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#### Key indicators

Single-crystal X-ray study  
 $T = 150$  K  
Mean  $\sigma(\text{C}-\text{C}) = 0.004$  Å  
 $R$  factor = 0.028  
 $wR$  factor = 0.067  
Data-to-parameter ratio = 20.1

For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.

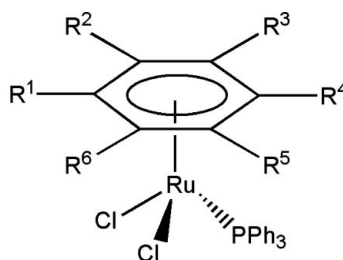
## Dichloro( $\eta^6$ -*p*-cymene)(triphenylphosphine)- ruthenium(II)

The title compound,  $[\text{Ru}(\text{C}_{10}\text{H}_{14})\text{Cl}_2(\text{C}_{18}\text{H}_{15}\text{P})]$ , crystallizes with two molecules in the asymmetric unit. It adopts the classic pseudo-tetrahedral piano-stool structure. A comparison of the Ru–P, Ru–Cl, Ru–C(av) bond lengths and the sum of the P–Ru–Cl1, P–Ru–Cl2 and Cl1–Ru–Cl2 angles (for both independent molecules) with those of previously determined compounds  $[(\eta^6\text{-arene})\text{Ru}(\text{PPh}_3)\text{Cl}_2]$  reveals that the nature of the  $\eta^6$ -arene ligand has a marginal effect on these structural parameters.

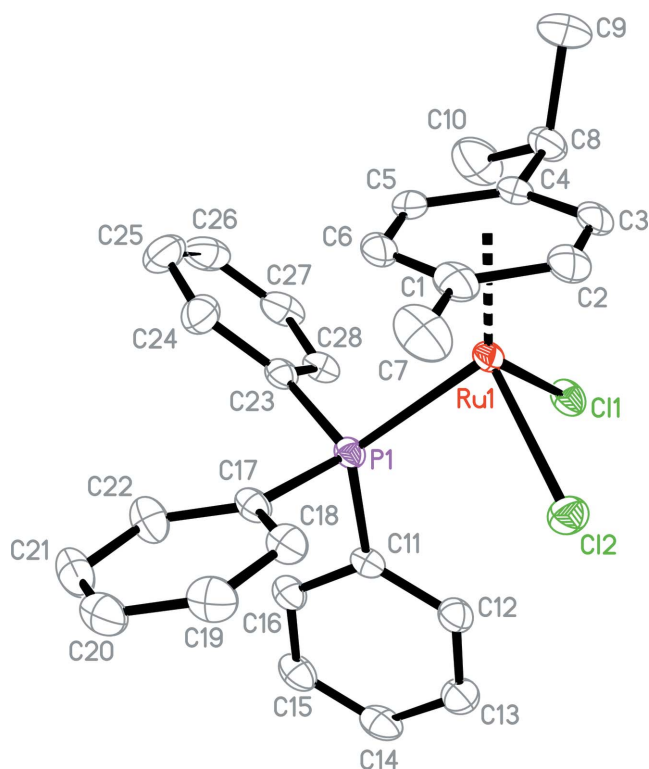
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#### Comment

Organometallic arene ruthenium(II) complexes have attracted much interest for a range of uses, including DNA-binding studies, chemosensors, highly selective receptors, catalysis and for the development of chiral half-sandwich compounds (Dorcier *et al.*, 2005; Buryak & Severin, 2005; Ion *et al.*, 2006; Morris *et al.*, 2006; Ganter, 2003). Tertiary phosphines, such as the ubiquitous triphenylphosphine, are known to rapidly cleave Ru–Cl–Ru bridges in dinuclear arene complexes to give achiral (Baldwin *et al.*, 2002; Hansen & Nelson, 2000; Therrien *et al.*, 2004) or chiral (Therrien & Süß-Fink, 2004; Vieille-Petit *et al.* (2003) mononuclear compounds of the type  $[(\eta^6\text{-arene})\text{Ru}(\text{PPh}_3)\text{Cl}_2]$ . Recently we reported (Dann *et al.*, 2006) the supramolecular chemistry of  $[(\eta^6\text{-}p\text{-cymene})\text{Ru}(\text{PR}_3)\text{Cl}_2]$  complexes with highly functionalized *P*-monodentate tertiary phosphines. During efforts to prepare a mixed-metal Cu/Ru complex using pyrazine-2,3-dicarboxylic acid as a bridging ligand, we isolated and crystallographically verified the structure of the title pseudo-tetrahedral ruthenium(II) triphenylphosphine complex, (I).



