

Five- and six-coordinate ruthenium complexes with the tridentate orthometallated aryl bisphosphine ligand $[2,6-(\text{Ph}_2\text{PCH}_2)_2\text{C}_6\text{H}_3]^-$

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Abstract

A series of ruthenium complexes with the orthometallated ligand $[2,6-(\text{Ph}_2\text{PCH}_2)_2\text{C}_6\text{H}_3]^-$ (PCP) was synthesized. Reaction of $\text{RuCl}_2(\text{PPh}_3)_3$ with $1,3-(\text{Ph}_2\text{PCH}_2)_2\text{C}_6\text{H}_4$ produced the coordinatively unsaturated complex $\text{RuCl}(\text{PPh}_3)(\text{PCP})$, which was characterized by X-ray crystallography. Treatment of $\text{RuCl}(\text{PPh}_3)(\text{PCP})$ with 4-phenylpyridine (pyph) yielded $\text{RuCl}(\text{pyph})(\text{PPh}_3)(\text{PCP})$. Treatment of $\text{RuCl}(\text{PPh}_3)(\text{PCP})$ with PMe_3 and CO generated $\text{RuCl}(\text{PMe}_3)_2(\text{PCP})$ and $\text{RuCl}(\text{CO})_2(\text{PCP})$ respectively. Reactions of $\text{RuCl}(\text{PPh}_3)(\text{PCP})$ with NaH in THF and NaBH_4 in methanol gave $\text{RuH}(\text{PPh}_3)(\text{PCP})$ and $\text{RuH}(\text{CO})(\text{PPh}_3)(\text{PCP})$ respectively. The hydride complex $\text{RuH}(\text{PMe}_3)_2(\text{PCP})$ was prepared by the reaction of $\text{RuCl}(\text{PMe}_3)_2(\text{PCP})$ with NaBH_4 .

Keywords: Ruthenium; Phosphine; Hydride

1. Introduction

Multidentate phosphine ligands have attracted considerable attention recently [1], since they can be designed to control the electronic and stereochemical properties of transition metal complexes. The family of bisphosphine ligands $1,3-(\text{R}_2\text{PCH}_2)_2\text{C}_6\text{H}_4$, where R = Bu^t, Ph, Cy, Me and Et, provides a good example of such control [2–8]. A common feature of the aryl phosphine ligands is that they undergo cyclometallation reactions to form complexes of tridentate $[(2,6-(\text{R}_2\text{PCH}_2)_2\text{C}_6\text{H}_3)]^-$. The cyclometallated ligands $[2,6-(\text{R}_2\text{PCH}_2)_2\text{C}_6\text{H}_3]^-$ are complementary to η^5 -cyclopentadienyls in that although both are six-electron donors and can be considered to occupy three-coordination sites, the former usually adopt meridional coordination while the latter are facially coordinated. Metal complexes of the cyclometallated ligands $[2,6-(\text{R}_2\text{PCH}_2)_2\text{C}_6\text{H}_3]^-$ have been reported for Ni, Pd, Pt, Rh and Ir [2–8]. Recently the chiral analogs $1,3-(\text{Ph}_2\text{PC}^*\text{HR})_2\text{C}_6\text{H}_4$ have also been synthesized [9]. The platinum complexes with these chiral ligands were reported to be catalytically active for aldol reactions of aldehydes and methylisocynoacetates [9].

In view of the rich chemical and catalytic properties of ruthenium complexes with η^5 -cyclopentadienyl lig-

ands [10] and polydentate phosphine ligands [11], it would be interesting to prepare analogous ruthenium complexes with ligands of the type $[2,6-(\text{R}_2\text{PCH}_2)_2\text{C}_6\text{H}_3]^-$. We report here the synthesis and characterization of a series of ruthenium complexes with $[2,6-(\text{Ph}_2\text{PCH}_2)_2\text{C}_6\text{H}_3]^-$ (PCP) including the coordinatively unsaturated ruthenium complex $\text{RuCl}(\text{PPh}_3)(\text{PCP})$ and hydride complexes such as $\text{RuH}(\text{L})_2(\text{PCP})$ (L = CO, PMe_3). It should be noted that the chemistry of metal complexes with the related ligand $[2,6-(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3]^-$ (NCN) and its derivatives has been intensively studied [12,13] and that several ruthenium complexes with NCN ligand (e.g. $\text{RuX}(\text{PPh}_3)(\text{NCN})$ (X = Cl, I) and $\text{RuX}(\text{NBD})(\text{NCN})$ (X = Cl, SO_3CF_3 ; NBD = norbornadiene) are known [12].

2. Experimental section

Microanalyses were performed by MEDAC Ltd. (Middlesex, UK) and M-H-W Laboratories (Phoenix, USA). ^1H and ^{31}P NMR spectra were collected on a JEOL EX-400 spectrometer (400 MHz) or a Bruker ARX-300 spectrometer (300 MHz). ^1H chemical shifts are relative to TMS, and ^{31}P NMR chemical shifts relative to 85% H_3PO_4 . IR spectra were collected on a Perkin Elmer 1600 spectrometer.

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All manipulations were carried out under nitrogen atmosphere using standard Schlenk techniques. Solvents were distilled under nitrogen from sodium–benzophenone (hexane, diethyl ether, THF), sodium (benzene), or calcium hydride (dichloromethane). The starting materials 1,3-(Ph₂PCH₂)₂C₆H₄ [7] and RuCl₂(PPh₃)₃ [14] were prepared according to literature methods. All other reagents were used as purchased from Aldrich.

