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## Coordinatively unsaturated $\sigma$ -aryl complexes of ruthenium(II) and osmium(II)

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### Abstract

The hydrido complexes  $MHCl(CO)(PPh_3)_3$  ( $M = Ru, Os$ ) react with the organomercury compounds  $R_2Hg$  ( $R = \text{phenyl, } p\text{-tolyl, } o\text{-tolyl, } \textit{trans}\text{-}\beta\text{-styryl}$ ) to give the five-coordinate,  $\sigma$  aryl and alkenyl complexes  $MRCI(CO)(PPh_3)_2$  in high yield. Bromide and iodide analogues of these compounds can be prepared through reaction with silver perchlorate followed by addition of excess bromide or iodide ions. The X-ray crystal structures of two of the complexes,  $Ru(p\text{-tolyl})Cl(CO)(PPh_3)_2$  and  $Ru(o\text{-tolyl})Cl(CO)(PPh_3)_2$ , have been determined.

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### Introduction

The use of organomercury compounds as reagents for the synthesis of transition metal alkyl and aryl complexes is now well established. Reactions can be broadly classified as involving either oxidative addition of  $RHgX$  or  $R_2Hg$  to low valent metal substrates, or exchange of organo-groups on mercury with metal halide or other anionic ligands [1–4].

Prior to our preliminary report [5], the interaction of transition metal hydrides with organomercurials was unknown as a route to transition metal alkyl and aryl complexes. We have now investigated this particular reaction in more detail, and have used it to prepare a number of new, coordinatively unsaturated  $\sigma$ -aryl and  $\sigma$ -alkenyl complexes of ruthenium and osmium. The full details of this work, along with the single crystal X-ray structure determinations of  $Ru(p\text{-tolyl})Cl(CO)(PPh_3)_2$  and  $Ru(o\text{-tolyl})Cl(CO)(PPh_3)_2$ , are reported in this paper.

### Results and discussion

On heating one equivalent of  $(p\text{-tolyl})_2Hg$  with  $RuHCl(CO)(PPh_3)_3$  in toluene under reflux, the solution turns red over a period of minutes and elemental mercury

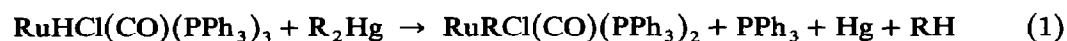
Table 1

IR data (cm<sup>-1</sup>) for ruthenium and osmium complexes<sup>a</sup>

Compound <sup>b</sup>	$\nu(\text{CO})$ <sup>c</sup>	Other bands
Ru( <i>p</i> -tolyl)Cl(CO)L <sub>2</sub>	1923	800m <sup>d</sup>
Ru( <i>p</i> -tolyl)Br(CO)L <sub>2</sub>	1917	797m <sup>d</sup>
Ru( <i>p</i> -tolyl)I(CO)L <sub>2</sub>	1927	796m <sup>d</sup>
Ru(phenyl)Cl(CO)L <sub>2</sub>	1922	1560m <sup>e</sup>
Ru( <i>o</i> -tolyl)Cl(CO)L <sub>2</sub>	1920sh, 1912	
Ru( <i>o</i> -tolyl)I(CO)L <sub>2</sub>	1927sh, 1917	
Ru( <i>trans</i> - $\beta$ -styryl)Cl(CO)L <sub>2</sub>	1916	1585m, 1560m ( <i>trans</i> - $\beta$ -styryl)
Ru( <i>trans</i> - $\beta$ -styryl)I(H <sub>2</sub> O)(CO)L <sub>2</sub>	1913	3520w, 3420w (H <sub>2</sub> O); 1595m, 1578w, 1545m ( <i>trans</i> - $\beta$ -styryl)
Ru( <i>trans</i> - $\beta$ -styryl)I(DMF)(CO)L <sub>2</sub>	1916	1643vs (DMF)
Os( <i>p</i> -tolyl)Cl(CO)L <sub>2</sub>	1906	798m <sup>d</sup>
Os(phenyl)Cl(CO)L <sub>2</sub>	1906	1564m <sup>e</sup>
Os( <i>p</i> -tolyl)I(CO)L <sub>2</sub>	1908	797m <sup>d</sup>
Os( <i>o</i> -tolyl)Cl(CO)L <sub>2</sub>	1912, 1900sh	

<sup>a</sup> Measured as Nujol mulls between KBr plates. <sup>b</sup> Satisfactory elemental analyses were obtained for all new compounds, L = PPh<sub>3</sub>. <sup>c</sup> All very strong. <sup>d</sup> Aromatic hydrogen "wag" of the *para*-substituted phenyl group. <sup>e</sup> Skeletal vibration of the metal-bound phenyl group.

is deposited. From this solution the red, coordinatively unsaturated  $\sigma$ -aryl complex Ru(*p*-tolyl)Cl(CO)(PPh<sub>3</sub>)<sub>2</sub> can be isolated in high (> 95%) yield. Other products of the reaction are triphenylphosphine and toluene (eq. 1)



(M = Ru, Os; R = *p*-tolyl, *o*-tolyl, phenyl, *trans*- $\beta$ -styryl)

The reaction can be extended to other diorganomercury compounds. Thus with R<sub>2</sub>Hg (R = *p*-tolyl, *o*-tolyl, phenyl, *trans*- $\beta$ -styryl) the corresponding five-coordinate organoruthenium compounds RuRCl(CO)(PPh<sub>3</sub>)<sub>2</sub> are formed in high yield (see Tables 1 and 2 for IR and <sup>1</sup>H NMR spectral data for all new compounds).