$\text{R}^1 = \text{CH}_3$ , $\text{R}^4 = \text{CH}(\text{CH}_3)_2$ , $\text{R}^2$ , $\text{R}^3$ , $\text{R}^5$ , $\text{R}^6 = \text{H}$	I
$\text{R}^1 = \text{CH}(\text{CH}_3)\text{CH}_2\text{OH}$ , $\text{R}^2 > \text{R}^6 = \text{H}$	II
$\text{R}^1 > \text{R}^6 = \text{H}$	III
$\text{R}^1 = \text{R}^3 = \text{R}^4 = \text{CH}_3$ , $\text{R}^2$ , $\text{R}^5$ , $\text{R}^6 = \text{H}$	IV
$\text{R}^1 > \text{R}^6 = \text{CH}_3$	V
$\text{R}^1 > \text{R}^6 = \text{CH}_2\text{CH}_3$	VI



**Figure 1**

The structure of one of the two independent molecules (I), showing the atom-labelling scheme; the other molecule is very similar. Displacement ellipsoids are drawn at the 50% probability level. All H atoms have been omitted for clarity.

There are two similar molecules in the asymmetric unit, so discussion will primarily focus on one of these independent molecules; see Fig. 1 for a view of one of the two independent molecules. The Ru atom has a typical piano-stool coordination environment, with an  $\eta^6$ -coordinated *p*-cymene ligand, two chlorides and a triphenylphosphine ligand. Both molecules adopt a conformation half way between staggered and eclipsed orientations with regard to the *p*-cymene ring and the other three coordinated atoms. The metric parameters around the Ru core (Table 1) compare well with those of similar three-legged piano-stool [ $\eta^6$ -arene]Ru(PPh<sub>3</sub>)Cl<sub>2</sub> complexes (II)–(VI) (Table 2). The two *p*-cymene alkyl substituents bend very slightly away from the metal by 0.03 Å at the methyl group and 0.05 Å at the isopropyl group (for molecule 1) and by 0.02 Å at the methyl group and 0.01 Å at the isopropyl group (for molecule 2). The average Ru–C distances are 2.218 (2) and 2.215 (2) Å for the two independent molecules, in the range found in compounds (II)–(VI) [2.202 (3)–2.249 (4) Å]. There is very little difference in the Ru–C<sub>centroid</sub> parameters (1.709 and 1.705 Å) for the two independent molecules in (I). We also find some evidence for bond-length alternation around the *p*-cymene ring: average long = 1.426; average short = 1.403 Å (molecule 1), (1.426 and 1.401 Å for molecule 2). In previous structures (Elsegood & Tocher, 1995; Therrien & Süß-Fink, 2004; Vieille-Petit *et al.* (2003), a *trans* bond lengthening has been observed in the Ru–C bonds *trans* to P donors such as PPh<sub>3</sub>. In the case of (I), the Ru1–C3, Ru1–

C4, Ru2–C31 and Ru2–C32 bonds are longer than the other Ru–C bonds, with C2/C3 *trans* to P1 and C30/C31 *trans* to P2. A comparison of the sum of the P–Ru–Cl1, P–Ru–Cl2 and Cl1–Ru–Cl2 angles for (I) with (II) reveals that both ( $\eta^6$ -arene) groups have similar steric hindrance. The sum of these angles is *ca* 4–8° larger than found in (III)–(VI) (Table 2).

In summary, we have shown that triphenylphosphine affords a classic pseudo-tetrahedral ( $\eta^6$ -*p*-cymene)ruthenium(II) chloro complex with typical Ru–P/Ru–Cl bond lengths and angles.

## Experimental

To a CH<sub>3</sub>OH (10 ml) solution of [( $\eta^6$ -*p*-cymene)RuCl<sub>2</sub>]<sub>2</sub> (0.043 g, 0.057 mmol) was added a CH<sub>3</sub>OH (10 ml) solution of Cu[2,3-pz(CO<sub>2</sub>)(CO<sub>2</sub>H)](PPh<sub>3</sub>)<sub>2</sub> (0.018 g, 0.028 mmol) (pz = pyrazine). The dark-orange solution was stirred at room temperature for 2 h. The mixture was evaporated to dryness under reduced pressure, affording a dark-orange solid which was redissolved in the minimum volume of CH<sub>2</sub>Cl<sub>2</sub> (*ca* 2 ml) and precipitated with diethyl ether (10 ml). The green solid was collected by suction filtration and dried *in vacuo*. Suitable X-ray quality crystals of (I) were obtained by slow evaporation of the CH<sub>2</sub>Cl<sub>2</sub>/diethyl ether filtrate.