2.1. RuCl(PPh₃)(PCP), 2

A mixture of 0.13 g of the ligand (Ph₂PCH₂)₂C₆H₄ (0.27 mmol) and 0.237 g of RuCl₂(PPh₃)₃ (0.247 mmol) in isopropanol was refluxed until a deep green solid separated from the solution. The solid was collected on a filter frit, washed with ether, and dried under vacuum overnight. Yield 0.18 g, 84%. Anal. Found: C, 68.43; H, 5.12. C₅₀H₄₂ClP₃Ru Calc.: C, 68.84; H, 4.85%. ¹H NMR (400 MHz, CDCl₃): δ 2.42 (d, *J*(HH) = 16.4 Hz, 2 H, CHH(C₆H₃)CHH), 3.47 (dt, *J*(HH) = 16.4 Hz, *J*(PH) = 5.9 Hz, 2 H, CHH(C₆H₃)CHH), 6.78–7.86 (m, 38 H, PPh₃, 2PPh₂, C₆H₃). ³¹P{¹H} NMR (161.70 MHz, CDCl₃): δ 32.5 (d, *J*(PP) = 27.7 Hz, PPh₂), 79.4 (t, *J*(PP) = 27.7 Hz, PPh₃).

2.2. RuCl(pyph)(PPh₃)(PCP), 3

A mixture of 0.104 g of RuCl(PPh₃)(PCP) (0.119 mmol) and 0.020 g of phenylpyridine (0.13 mmol) in 20 ml of chloroform was stirred at room temperature for 10 min to give a dark yellow solution. The volume of the reaction mixture was then reduced to ca. 1 ml under vacuum and a yellow solid was formed after addition of 20 ml of hexane. The solid was collected on a filter frit and dried under vacuum overnight. Yield 0.098 g, 80%. Anal. Found: C, 65.54; H, 4.77; N, 1.20. C₆₁H₅₁ClN₃P₃Ru · CHCl₃ Calc.: C, 64.93; H, 4.57; N, 1.22%. ¹H NMR (400 MHz, CDCl₃): δ 3.62 (br, 4 H, 2 CH₂), 6.0–7.8 (m, PPh₃, 2PPh₂, C₆H₃, pyph), 9.96 (d, *J*(HH) = 4.4 Hz, 2 H, py–ph). ³¹P{¹H} NMR (161.70 MHz, C₆D₆): δ 23.9 (d, *J*(PP) = 33.3 Hz, PPh₂), 37.6 (t, *J*(PP) = 33.3 Hz, PPh₃).

2.3. RuCl(PMe₃)₂(PCP), 4

Trimethylphosphine in tetrahydrofuran (1 M, 0.7 ml, 0.7 mmol) was added to a dichloromethane solution (15 ml) of 0.28 g of RuCl(PPh₃)(PCP) (0.32 mmol). The color of the reaction mixture changed immediately from green to orange. The solution was stirred for 2 h at room temperature. Then the solvent was removed completely under vacuum. Addition of 15 ml of methanol gave a yellow solid. The solid was collected on a filter frit and dried under vacuum overnight. Yield 0.21 g, 87%. Anal. Found: C, 60.00; H, 5.78. C₃₈H₄₅ClP₃Ru Calc.: C, 59.88; H, 5.95%. ¹H NMR (400 MHz, CDCl₃): δ 0.75 (t, *J*(PH) = 3.0 Hz, 18 H, 2 PMe₃), 3.80 (br, 4 H, 2

CH₂), 6.94–7.72 (m, 23 H, 2PPh₂, C₆H₃). ³¹P{¹H} NMR (161.70 MHz, CDCl₃): δ -13.6 (t, *J*(PP) = 38.9 Hz, PMe₃), 35.7 (t, *J*(PP) = 38.9 Hz, PPh₂).

2.4. RuCl(CO)₂(PCP), 5

Carbon monoxide was bubbled into a solution of 0.15 g of RuCl(PPh₃)(PCP) (0.17 mmol) in dichloromethane (15 ml) for 1 min. The color immediately changed from green to brown. The solvent was pumped away completely and 30 ml of methanol was added to give a white solid. The solid was collected on a filter frit and dried under vacuum overnight. Yield 0.10 g, 91%. Anal. Found: C, 61.50; H, 4.16. C₃₄H₂₇ClO₂P₂Ru Calc.: C, 61.31; H, 4.09%. IR (KBr, cm⁻¹): ν(CO) 2028 s, 1966 s. ¹H NMR (300 MHz, CDCl₃): δ 3.97 (dt, *J*(HH) = 16.0 Hz, *J*(PH) = 4.4 Hz, 2 H, CHH(C₆H₃)CHH), 4.61 (dt, *J*(HH) = 16.0 Hz, *J*(PH) = 5.0 Hz, 2 H, CHH(C₆H₃)CHH), 7.10–7.97 (m, 23 H, 2PPh₂, C₆H₃). ³¹P{¹H} NMR (121.50 MHz, CDCl₃): δ 50.9 (s).

2.5. RuH(PPh₃)(PCP), 6

10 mg of RuCl(PPh₃)(PCP), excess NaH and 0.5 ml of degassed tetrahydrofuran-*d*₈ was added to an NMR tube. ¹H and ³¹P NMR were obtained immediately. ¹H NMR (300 MHz, THF-*d*₈): δ -17.90 (q, *J*(PH) = 27 Hz), 2.47 (d, *J*(HH) = 16.2 Hz, 2 H, CHH(C₆H₃)CHH), 3.58 (dt, *J*(HH) = 16.2 Hz, *J*(PH) = 6.1 Hz, 2 H, CHH(C₆H₃)CHH), 6.86–7.43 (m, 38 H, PPh₃, 2PPh₂, C₆H₃). ³¹P{¹H} NMR (121.50 MHz, THF-*d*₈): δ 32.9 (d, *J*(PP) = 32.1 Hz, PPh₂), 78.4 (t, *J*(PP) = 32.1 Hz, PPh₃).