The osmium hydride OsHCl(CO)(PPh<sub>3</sub>)<sub>3</sub> also reacts cleanly with the diaryl mercury compounds R<sub>2</sub>Hg (R = *p*-tolyl, *o*-tolyl, phenyl) giving the five-coordinate  $\sigma$ -aryls OsRCl(CO)(PPh<sub>3</sub>)<sub>2</sub>. However, in contrast to the ruthenium reactions, no  $\sigma$ -alkenyl compound was formed on reaction with Hg(*trans*- $\beta$ -styryl)<sub>2</sub>. Elemental mercury was deposited but only OsHCl(CO)(PPh<sub>3</sub>)<sub>3</sub> was isolated (in good yield) from solution. The most likely explanation is that  $\beta$ -hydride elimination from a five-coordinate intermediate alkenyl compound leads to the reformation of OsHCl(CO)(PPh<sub>3</sub>)<sub>3</sub> after coordination of triphenylphosphine.

There have been a few reports in the literature of transition metal hydrides reacting with mercuric halides [6–11], and products with transition metal–mercury bonds [7] or bridging hydride ligands [11] have been isolated. However there appears to be no previous reports of reactions between transition metal hydrides and organomercury compounds to give  $\sigma$ -organo transition metal derivatives.

There are several plausible possibilities for the mechanism by which these organo-transfer reactions proceed. One of the simplest involves an oxidative addition–reductive elimination sequence followed by elimination of elemental mercury from the resulting M–Hg–R containing intermediate (Scheme 1). There is ample literature precedent for both the key steps in this mechanism [4,12]. Alternatively,

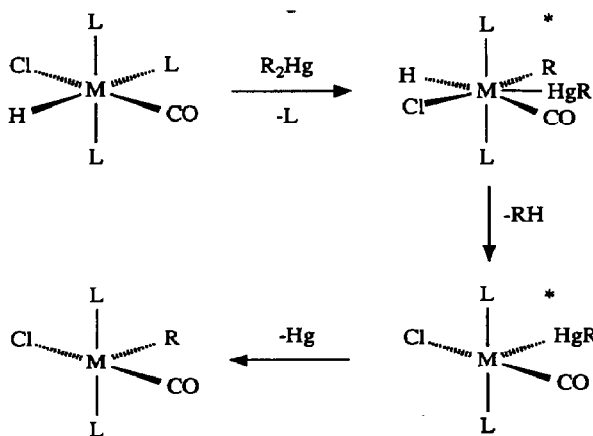
Table 2

<sup>1</sup>H NMR data for ruthenium and osmium complexes <sup>a</sup>

Compound <sup>b</sup>	Chemical shift (ppm) and coupling constants (Hz)
Ru( <i>p</i> -tolyl)Cl(CO)L <sub>2</sub>	2.13, s, 3H, C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> ; 6.32, d, 2H, 6.66, d, 2H, C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> ; 7.20–7.45, m, 30H, C <sub>6</sub> H <sub>5</sub>
Ru( <i>p</i> -tolyl)Br(CO)L <sub>2</sub>	
Ru( <i>p</i> -tolyl)I(CO)L <sub>2</sub>	2.13, s, 3H, C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> ; 6.34, s, 4H, C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> ; 7.20–7.70, m, 30H, C <sub>6</sub> H <sub>5</sub>
Ru(phenyl)Cl(CO)L <sub>2</sub>	6.40–6.90, m, 5H, C <sub>6</sub> H <sub>5</sub> ; 7.20–7.45, m, 30H, C <sub>6</sub> H <sub>5</sub>
Ru( <i>o</i> -tolyl)Cl(CO)L <sub>2</sub>	1.07, s, ca. 2H, 1.5, s, ca. 1H, CH <sub>3</sub> <sup>d</sup> ; 6.00–6.70, m, 4H, C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> ; 7.10–7.60, m, 30H, C <sub>6</sub> H <sub>5</sub>
Ru( <i>o</i> -tolyl)I(CO)L <sub>2</sub>	0.84, s, ca. 2H, 0.97, s, ca. 1H, CH <sub>3</sub> <sup>d</sup> ; 5.90–6.70, m, 4H, C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> ; 7.15–7.55, m, 30H, C <sub>6</sub> H <sub>5</sub>
Ru( <i>trans</i> -β-styryl)Cl(CO)L <sub>2</sub>	5.57, dt, 1H, =CHPh, <sup>4</sup> J(HP) 1.8, <sup>3</sup> J(HH) 13, 8.45, dt, 1H, CH=, <sup>3</sup> J(HP) 2.4, <sup>3</sup> J(HH) 13, 6.60–7.80, m, 35H, C <sub>6</sub> H <sub>5</sub>
Ru( <i>trans</i> -β-styryl)I(H <sub>2</sub> O)(CO)L <sub>2</sub>	1.50, s, 2H, H <sub>2</sub> O <sup>e</sup>
Ru( <i>trans</i> -β-styryl)I(DMF)(CO)L <sub>2</sub>	2.32, s, 3H, N-CH <sub>3</sub> ; 2.46, s, 3H, N-CH <sub>3</sub> ; 6.70–8.10, m, 37H, C <sub>6</sub> H <sub>5</sub> , CH=, CHPh <sup>c</sup>
Os( <i>p</i> -tolyl)Cl(CO)L <sub>2</sub>	
Os(phenyl)Cl(CO)L <sub>2</sub>	6.30–6.65, m, 5H, C <sub>6</sub> H <sub>5</sub> ; 7.20–7.50, m, 30H, C <sub>6</sub> H <sub>5</sub>
Os( <i>p</i> -tolyl)I(CO)L <sub>2</sub>	2.02, s, 3H, C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> ; 6.28, s, 4H, C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> <sup>f</sup> ; 7.10–7.65, m, 30H, C <sub>6</sub> H <sub>5</sub>
Os( <i>o</i> -tolyl)Cl(CO)L <sub>2</sub>	1.14, s, ca. 1.5H, 1.43, s, ca. 1.5H, C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> <sup>d</sup> ; 6.14–6.95, m, 4H, C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> ; 7.10–7.60, m, 30H, C <sub>6</sub> H <sub>5</sub>