### Crystal data

[Ru(C<sub>10</sub>H<sub>14</sub>)Cl<sub>2</sub>(C<sub>18</sub>H<sub>15</sub>P)]  
*M<sub>r</sub>* = 568.45  
 Monoclinic, *P*2<sub>1</sub>/*n*  
*a* = 15.4858 (8) Å  
*b* = 9.1887 (5) Å  
*c* = 35.0089 (19) Å  
 $\beta$  = 96.568 (2)°  
*V* = 4948.9 (5) Å<sup>3</sup>

*Z* = 8  
*D<sub>x</sub>* = 1.526 Mg m<sup>-3</sup>  
 Mo *K*α radiation  
 $\mu$  = 0.93 mm<sup>-1</sup>  
*T* = 150 (2) K  
 Plate, red  
 0.71 × 0.28 × 0.10 mm

### Data collection

Bruker SMART 1000 CCD diffractometer  
 $\omega$  scans  
 Absorption correction: multi-scan (SADABS; Sheldrick, 2003)  
*T<sub>min</sub>* = 0.558, *T<sub>max</sub>* = 0.913

42058 measured reflections  
 11719 independent reflections  
 9288 reflections with *I* > 2σ(*I*)  
*R<sub>int</sub>* = 0.023  
 $\theta_{\max}$  = 29.0°

### Refinement

Refinement on *F*<sup>2</sup>  
*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.028  
*wR*(*F*<sup>2</sup>) = 0.067  
*S* = 1.06  
 11719 reflections  
 583 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0233P)^2 + 4.6393P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.002$   
 $\Delta\rho_{\max} = 0.52 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\min} = -0.59 \text{ e \AA}^{-3}$

**Table 1**

Selected bond lengths (Å).

Ru1–C1	2.213 (2)	Ru2–C29	2.210 (2)
Ru1–C2	2.216 (2)	Ru2–C30	2.212 (2)
Ru1–C3	2.245 (2)	Ru2–C31	2.247 (2)
Ru1–C4	2.247 (2)	Ru2–C32	2.239 (2)
Ru1–C5	2.213 (2)	Ru2–C33	2.207 (2)
Ru1–C6	2.176 (2)	Ru2–C34	2.173 (2)

**Table 2**

Selected geometric parameters (Å, °) for (I) and comparison with reported compounds (II)–(VI).

	(I)	(II)	(III)	(IV)	(V)	(VI)
Ru–P	2.3438 (6) [2.3442 (6)]	2.3530 (10)	2.3637 (12)	2.3533 (14)	2.3607 (10)	2.388 (1)
Ru–Cl1	2.4154 (6) [2.4154 (6)]	2.4134 (9)	2.406 (2)	2.4008 (18)	2.4117 (10)	2.423 (1)
Ru–Cl2	2.4151 (6) [2.4131 (6)]	2.3995 (10)	2.4118 (10)	2.4299 (15)	2.4118 (10)	2.412 (1)
Ru–C(av)	2.218 (2) [2.215 (2)]	2.215 (4)	2.202 (3)	2.230 (7)	2.249 (4)	2.231 (5)
P–Ru–Cl1	87.094 (19) [89.78 (2)]	91.81 (3)	86.15 (4)	85.82 (5)	84.99 (3)	86.83 (5)
P–Ru–Cl2	90.27 (2) [87.518 (19)]	86.34 (4)	86.15 (4)	91.46 (5)	88.22 (4)	82.63 (4)
Cl1–Ru–Cl2	88.41 (2) [88.91 (2)]	86.62 (4)	88.18 (3)	86.40 (6)	88.16 (4)	87.99 (4)
Σ angles	265.77 [266.21]	264.77	260.48	263.68	261.37	257.45

References: (II): Vieille-Petit *et al.* (2003); (III) Elsegood & Tocher (1995); (IV): Therrien & Süß-Fink (2004); (V): Hansen & Nelson (2000); (VI): Baldwin *et al.* (2002). Value in square brackets is for the second independent molecule. Σ angles = the sum of the P–Ru–Cl1, P–Ru–Cl2 and Cl1–Ru–Cl2 angles.

H atoms were positioned geometrically (C–H = 0.95 Å for aryl, 0.98 Å for methine and 1.00 Å for methyl H atoms) and refined using a riding model;  $U_{\text{iso}}$  values were set at  $1.2U_{\text{eq}}(\text{C})$  ( $1.5U_{\text{eq}}$  for methyl H atoms).

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and local programs.

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