2.6. RuH(CO)(PPh₃)(PCP), 7

A mixture of 0.30 g of RuCl(PPh₃)(PCP) (0.34 mmol) and 0.12 g of NaBH₄ (3.5 mmol) in methanol was refluxed for 6 h. The green suspension gradually changed to pale brown. The solid was collected on a filter frit and dried under vacuum overnight. Yield 0.26 g, 87%. Anal. Found: C, 70.57; H, 5.16. C₅₁H₄₃OP₃Ru Calc.: C, 70.74; H, 5.01%. IR (KBr, cm⁻¹): ν(CO) 1965 s, ν(Ru–H) 1950 m. ¹H NMR (300 MHz, C₆D₆): δ -5.11 (q, *J*(PH) = 21 Hz, 1 H, RuH), 3.80 (dt, *J*(HH) = 15.1 Hz, *J*(PH) = 4.3 Hz, 2 H, CHH(C₆H₃)CHH), 4.35 (d, *J*(HH) = 15.1 Hz, 2 H, CHH(C₆H₃)CHH), 6.69–8.00 (m, 38 H, PPh₃, 2PPh₂, C₆H₃). ³¹P{¹H} NMR (121.49 MHz, C₆D₆): δ 46.9 (t, *J*(PP) = 19.0 Hz, PPh₃), 62.0 (d, *J*(PP) = 19.0 Hz, PPh₂).

2.7. RuH(PMe₃)₂(PCP), 8

A mixture of 0.07 g of RuCl(PMe₃)₂(PCP) (0.09 mmol) and 35 mg sodium borohydride (0.9 mmol) in 20 ml methanol was refluxed for 15 min to give a light orange solution. Then the reaction mixture was

cooled down to room temperature. The solvent was then removed completely under vacuum, and the residue was extracted with 20 ml of benzene, which was removed subsequently to give a yellow solid. The solid was dried under vacuum overnight. Yield 43 mg, 64%. Anal. Found: C, 62.62; H, 6.54. $C_{38}H_{46}P_4Ru$ Calc.: C, 62.72; H, 6.37%. 1H NMR (300 MHz, CD_2Cl_2): δ -8.68 (dq, $J(PH) = 72.9, 22.5$ Hz, 1 H, RuH), 0.6 (d, $J(PH) = 5.5$ Hz, 9 H, PMe_3), 1.18 (d, $J(PH) = 5.9$ Hz, 9 H, PMe_3), 3.72 (dt, $J(HH) = 15.9$ Hz, $J(PH) = 4.9$ Hz, 2 H, $CHH(C_6H_3)CHH$), 3.99 (d, $J(HH) = 16.0$ Hz, 2 H, $CHH(C_6H_3)CHH$), 6.67 (t, $J(HH) = 7.2$ Hz, 1 H, Ph), 6.93 (d, $J(HH) = 7.2$ Hz, 2 H, Ph), 7.18–7.91 (m, 20 H, PPh_2). $^{31}P\{^1H\}$ NMR (121.49 MHz, CD_2Cl_2): δ -18.0 (q, $J(PP) = 19.8$ Hz, PMe_3), -13.5 (q, $J(PP) = 23.6$ Hz, PMe_3), 63.9 (dd, $J(PP) = 23.6, 18.7$ Hz, PPh_2).

2.8. $[Ru(CO)(PPh_3)(PCP)]BF_4 \cdot 9$

One equiv. $HBF_4 \cdot Et_2O$ was dropped into a solution of 0.30 g of $RuH(CO)(PPh_3)(PCP)$ (0.34 mmol) in 15 ml

Table 1
Crystal data and refinement details for $RuCl(PPh_3)(PCP) \cdot CH_2Cl_2$

formula	$C_{51}H_{42}Cl_3P_3Ru$
fw	955.2
color and habit	dark, prism
crystal dimensions (mm^3)	$0.55 \times 0.30 \times 0.18$
crystal system	monoclinic
space group	$P2_1/c$
a (Å)	13.964(2)
b (Å)	12.366(2)
c (Å)	25.303(2)
β (deg)	90.89(2)
V (Å ³)	4369.0(12)
Z	4
d_{calc} ($g\ cm^{-3}$)	1.452
absorption coefficient (mm^{-1})	0.688
$F(000)$	1952
radiation	Mo $K\alpha$ ($\lambda = 0.71073$ Å)
2θ range (deg)	3.0–50.0
scan type	$2\theta - \theta$
scan speed ($deg\ min^{-1}$)	variable, 3.0–50.00 in ω
scan range (ω)	0.72° plus $K\alpha$ separation
T (K)	198
standard reflections	3 measured every 150 reflections
index range	$0 \leq h \leq 16, 0 \leq k \leq 14, -30 \leq l \leq 40$
reflection collected	7697
independent reflections	7675 ($R_{int} = 2.23\%$)
observed reflections	5713 ($F > 4.0\sigma(F)$)
absorption correction	semi-empirical
min./max. transmission	0.88/0.98
system used	Siemens SHELXTL IRIS
quantity minimized	$\sum w(F_o - F_c)^2$
hydrogen atoms	riding model, fixed isotropic U
weight scheme	$w^{-1} = \sigma^2(F) + 0.0003F^2$
no. of parameters refined	549
final R indices (obs. data)	$R = 3.78\%, R_w = 3.86\%$
R indices (all data)	$R = 5.86\%, R_w = 4.21\%$

Table 2
Selected bond distances (Å) and angles (deg) for $RuCl(PPh_3)(PCP) \cdot CH_2Cl_2$