<sup>a</sup> CDCl<sub>3</sub> solution, TMS (0.00 ppm) internal standard. <sup>b</sup> L = PPh<sub>3</sub>. <sup>c</sup> Too insoluble to obtain a satisfactory spectrum. <sup>d</sup> Two resonances observed for the methyl protons, see discussion. <sup>e</sup> Signal disappears on addition of D<sub>2</sub>O. <sup>f</sup> Signals coincident.

instead of an initial oxidative addition process, the reaction may proceed to the M–Hg–R species via an intermediate in which the hydride bridges both ruthenium and mercury metal centres. Intermediates such as this have been proposed for the



Scheme 1. Possible mechanism for the formation of the coordinatively unsaturated organo-complexes of ruthenium and osmium. (M = Ru, Os; L = PPh<sub>3</sub>; R = *p*-tolyl, *o*-tolyl, phenyl, *trans*-β-styryl); \* proposed intermediates.

binuclear reductive elimination of methane from  $\text{OsHMe}(\text{CO})_{14}$  [13], and recently compounds with hydride ligands bridging both platinum and mercury or iridium and mercury have been isolated at low temperatures [11]. At present, however, we have not established the precise mechanism of these organo-transfer reactions.

The five-coordinate organo-complexes  $\text{MRCl}(\text{CO})(\text{PPh}_3)_2$  are all intensely coloured (orange-red), crystalline solids with surprisingly high thermal stability. For example  $\text{Ru}(\textit{o}\text{-tolyl})\text{Cl}(\text{CO})(\text{PPh}_3)_2$  can be recovered in very good yield after heating under reflux in benzene under a nitrogen atmosphere for 48 h. Benzene or toluene solutions of these compounds also do not react appreciably with oxygen or water at room temperature, even after contact for many hours.

The chloride ligand in  $\text{MRCl}(\text{CO})(\text{PPh}_3)_2$  can be conveniently replaced by other halides through the use of silver perchlorate. On stirring solutions of  $\text{MRCl}(\text{CO})(\text{PPh}_3)_2$  with silver perchlorate in dichloromethane/ethanol, silver chloride precipitates. After removal by filtration and addition of  $\text{NaX}$  ( $\text{X} = \text{Br}, \text{I}$ ) the new complexes  $\text{MRX}(\text{CO})(\text{PPh}_3)_2$  are formed in high yield. The intermediate perchlorate salts,  $[\text{MR}(\text{solvent})(\text{CO})(\text{PPh}_3)_2]\text{ClO}_4$ , were not isolated in analytically pure forms.

The bromo and iodo derivatives are also all highly coloured, except for the iodostyryl complex which is pale yellow. Examination of the IR spectrum for this compound reveals broad, weak absorptions at 3520 and 3420  $\text{cm}^{-1}$ . There is also a signal in the  $^1\text{H}$  NMR spectrum at 1.50 ppm which integrates for approximately two protons and which disappears on addition of  $\text{D}_2\text{O}$ . This is consistent with the presence of coordinated water and the complex is formulated as  $\text{Ru}(\textit{trans}\text{-}\beta\text{-styryl})\text{I}(\text{H}_2\text{O})(\text{CO})(\text{PPh}_3)_2$ . On recrystallization from solutions containing *N,N*-dimethylformamide (DMF) the aquo ligand is displaced and the pale yellow crystalline complex  $\text{Ru}(\textit{trans}\text{-}\beta\text{-styryl})\text{I}(\text{DMF})(\text{CO})(\text{PPh}_3)_2$  is obtained. Of all the coordinatively unsaturated,  $\sigma$ -organo compounds reported in this paper, the iodostyryl derivative of ruthenium is the only one that strongly coordinates water.

In keeping with their coordinative unsaturation, other small Lewis bases readily add to  $\text{MRX}(\text{CO})(\text{PPh}_3)_2$ . Thus with CO, CNR and NCMe the corresponding octahedral complexes are rapidly formed. (In some instances these then rearrange to the corresponding *dihapto*-acyl or *dihapto*-iminoacyl derivatives [5,14,15]). It is reasonable to assume that addition occurs *trans* to the  $\sigma$ -organo group, the group with the largest *trans*-influence. These addition reactions can sometimes be reversed. For example heating  $\text{Ru}(\textit{p}\text{-tolyl})\text{Cl}(\text{CO})_2(\text{PPh}_3)_2$  under reflux in benzene while purging the solution with nitrogen slowly returns red  $\text{Ru}(\textit{p}\text{-tolyl})\text{Cl}(\text{CO})(\text{PPh}_3)_2$ . Potentially bidentate anions such as acetate and formate also rapidly add to  $\text{MRX}(\text{CO})(\text{PPh}_3)_2$  displacing chloride and forming the coordinatively saturated derivatives,  $\text{MR}(\eta^2\text{-O}_2\text{CR})(\text{CO})(\text{PPh}_3)_2$  [16]. In contrast, sterically demanding Lewis bases such as triphenylphosphine are not coordinated by  $\text{MRX}(\text{CO})(\text{PPh}_3)_2$ . Thus the large *trans*-influence of the  $\sigma$ -organo groups [17,18] together with the steric restraints imposed by the other coordinated ligands strongly influence the coordination properties of  $\text{MRX}(\text{CO})(\text{PPh}_3)_2$ .

