. Dusausoy, Inorg. Chem. 22 (1983) 2043. (b) P Braunstein, Y. Chauvin, J. Nhring, A. DeCian, J. Fischer, J. Chem. Soc. Dalton Trans. (1995) 863.
[13] E. Lindner, Q. Wang, H.A. Mayer, A. Bader, H. Kühbauch, P. Wegner, Organometallics 12 (1993) 3291.
[14] C.A. Tolman, Chem. Rev. 77 (1977) 313.
[15] (a) E. Lindner, M. Haustein, H.A. Mayer, K. Gierling, R. Fawzi, M. Steimann, Organometallics 14 (1995) 2245. (b) E. Lindner, H.A. Mayer, R. Fawzi, M. Steimann, Organometallics 12 (1993) 1865.
[16] E. Lindner, M. Haustein, R. Fawzi, M. Steimann, P. Wegner, Organometallics 13 (1994) 5021.