Interatomic distances			
Ru(1)–Cl(1)	2.459(1)	Ru(1)–P(1)	2.297(1)
Ru(1)–P(2)	2.284(1)	Ru(1)–P(3)	2.196(1)
Ru(1)–C(1)	2.070(4)	P(1)–C(11)	1.826(4)
P(1)–C(21)	1.818(4)	P(1)–C(31)	1.811(4)
P(2)–C(37)	1.817(4)	P(2)–C(41)	1.814(4)
P(2)–C(51)	1.820(4)	P(3)–C(61)	1.844(4)
P(3)–C(71)	1.833(4)	P(3)–C(81)	1.844(4)
C(1)–C(32)	1.414(5)	C(1)–C(36)	1.413(5)
C(31)–C(32)	1.504(5)	C(32)–C(33)	1.388(6)
C(33)–C(34)	1.384(6)		
Intermolecular angles			
P(1)–Ru(1)–Cl(1)	96.1(1)	P(1)–Ru(1)–P(2)	150.4(1)
P(1)–Ru(1)–P(3)	102.3(1)	P(1)–Ru(1)–C(1)	79.4(1)
P(2)–Ru(1)–Cl(1)	95.0(1)	P(2)–Ru(1)–P(3)	98.1(1)
P(2)–Ru(1)–C(1)	81.5(1)	P(3)–Ru(1)–Cl(1)	113.6(1)
P(3)–Ru(1)–C(1)	84.8(1)	C(1)–Ru(1)–Cl(1)	161.6(1)

dichloromethane. After stirring for 10 min at room temperature, the volume of the reaction mixture was reduced to 1 ml. Addition of 50 ml of hexane produced a gray solid. The solid was collected by filtration, washed with water and hexane and dried under vacuum. Yield 0.25 g, 76%. Anal. Found: C, 61.68; H, 4.97. $C_{51}H_{42}BF_4OP_3Ru \cdot 2H_2O$ Calc.: C, 62.07; H, 4.69%. IR (KBr, cm^{-1}): $\nu(CO)$ 1944 s. 1H NMR (300 MHz, $CDCl_3$): δ 3.78 (dt, $J(HH) = 16.5$ Hz, $J(PH) = 4.1$ Hz, 2 H, $CHH(C_6H_3)CHH$), 3.94 (dt, $J(HH) = 16.5$ Hz, $J(PH) = 3.8$ Hz, 2 H, $CHH(C_6H_3)CHH$), 6.86–7.77 (m, 38 H, $PPh_3, 2PPh_2, C_6H_3$). $^{31}P\{^1H\}$ NMR (121.50 MHz, $CDCl_3$): δ 23.1 (d, $J(PP) = 17.1$ Hz, PPh_2), 42.4 (t, $J(PP) = 17.1$ Hz, PPh_3).

2.9. Crystallographic analysis of $RuCl(PPh_3)(PCP) \cdot CH_2Cl_2$

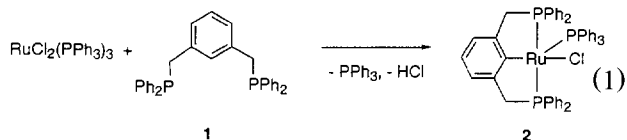
Suitable crystals for X-ray diffraction study were obtained by slow diffusion of MeOH into a CH_2Cl_2 solution of $RuCl(PPh_3)(PCP)$ at room temperature. A specimen of dimensions $0.55 \times 0.30 \times 0.18\ mm^3$ was mounted on a glass fiber and used for X-ray structure determination. The crystal system was monoclinic, with space group $P2_1/c$. A total of 7697 intensity measurements were made using the $2\theta - \theta$ scan technique in the range $3^\circ \leq 2\theta \leq 50^\circ$ (Mo $K\alpha$ radiation). Of these 7675 were unique ($R_{merge} = 2.23\%$) and 5713 observed $F \geq 4\sigma(F)$, which were used for structure solution and refinement using the SHELXTL PLUS [15] program package. Solution by direct methods yielded the positions of all non-hydrogen atoms. Refinement by full-matrix least-squares resulted in final discrepancy indices $R = 0.0378$, $R_w = 0.0386$ with GOF = 1.16. All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogens were revealed in difference Fourier

maps, but then placed in geometrically determined positions $d_{C-H} = 0.96 \text{ \AA}$ and refined isotropically with riding constraints and group thermal parameters. The data:parameter ratio was 10.4:1 and the residual electron density $+0.47 / -0.41 \text{ e \AA}^{-3}$, with the largest peak associated with the disordered CH_2Cl_2 . Further crystallographic details for $\text{RuCl}(\text{PPh}_3)(\text{PCP}) \cdot \text{CH}_2\text{Cl}_2$ are given in Table 1. Selected bond distances and angles are given in Table 2.

3. Results and discussion

3.1. Synthesis and characterization of $\text{RuCl}(\text{PPh}_3)(\text{PCP})$

Refluxing a mixture of $\text{RuCl}_2(\text{PPh}_3)_3$ and slightly over one equiv. of the ligand **1** in isopropanol produced the monomeric green compound $\text{RuCl}(\text{PPh}_3)(\text{PCP})$, **2** (Eq. (1)). Thus orthometallation occurred during the reaction. Orthometallation reactions were observed previously in the reactions of 1,3- $(\text{R}_2\text{PCH}_2)_2\text{C}_6\text{H}_4$ and related ligands with metal complexes such as $\text{PdCl}_2(\text{PhCN})_2$, $\text{PtCl}_2(\text{PPh}_3)_2$ and $[\text{RhCl}(\text{COD})]_2/\text{PPh}_3$ [2,4,6–9].