The organo-transfer reactions from mercury to ruthenium and osmium described above do not represent the limits of this reaction.  $\text{Ru}(\textit{p}\text{-tolyl})\text{Cl}(\text{CO})(\text{PPh}_3)_2$  can be prepared through the reaction of  $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$  with *p*-tolylmercuric chloride. The yield in this instance is lower (ca. 70%) and the product much less pure than when di(*p*-tolyl)mercury is used. In addition to elemental mercury and triphenyl-

phosphine, hydrogen chloride is formed in this reaction and this cleaves the tolyl groups from some of the product  $\text{Ru}(p\text{-tolyl})\text{Cl}(\text{CO})(\text{PPh}_3)_2$ . No  $\text{Os}(p\text{-tolyl})\text{Cl}(\text{CO})(\text{PPh}_3)_2$  is formed when  $p\text{-tolylmercuric}$  chloride reacts with  $\text{OsHCl}(\text{CO})(\text{PPh}_3)_3$ , but with the thiocarbonyl analogue,  $\text{Os}(p\text{-tolyl})\text{Cl}(\text{CS})(\text{PPh}_3)_2$  is formed in good yield [19]. The group 9 hydride,  $\text{IrHCl}_2(\text{PPh}_3)_3$ , also reacts with di( $p\text{-tolyl}$ )mercury, in this instance to give the coordinatively unsaturated compound  $\text{Ir}(p\text{-tolyl})\text{Cl}_2(\text{PPh}_3)_2$  [20]. Other groups can also be transferred from mercury. We have already reported that bis(trichloromethyl)mercury provides a convenient route to dichlorocarbene complexes of ruthenium, osmium and iridium via transfer and subsequent rearrangement of the trichloromethyl group [21,22]. In a similar manner a coordinatively unsaturated trimethylsilylosmium complex is obtained with bis(trimethylsilyl)mercury [23]. The full scope of this reaction has not yet been explored and we are currently investigating other related reactions.

### Structures of $\text{Ru}(p\text{-tolyl})\text{Cl}(\text{CO})(\text{PPh}_3)_2$ and $\text{Ru}(o\text{-tolyl})\text{Cl}(\text{CO})(\text{PPh}_3)_2$

Single crystal X-ray structure determinations have been completed for  $\text{Ru}(p\text{-tolyl})\text{Cl}(\text{CO})(\text{PPh}_3)_2$  and  $\text{Ru}(o\text{-tolyl})\text{Cl}(\text{CO})(\text{PPh}_3)_2$ . The molecular geometries of

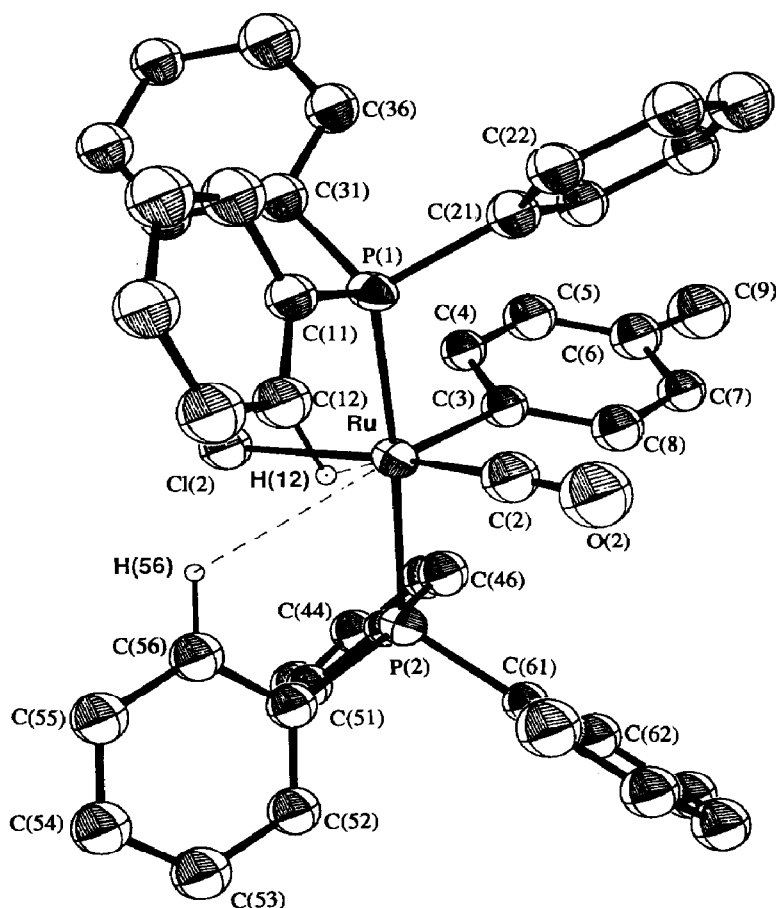


Fig. 1. Molecular structure of  $\text{Ru}(p\text{-tolyl})\text{Cl}(\text{CO})(\text{PPh}_3)_2$ .