The spectroscopic data of the green compound **2** are consistent with a square-pyramidal complex with PPh_3 occupying the apical position. The ^{31}P NMR spectrum of the green compound in CDCl_3 showed a doublet for the PPh_2 group at 32.5 ppm and a triplet at 79.4 ppm ($J(\text{PP}) = 27.7 \text{ Hz}$) for the PPh_3 ligand. Thus the PPh_3 is significantly deshielded compared to the PPh_2 groups. Such a ^{31}P NMR pattern has been observed for several similar square-pyramidal ruthenium dichloro complexes with apical phosphines, such as $\text{RuCl}_2(\text{PR}_3)_3$ ($\text{PR}_3 = \text{PPh}_3, \text{PEtPh}_2$) [16], $\text{RuCl}_2(\text{PPh}_3)(\text{L}_2)$ ($\text{L}_2 = \text{dppb}, \text{dppp}$) [17], $\text{Ru}_2\text{Cl}_4(\text{diop})_3$ [18] and $\text{RuCl}_2(\text{Cytpt})$ ($\text{Cytpt} = \text{PhP}(\text{CH}_2\text{CH}_2\text{CH}_2\text{PCy}_2)_2$) [19]. For example, the resonance for the apical PPh_3 appeared at 75.0 ppm and the basal PPh_3 at 23.3 ppm in $\text{RuCl}_2(\text{PPh}_3)_3$ [16]. It is interesting to note that some of the square-pyramidal ruthenium dichloro complexes, for example $\text{RuCl}_2(\text{Cytpt})$, $\text{RuCl}_2(\text{PEtPh}_2)_3$ and $\text{Ru}_2\text{Cl}_4(\text{diop})_3$, are also green in color. Consistent with the structure, the ^1H NMR of the compound displayed a virtual doublet of triplet signal at 3.47 ppm for two of the methylene protons, indicating that the two PPh_2 groups are *trans* to each other [20]. The structure has been confirmed by an X-ray diffraction study of **2** (see below).

It may be noted that although both $[2,6-(\text{Ph}_2\text{PCH}_2)_2\text{C}_6\text{H}_3]^-$ and η^5 -cyclopentadienyls are six-

electron donors, Cp or Cp^* can form stable complexes $\text{CpRuCl}(\text{PPh}_3)_2$ [21] or $\text{Cp}^*\text{RuCl}(\text{PPh}_3)_2$ [22], whereas $[2,6-(\text{Ph}_2\text{PCH}_2)_2\text{C}_6\text{H}_3]^-$ does not form the analogous 18-electron complexes $\text{RuCl}(\text{PPh}_3)_2(\text{PCP})$, probably due to its bulkiness and better electron donating capability. Very bulky phosphines such as PCy_3 and P^iPr_3 are known to form stable 16-electron complexes with η^5 -pentamethylcyclopentadienyl, $\text{Cp}^*\text{RuCl}(\text{PR}_3)_3$, which are deep blue in color [23,24].

3.2. Description of the structure of $\text{RuCl}(\text{PPh}_3)(\text{PCP})$

The molecular geometry of **2** is depicted in Fig. 1. Selected bond distances and angles are listed in Table 2.

The structure of **2** can be viewed as a distorted square pyramid with the PPh_3 ligand located at the apex. The four atoms $\text{Cl}(1)$, $\text{P}(1)$, $\text{C}(1)$ and $\text{P}(2)$ form the base and the ruthenium center is above the square base towards the apical position. The structure is quite similar to that of $\text{Ru}(\text{PPh}_3)(\text{NCN})$ ($\text{NCN} = 2,6-(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3$) reported recently [12]. The $\text{P}(1)-\text{Ru}(1)-\text{P}(2)$ angle is $150.4(1)^\circ$ and the $\text{C}(1)-\text{Ru}(1)-\text{Cl}(1)$ angle is $161.6(1)^\circ$. The $\text{P}(1)-\text{Ru}(1)-\text{P}(2)$ angle of $150.4(1)^\circ$ is smaller than those observed typically in meridional triphosphine ruthenium complexes, for example *cis-mer*- $\text{RuH}_2(\text{N}_2)(\text{Cytpt})$ ($\text{P}(1)-\text{Ru}-\text{P}(1') = 163.26(6)^\circ$) [25], *mer*- $\text{Ru}(\text{C}\equiv\text{CPh})(\eta^3\text{-PhC}_3\text{CHPh})(\text{Cytpt})$ ($\text{P}(1)-\text{Ru}-\text{P}(1') = 176.2(1)^\circ$) [26]. However, the $\text{P}(1)-\text{Ru}(1)-\text{P}(2)$ angle of $150.4(1)^\circ$ is close to that of the $\text{N}-\text{Ru}-\text{N}$ angle ($147.59(7)^\circ$) in $\text{Ru}(\text{PPh}_3)(\text{NCN})$ [12]. The smaller angles in the PCP and NCN complexes are likely due to the smaller bite angles of these ligands.

The $\text{Ru}(1)-\text{C}(1)$ bond length of $2.070(4) \text{ \AA}$ is close to the $\text{Ru}-\text{C}(\text{sp}^2)$ single bonds reported in other complexes. For example, the $\text{Ru}-\text{C}(\text{sp}^2)$ distances are $1.967(2)$, $2.056(5)$ and $2.04(3) \text{ \AA}$ in the five-coordinate

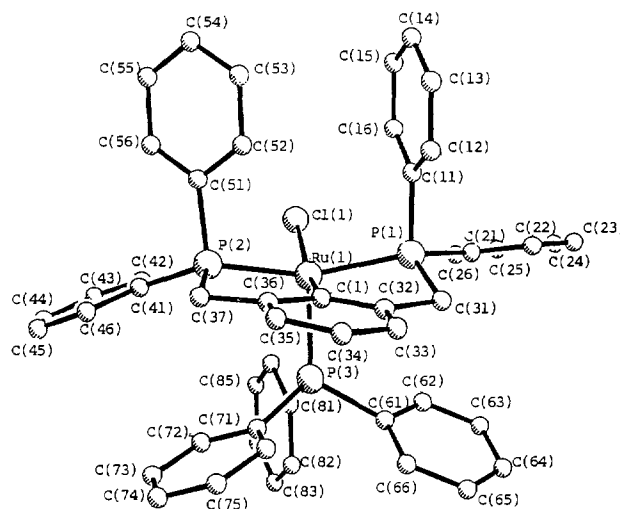


Fig. 1. The molecular structure of $\text{RuCl}(\text{PPh}_3)(\text{PCP})$. Hydrogen atoms are omitted for clarity.

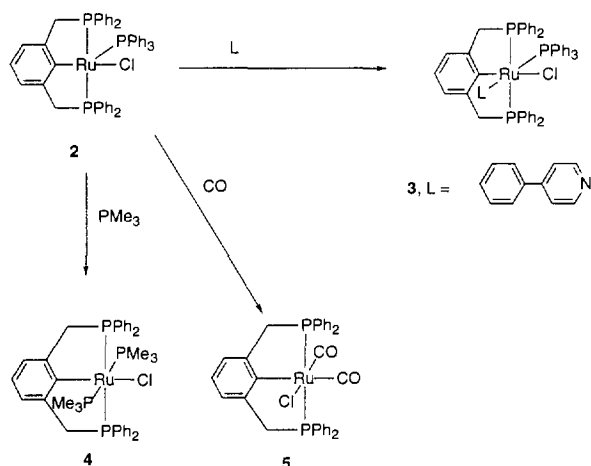
complexes $\text{RuI}(\text{PPh}_3)(\text{NCN})$ [12], $\text{RuCl}(p\text{-tolyl})(\text{CO})(\text{PPh}_3)_2$ and $\text{RuCl}(o\text{-tolyl})(\text{CO})(\text{PPh}_3)_2$ respectively [27]. The $\text{Ru}-\text{C}(\text{sp}^2)$ distance is $2.018(10)\text{ \AA}$ in the orthometallated complex $\text{Ru}(\text{C}_6\text{F}_4\text{-N}=\text{NC}_6\text{F}_5)(\text{PPh}_2\text{-C}_6\text{H}_4\text{-}\eta^5\text{-C}_5\text{H}_4)$ [28]. The $\text{Ru}(1)\text{-P}(3)$ bond is shorter than the mutually *trans* disposed $\text{Ru}(1)\text{-P}(1)$ and $\text{Ru}(1)\text{-P}(2)$ bonds. These bonding patterns and bond distances are normal compared to related meridional complexes, for example $\text{RuH}(\text{O}_2\text{CH})(\text{PPh}_3)_3$ [29], $\text{RuH}(\text{O}_2\text{CCH}_3)(\text{PPh}_3)_3$ [30], $\text{RuHCl}(\text{PPh}_3)_3$ [31] and $\text{RuCl}_2(\text{PPh}_3)_3$ [32].

Theoretical study shows that in the absence of steric effects, a square pyramid is favored over trigonal bipyramidal geometry for complexes with d^6 electronic configuration [33]. It is noted that most other structurally characterized square pyramidal geometry d^6 complexes of Group 8 and 9 metals have the largest *trans* influence group occupying the apical position [31,32,34,35], as for example in $\text{RuCl}(p\text{-tolyl})(\text{CO})(\text{PPh}_3)_2$ [27] and $\text{RuCl}(\text{CH}=\text{CHPh})(\text{CO})(\text{PPh}_3)_2$ [34]. In the complex $\text{RuCl}(\text{PPh}_3)(\text{PCP})$, the PPh_3 instead of the orthometallated aryl takes the apical position, most likely for steric reasons.

3.3. Reactions of $\text{RuCl}(\text{PPh}_3)(\text{PCP})$ with simple two-electron donor ligands

As expected the unsaturated complex **2** reacted with 4-phenylpyridine to give the simple $18e^-$ octahedral adduct **3** (see Scheme 1). The ^{31}P NMR of the adduct in CDCl_3 showed a doublet for the two PPh_2 groups and a triplet for the PPh_3 ligand. The NMR data are consistent with the PCP ligand coordinating in a meridional fashion as shown in Scheme 1, although we cannot exclude another possible isomer in which the 4-phenylpyridine ligand is *trans* to the orthometallated carbon atom.

With stronger coordinating ligands, the PPh_3 ligand can also be substituted. Thus the bis(trimethylphos-



Scheme 1.

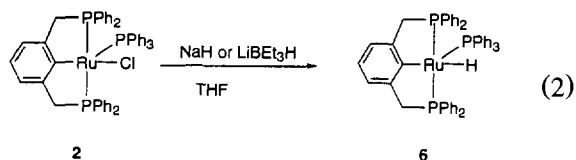
phine) compound $\text{RuCl}(\text{PMe}_3)_2(\text{PCP})$, **4**, was isolated upon treatment of compound **2** with two equivalents of PMe_3 at room temperature. A mixture of starting material **2** and compound **4** was obtained when less than two equivalents of PMe_3 ligand was used. The easy substitution of PPh_3 ligand in $\text{RuCl}(\text{PPh}_3)(\text{PCP})$ is in sharp contrast with the more forcing conditions used in the replacement of the PPh_3 ligand in $\text{CpRuCl}(\text{PPh}_3)_2$ with PR_3 to give $\text{CpRuCl}(\text{PR}_3)_2$ [36]. Compound **4** is soluble in non-polar solvents such as benzene and insoluble in polar solvents such as methanol, indicating that it is a neutral compound. The ^{31}P NMR of the PMe_3 compound **4** in CDCl_3 showed a triplet at -13.6 ppm for the PMe_3 ligand and a triplet at 35.7 ppm ($J(\text{PP}) = 38.9\text{ Hz}$) for the PPh_2 groups. The ^{31}P NMR data indicate that the PCP ligand is still in a meridional fashion and that the two PMe_3 ligands are *trans* to each other.