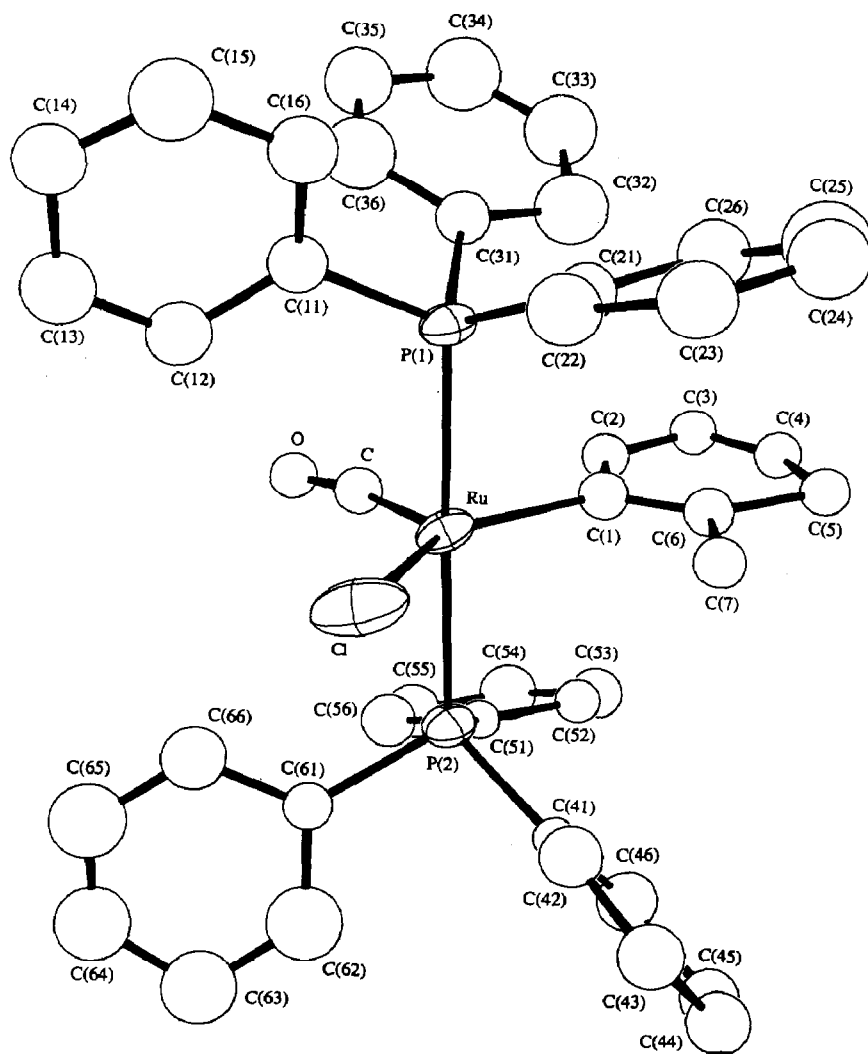


Fig. 2. Molecular structure of  $\text{Ru}(o\text{-tolyl})\text{Cl}(\text{CO})(\text{PPh}_3)_2$ .

these compounds are depicted in Fig. 1 and 2 although no attempt was made to determine absolute structures. Important bond lengths and angles are listed in Tables 3 and 4.

For  $\text{Ru}(p\text{-tolyl})\text{Cl}(\text{CO})(\text{PPh}_3)_2$  the Cl and CO ligands are disordered and are randomly distributed over two sites. Accordingly their coordinates and bond lengths are subject to large errors. The arrangement of ligands about ruthenium shows only small deviations from a regular square pyramidal geometry with the aryl group in the apical position and the triphenylphosphine ligands mutually *trans* in the basal plane. The angles  $\text{C}(3)\text{-Ru-P}(1)$  ( $91.6^\circ$ ),  $\text{C}(3)\text{-Ru-P}(2)$  ( $95.5^\circ$ ),  $\text{C}(3)\text{-Ru-Cl}$  ( $94.0^\circ$ ) and  $\text{C}(3)\text{-Ru-C}$  ( $96.0^\circ$ ) illustrate the regularity of the structure. Most other structurally characterised, five-coordinate,  $d^6$  complexes of the group 8 and 9 metals have also been described in terms of this idealized geometry with the largest *trans*-influence group occupying the apical position [24–29]. Theoretical studies

Table 3

Bond distances (Å) and angles (°) for Ru(*p*-tolyl)Cl(CO)(PPh<sub>3</sub>)<sub>2</sub>