Reaction of CO with $\text{RuCl}(\text{PPh}_3)(\text{PCP})$ also leads to replacement of the PPh_3 ligand. Thus the white compound $\text{RuCl}(\text{CO})_2(\text{PCP})$, **5**, was produced when CO gas was briefly bubbled into a solution of $\text{RuCl}(\text{PPh}_3)(\text{PCP})$. The ^{31}P NMR of compound **5** showed only a singlet at 50.9 ppm for the PPh_2 groups. The ^1H NMR spectra showed two sets of virtual doublets of triplets at 4.61 and 3.97 ppm for the methylene protons, indicating that the PCP ligand is meridional. The infrared spectrum showed two CO stretching bands with similar intensity at 2028 and 1966 cm^{-1} , which implies that the two CO ligands are *cis* to each other [37]. Thus the structure of $\text{RuCl}(\text{CO})_2(\text{PCP})$ is different from that of $\text{RuCl}(\text{PMe}_3)_2(\text{PCP})$ in which the two PMe_3 ligands are *trans* to each other. The structural difference between the CO complex **5** and the PMe_3 complex **4** can be attributed to the fact that CO is a very strong π -acceptor and thus the two COs avoid being *trans* to each other so as not to compete for the π -electrons of ruthenium. It is noted that substitution of PPh_3 with CO in $\text{CpRuCl}(\text{PPh}_3)_2$ or $\text{Cp}^*\text{RuCl}(\text{PPh}_3)_2$ could not be achieved so easily. All attempts to prepare the dicarbonyl species $\text{CpRuCl}(\text{CO})_2$ via substitution reactions of $\text{CpRuCl}(\text{PPh}_3)_2$ with CO have been unsuccessful. Thus only $\text{CpRuCl}(\text{CO})(\text{PPh}_3)$ was formed from the forcing carbonylation reactions of $\text{CpRuCl}(\text{PPh}_3)_2$ (150 atm CO, or 2 atm CO in the presence of S, or via the addition of $\text{Fe}_2(\text{CO})_9$ in THF) [38]. A mixture of $\text{Cp}^*\text{RuCl}(\text{CO})(\text{PPh}_3)$ and $\text{Cp}^*\text{RuCl}(\text{CO})_2$ was obtained from the reaction of 5 atm CO and $\text{Cp}^*\text{RuCl}(\text{PPh}_3)_2$ in refluxing toluene [39]. The easy replacement of PPh_3 in **2** is likely due to the steric congestion and more electron richness in the PCP complex.

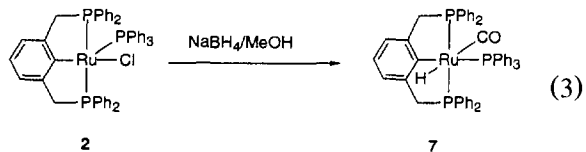
3.4. Preparation of hydride complexes

The monohydride complex $\text{RuH}(\text{PPh}_3)(\text{PCP})$, **6**, could be produced from the reaction of $\text{RuCl}(\text{PPh}_3)(\text{PCP})$ with NaH or LiBEt_3H in THF (Eq.

(2)). Due to its low stability, compound **6** could not be isolated in analytically pure form. The ^{31}P NMR spectrum of the hydride compound in $\text{THF-}d_8$ showed a triplet at 78.4 ppm for the PPh_3 ligand and a doublet at 32.9 ppm ($J(\text{PP}) = 32.1$ Hz) for the PPh_2 group. The ^{31}P NMR data are very similar to those of the chloride complex $\text{RuCl}(\text{PPh}_3)(\text{PCP})$, which implies that the two compounds presumably have very similar structures. Consistent with this, the ^1H NMR spectrum in $\text{THF-}d_8$ displayed a quartet hydride signal at -17.90 ppm with $J(\text{PH}) = 27$ Hz. It is noted that reaction of the 16-electron species $\text{Cp}^*\text{RuCl}(\text{PR}_3)$ with LiEt_3H in THF produced $\text{Cp}^*\text{RuH}_3(\text{PR}_3)$ [23].



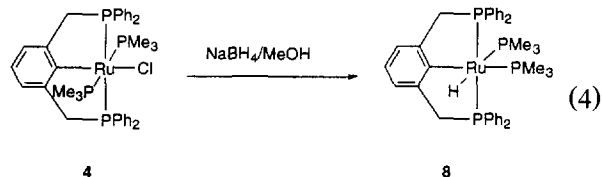
Treatment of $\text{RuCl}(\text{PPh}_3)(\text{PCP})$ with NaBH_4 in methanol produced the CO-containing compound $\text{RuH}(\text{CO})(\text{PPh}_3)(\text{PCP})$, **7**, in 87% yield (Eq. (3)). Although the detailed mechanism for this reaction was not investigated, complex **7** is likely formed from the hydride intermediate $\text{RuH}(\text{PPh}_3)(\text{PCP})$ which reacted further with methanol to give the CO-containing product **7**. This was confirmed by the reaction of methanol with $\text{RuH}(\text{PPh}_3)(\text{PCP})$ prepared from the reaction of $\text{RuCl}(\text{PPh}_3)(\text{PCP})$ with NaH in THF. There are many reported examples of production of CO-containing complexes from the reactions of low valent metal complexes with alcohols [40].



The ^{31}P NMR of complex **7** in C_6D_6 showed a triplet at 46.9 ppm for the PPh_3 ligand and a doublet at 62.0 ppm ($J(\text{PP}) = 19.0$ Hz) for the PPh_2 groups. These ^{31}P NMR data are consistent with a structure in which the PCP ligand is meridional and the PPh_3 ligand is *cis* to both the PPh_2 groups. The ^1H NMR spectrum in C_6D_6 displayed a pseudo-quartet hydride signal at -5.11 ppm with $J(\text{PH}) = 21$ Hz. The magnitude of the coupling constant indicates that the hydride is *cis* to all three phosphorus atoms [41]. The low field chemical shift for the hydride signal implies that the hydride is *trans* to the strong *trans* influence ligand CO. For comparison, the signals for the hydride *trans* to CO were observed at -3.87 ppm for $[\text{RuH}(\text{CO})(\text{dppm})_2]\text{Cl}$ and at -5.05 ppm for $[\text{RuH}(\text{CO})(\text{dppp})_2]\text{Cl}$, the signal for the hydride *trans* to Cl was observed at -13.59 ppm for $\text{RuHCl}(\text{CO})(\text{PPh}_3)(\text{dppm})$ [42]. The structure assign-

ment is confirmed by NOE experiment. In this experiment, a positive NOE effect was observed for the methylene protons ($\delta = 4.35$ ppm) on the same side of the hydride, when the hydride signal at -5.11 ppm was irradiated.

Reaction of $\text{RuCl}(\text{PMe}_3)_2(\text{PCP})$ with NaBH_4 in refluxing methanol produced the hydride complex $\text{RuH}(\text{PMe}_3)_2(\text{PCP})$, **8**, in 64% (Eq. (4)). In the ^{31}P NMR in CD_2Cl_2 , the signals for PMe_3 were observed at -18.0 ppm (q, $J = 19.8$ Hz) and -13.5 ppm (q, $J = 23.6$ Hz), and that for the PPh_2 groups was observed at 63.9 ppm (dd, $J = 23.6, 18.7$ Hz). The ^{31}P NMR data indicate that the two PMe_3 ligands are *cis* to each other and that the PCP ligand is in a meridional geometry. Consistent with this structure, the ^1H NMR in CD_2Cl_2 displayed a doublet of triplet hydride signal at -8.68 ppm with $J(\text{PH})$ constants of 72.9 and 22.5 Hz, suggesting that the hydride is *trans* to one phosphorus and *cis* to the other three. It is interesting to note that the two PMe_3 ligands are *trans* to each other in $\text{RuCl}(\text{PMe}_3)_2(\text{PCP})$ but are *cis* to each other in $\text{RuH}(\text{PMe}_3)_2(\text{PCP})$. The structural difference is likely due to the fact that both hydride and aryl are strong σ -donors and *cis* deposition of the two PMe_3 ligands in **8** would avoid the *trans* arrangement of the two ligands.



The hydride complexes $\text{RuH}(\text{CO})(\text{PPh}_3)(\text{PCP})$ and $\text{RuH}(\text{PMe}_3)_2(\text{PCP})$ can be viewed as analogs of complexes $(\eta^5\text{-C}_5\text{R}_5)\text{RuH}(\text{CO})(\text{PR}_3)$ and $(\eta^5\text{-C}_5\text{R}_5)\text{RuH}(\text{PR}_3)_2$. Protonation of $(\eta^5\text{-C}_5\text{R}_5)\text{RuH}(\text{L})(\text{PR}_3)$ ($\text{L} = \text{CO}, \text{PR}_3$) with HBF_4 could lead to either $[(\eta^5\text{-C}_5\text{R}_5)\text{Ru}(\text{H}_2)(\text{L})(\text{PR}_3)]^+$ or $(\eta^5\text{-C}_5\text{R}_5)\text{RuH}_2(\text{L})(\text{PR}_3)^+$ [43]. However the corresponding dihydride or dihydrogen complexes could not be obtained from protonation of $\text{RuH}(\text{CO})(\text{PPh}_3)(\text{PCP})$ and $\text{RuH}(\text{PMe}_3)_2(\text{PCP})$. Protonation of $\text{RuH}(\text{PMe}_3)_2(\text{PCP})$ with $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ led to an unidentified mixture and protonation of $\text{RuH}(\text{CO})(\text{PPh}_3)(\text{PCP})$ led to the formation of $[\text{Ru}(\text{CO})(\text{PPh}_3)(\text{PCP})]^+$ (or solvated complex), **9**, as indicated by the spectroscopic data.

4. Conclusion

We have synthesized and characterized a series of ruthenium complexes with the orthometallated ligand $[(2,6\text{-}(\text{Ph}_2\text{PCH}_2)_2\text{C}_6\text{H}_3)]^-$ (PCP). Although ligand $[2,6\text{-}(\text{Ph}_2\text{PCH}_2)_2\text{C}_6\text{H}_3]^-$ and cyclopentadienyls are all six-electron donors, their metal complexes display different structural and chemical properties. For example, substi-

tution reactions of $\text{RuCl}(\text{PPh}_3)(\text{PCP})$ with CO and PMe_3 ligands are much faster than those in $\text{CpRuCl}(\text{PPh}_3)_2$ or $\text{Cp}^*\text{RuCl}(\text{PPh}_3)_2$; the protonation behavior of $\text{RuH}(\text{L})_2(\text{PCP})$ ($\text{L} = \text{CO}, \text{PMe}_3$) are also different from their Cp or Cp^* analogs ($\eta^5\text{-C}_5\text{R}_5$) $\text{RuH}(\text{L})(\text{PR}_3)$. The difference could be related to the sterically more bulky, electronically more rich properties of the PCP ligand.

5. Supplementary material

Tables of atomic coordinates, bond distances, bond angles, anisotropic displacement coefficients, H-atom coordinates and isotropic displacement coefficients for $\text{RuCl}(\text{PPh}_3)(\text{PCP}) \cdot \text{CH}_2\text{Cl}_2$ (total 9 pages) are available from the authors.

Acknowledgements

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