Ru–P(1)	2.363(4)	P(1)–C(11)	1.842(7)
Ru–P(2)	2.399(4)	P(1)–C(21)	1.849(7)
Ru–Cl(1)	2.522(9)	P(1)–C(31)	1.873(7)
Ru–Cl(2)	2.496(12)	P(2)–C(41)	1.807(7)
Ru–C(1)	1.63(3)	P(2)–C(51)	1.835(7)
Ru–C(2)	1.75(4)	P(2)–C(61)	1.791(7)
Ru–C(3)	2.056(3)	C(1)–O(1)	1.25(4)
Ru–H(12)	2.85	C(2)–O(2)	1.12(5)
Ru–H(56)	2.77	C(6)–C(9)	1.54(1)
P(1)–Ru–P(2)	173.0(1)	Ru–P(2)–C(41)	115.0(3)
P(1)–Ru–Cl(1)	85.8(2)	Ru–P(2)–C(51)	108.1(3)
P(1)–Ru–Cl(2)	94.7(3)	Ru–P(2)–C(61)	119.5(4)
P(1)–Ru–C(1)	90(1)	Ru–C(1)–O(1)	164(3)
P(1)–Ru–C(2)	81(1)	Ru–C(2)–O(2)	161(3)
P(1)–Ru–C(3)	93.7(4)	Ru–C(3)–C(4)	188.7(3)
P(2)–Ru–Cl(1)	92.3(2)	Ru–C(3)–C(8)	121.2(3)
P(2)–Ru–Cl(2)	85.4(3)	P(1)–C(11)–C(12)	119.9(3)
P(2)–Ru–C(1)	90(1)	P(1)–C(11)–C(16)	120.1(3)
P(2)–Ru–C(2)	98(1)	P(1)–C(21)–C(22)	124.4(3)
P(2)–Ru–C(3)	93.3(4)	P(1)–C(21)–C(26)	115.5(3)
Cl(1)–Ru–C(1)	167(1)	P(1)–C(31)–C(32)	121.6(3)
Cl(1)–Ru–C(3)	96.5(4)	P(1)–C(31)–C(36)	118.4(3)
Cl(2)–Ru–C(2)	172(1)	P(2)–C(41)–C(42)	119.6(3)
Cl(2)–Ru–C(3)	97.8(4)	P(2)–C(41)–C(46)	120.4(3)
C(1)–Ru–C(3)	97(1)	P(2)–C(51)–C(52)	121.9(3)
C(2)–Ru–C(3)	90(1)	P(2)–C(51)–C(56)	118.1(3)
Ru–P(1)–C(11)	109.4(3)	P(2)–C(61)–C(62)	128.5(3)
Ru–P(1)–C(21)	117.0(4)	P(2)–C(61)–C(66)	111.5(3)
Ru–P(1)–C(31)	118.5(4)	C(5)–C(6)–C(9)	121(1)
		C(7)–C(6)–C(9)	119(1)

Table 4

Selected bond distances (Å) and angles (°) for Ru(*o*-tolyl)Cl(CO)(PPh<sub>3</sub>)<sub>2</sub>

Ru–P(1)	2.385(6)	P(1)–C(11)	1.84(3)
Ru–P(2)	2.391(6)	P(1)–C(21)	1.84(3)
Ru–Cl	2.438(8)	P(1)–C(31)	1.87(3)
Ru–C	1.76(4)	P(2)–C(41)	1.81(2)
Ru–C(1)	2.04(3)	P(2)–C(51)	1.82(2)
Ru–H	2.11	P(2)–C(61)	1.81(3)
C–O	1.09(4)		
P(1)–Ru–P(1)	178.4(3)	Cl–Ru–C(1)	140.1(8)
P(1)–Ru–Cl	89.6(2)	C–Ru–C(1)	93.8(1.4)
P(1)–Ru–C	91.4(9)	Ru–P(1)–C(11)	116.5(8)
P(1)–Ru–C(1)	87.5(1.3)	Ru–P(1)–C(21)	110.8(1.0)
P(2)–Ru–Cl	90.8(2)	Ru–P(1)–C(31)	115.5(8)
P(2)–Ru–C	89.6(9)	Ru–P(2)–C(41)	119.1(7)
P(2)–Ru–C(1)	91.2(1.3)	Ru–P(2)–C(51)	112.2(8)
Cl–Ru–C	126.1(1.1)	Ru–P(2)–C(61)	116.1(8)

indicate that in the absence of steric effects, square pyramidal rather than trigonal bipyramidal geometry is favoured for complexes with  $d^6$  electronic configurations [30,31].

The Ru–C(3) bond length of 2.056 Å is close to the Ru–C( $sp^2$ ) single bond distances reported in other complexes. For example in the five-coordinate, *ortho*-metallated complex  $\text{Ru}(\text{CN}[\textit{p}\text{-tolyl}][\text{CH}_2]_2\text{N}[4\text{-MeC}_6\text{H}_3])\text{Cl}(\text{PEt}_3)_2$  the Ru–C distance is 1.994 Å [32] and in the six coordinate  $\text{Ru}(\text{C}_6\text{F}_4\text{N}=\text{NC}_6\text{F}_5)(\text{Ph}_2\text{PC}_6\text{H}_4\text{-}\eta^5\text{-C}_5\text{H}_4)$  it is 2.014 Å [33], although in both these cases the aryl group forms part of a chelate ring. The  $\sigma$ -alkenyl complex,  $\text{Ru}(\text{CPh}=\text{CHPh})\text{Cl}(\text{CO})(\text{PPh}_3)_2$ , has a Ru–C( $sp^2$ ) distance of 2.03 Å [34].

In the solid state the open coordination site opposite the *p*-tolyl ligand in  $\text{Ru}(\textit{p}\text{-tolyl})\text{Cl}(\text{CO})(\text{PPh}_3)_2$  is occupied by two triphenylphosphine, *o*-phenyl hydrogen atoms (see Fig. 1). The Ru–H distances are calculated to be 2.73 and 2.91 Å. These are very similar to the values reported for the “weak” metal–hydrogen agostic interactions in other coordinatively unsaturated complexes, for example 2.85 Å in  $\text{RuHCl}(\text{PPh}_3)_3$  [25], 2.95 Å in  $\text{RuCl}_2(\text{PPh}_3)_3$  [24], 2.79 Å in  $\text{RhHCl}(\text{SiCl}_3)\text{-}(\text{PPh}_3)_2$  [28] and 2.86, 2.80 Å in  $\text{Ru}(\text{SC}_6\text{F}_5)_2(\text{PPh}_3)_2$  [35].

The Ru–CO distance of 1.63 Å in this compound is apparently much shorter than normally observed for ruthenium carbonyl complexes [34,38]. However, this and the Ru–Cl distance are not reliable because of the disorder problem involving Cl and CO.

The structure of  $\text{Ru}(\textit{o}\text{-tolyl})\text{Cl}(\text{CO})(\text{PPh}_3)_2$  is depicted in Fig. 2. In contrast to the *p*-tolyl derivative, the structure of  $\text{Ru}(\textit{o}\text{-tolyl})\text{Cl}(\text{CO})(\text{PPh}_3)_2$  is most conveniently viewed in terms of a distorted trigonal bipyramidal arrangement of ligands about ruthenium with *trans*, axial triphenylphosphines. The relevant angles are P(1)–Ru–P(2) 178.4°, C(1)–Ru–C 95.3°, C–Ru–Cl 125.1° and Cl–Ru–C(1) 139.6°. A very similar arrangement has been reported for  $\text{Ru}(\text{CPh}=\text{CHPh})\text{Cl}(\text{CO})\text{-}(\text{PPh}_3)_2$  [34]. Undoubtedly the large steric demands of the *o*-tolyl and the diphenylethenyl groups preclude the formation of a square pyramidal arrangement as found in  $\text{Ru}(\textit{p}\text{-tolyl})\text{Cl}(\text{CO})(\text{PPh}_3)_2$ .

There was some evidence of disorder in the *o*-tolyl group in that the plane of the phenyl ring was slightly twisted about the Ru–C(1) axis bringing the methyl group slightly above the equatorial plane in some instances and slightly below it in others. The structure in Fig. 2 is drawn with the phenyl group in the average, in-plane position. In this arrangement the closest approach the methyl hydrogen atoms can make to ruthenium is ca. 1.9 Å “Strong” transition metal–hydrogen interactions are typically close to this value, for example metal–hydrogen distances of 2.2, 1.88, and 2.2 Å have been reported for  $\text{Ru}(\text{CN}[\textit{p}\text{-tolyl}][\text{CH}_2]_2\text{N}[4\text{-MeC}_6\text{H}_3])\text{Cl}(\text{PEt}_3)_2$  [32],  $[\text{Fe}(\eta^3\text{-C}_8\text{H}_{13})\{\text{P}(\text{OMe})_3\}_3]\text{BF}_4$  [36] and  $\text{Mo}(\eta^3\text{-CH}_2\text{C}(\text{Ph})\text{CH}_2)\text{Et}_2\text{B}(\text{pyrazolyl})_2(\text{CO})_2$  [37] respectively. In the  $^1\text{H}$  NMR spectrum of  $\text{Ru}(\textit{o}\text{-tolyl})\text{Cl}(\text{CO})\text{-}(\text{PPh}_3)_2$  the methyl signal does not appear as a single resonance. Instead, two broad signals at 1.07 and 1.50 ppm (together integrating for three protons versus the triphenylphosphine resonances) are observed with the ratio of the two integrals approximately 2/1. This indicates that the methyl protons find themselves in two different magnetic environments and that the interconversion between them is slow on the  $^1\text{H}$  NMR time scale. If the solid state structure depicted in Fig. 2 is retained in solution, orientation of the methyl protons so that only one of them sits in the equatorial plane (either pointing to the ruthenium atom or away from it) would give



rise to such a spectrum. The other *o*-tolyl complexes display a similar pattern of resonances for their methyl protons (see Table 2), although for  $\text{Os}(o\text{-tolyl})\text{Cl}(\text{CO})(\text{PPh}_3)_2$  the two signals have almost equal integrals.

The Ru–C(1) bond length is 2.04 Å and this is almost identical to the corresponding distance in the *p*-tolyl analogue. At 1.76 Å the Ru–CO distance is very similar to that reported for  $\text{Ru}(\text{CPh}=\text{CHPh})\text{Cl}(\text{CO})(\text{PPh}_3)_2$  and is only slightly shorter than other Ru–CO distances [34,38]. The Ru–P and Ru–Cl distances do not deviate significantly from expected values [22,39].

## Conclusions

Reaction of the group 8 hydrides  $\text{MHCl}(\text{CO})(\text{PPh}_3)_3$  ( $\text{M} = \text{Ru}, \text{Os}$ ) with  $\text{R}_2\text{Hg}$  ( $\text{R} = \text{phenyl}, p\text{-tolyl}, o\text{-tolyl}, \text{trans-}\beta\text{-styryl}$ ) provides a simple, efficient route to the stable, coordinatively unsaturated  $\sigma$ -organo-compounds  $\text{MRCl}(\text{CO})(\text{PPh}_3)_2$ . These reactions appear to represent a new route by which organo group can be transferred from mercury to transition metals. Some extensions to other platinum group hydrides and mercury derivatives have been made and the full scope of the reaction is still under investigation.

The structures of  $\text{Ru}(p\text{-tolyl})\text{Cl}(\text{CO})(\text{PPh}_3)_2$  and  $\text{Ru}(o\text{-tolyl})\text{Cl}(\text{CO})(\text{PPh}_3)_2$  confirm the five-coordinate,  $\sigma$ -aryl formulations for these compounds. The overall arrangement of the ligands about the ruthenium atom in this latter compound appears to be significantly influenced by the sterically demanding *o*-tolyl group and the methyl protons interact strongly with the ruthenium atom.

The complexes  $\text{MRCl}(\text{CO})(\text{PPh}_3)_2$  undergo a range of interesting reactions, some of which have already been reported [5,14,15,16,46].

## Experimental

**General.** Solvents were degassed by the freeze-thaw method using nitrogen or by passing a stream of nitrogen through the boiling solvent for ten minutes before use. The new compounds were characterized by elemental analysis, IR and  $^1\text{H}$  NMR spectroscopy. Analytical data were obtained from the Microanalytical Laboratory, University of Otago. IR spectra ( $4000\text{--}400\text{ cm}^{-1}$ ) were recorded on Perkin Elmer 397 or 597 spectrometers as Nujol mulls between KBr plates.  $^1\text{H}$  NMR spectra were recorded on a Varian Associates T60 spectrometer with tetramethylsilane (0.00 ppm) as internal reference. Melting points (uncorrected) were measured on a Reichert hot-stage microscope. Osmium tetroxide and ruthenium trichloride were obtained commercially from Johnson Matthey Chemicals Ltd.  $\text{OsHCl}(\text{CO})(\text{PPh}_3)_3$  [40],  $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$  [41],  $\text{Hg}(p\text{-tolyl})\text{Cl}$  [42],  $\text{Hg}(p\text{-tolyl})_2$  [42,43],  $\text{Hg}(o\text{-tolyl})_2$  [44], and  $\text{Hg}(\text{trans-}\beta\text{-styryl})_2$  [43,45] were prepared by published methods.

### Syntheses

The syntheses of (a)  $\text{Ru}(p\text{-tolyl})\text{Cl}(\text{CO})(\text{PPh}_3)_2$ , (b)  $\text{Ru}(\text{phenyl})\text{Cl}(\text{CO})(\text{PPh}_3)_2$ , (c)  $\text{Ru}(o\text{-tolyl})\text{Cl}(\text{CO})(\text{PPh}_3)_2$  and (d)  $\text{Os}(o\text{-tolyl})\text{Cl}(\text{CO})(\text{PPh}_3)_2$  have been described previously in reference 46.

(e)  $\text{Ru}(\text{trans-}\beta\text{-styryl})\text{Cl}(\text{CO})(\text{PPh}_3)_2$ . A solution of  $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$  (1.20 g) and  $\text{Hg}(\text{trans-}\beta\text{-styryl})_2$  (0.60 g) in benzene (925 ml) was heated under reflux for 5 min. The solution was allowed to cool and filtered through a Celite pad, and the benzene removed under reduced pressure after the addition of ethanol (25 ml). The

resulting red product was recrystallized from dichloromethane/ethanol to give deep red crystals (0.92 g, 92%). M.p. 175–176°C. Anal. Found: C, 67.98; H, 4.77.  $C_{45}H_{37}ClOP_2Ru$  calcd.: C, 68.22; H, 4.71%.

(f)  $Os(p\text{-tolyl})Cl(CO)(PPh_3)_2$ . A solution of  $OsHCl(CO)(PPh_3)_3$  (1.00 g) and  $Hg(p\text{-tolyl})_2$  (0.45 g) in toluene (50 ml) was heated under reflux for 15 min. The solution was allowed to cool and the deep-burgundy product filtered off and dissolved in dichloromethane. The solution was filtered through a Celite pad to remove mercury and ethanol (50 ml) was added to the filtrate and the dichloromethane removed under reduced pressure to give deep burgundy crystals (0.74 g, 93%). M.p. 229–231°C. Anal. Found: C, 60.14; H, 4.55.  $C_{44}H_{37}ClOOSp_2$  calcd.: C, 60.79; H, 4.29%.

(g)  $Os(phenyl)Cl(CO)(PPh_3)_2$ .  $OsHCl(CO)(PPh_3)_3$  (1.00 g) and  $Hg(phenyl)_2$  (0.45 g) were treated as in (f) above. On recrystallization from dichloromethane/ethanol deep-burgundy crystals were obtained (0.76 g, 92%). M.p. 209–211°C. Anal. Found: C, 60.20; H, 4.20.  $C_{43}H_{35}ClOOSp_2$  calcd.: C, 60.38; H, 4.12%.

(h)  $Ru(p\text{-tolyl})I(CO)(PPh_3)_2$ . To a solution of  $Ru(p\text{-tolyl})Cl(CO)(PPh_3)_2$  (0.300 g) in dichloromethane (30 ml) was added one of silver perchlorate (0.079 g) in ethanol (20 ml). After 5 min stirring the silver chloride precipitate was removed by filtration through a Celite pad and a solution of sodium iodide (0.065 g) in a water/ethanol mixture (1 ml/20 ml) was added to the filtrate. Dark red crystals formed as the dichloromethane was removed under reduced pressure. These were removed by filtration, dissolved in dichloromethane, and purified by column chromatography on silica gel with dichloromethane as eluant. The dark red band was collected and crystals of the same colour obtained by adding ethanol and removing the dichloromethane under reduced pressure (0.315 g, 94%). M.p. 222–227°C. Anal. Found: C, 60.21; H, 4.44; P, 7.10.  $C_{44}H_{37}IOP_2Ru$  calcd.: C, 60.63; H, 4.28; P, 7.11%.

Table 5

Crystal data for  $C_{44}H_{37}ClOP_2Ru$ 

	I	II
Crystal system	monoclinic	orthorhombic
Space group	<i>Cc</i>	<i>Pna2<sub>1</sub></i>
<i>a</i> (Å)	12.967(1)	29.944(3)
<i>b</i> (Å)	13.801(1)	10.235(2)
<i>c</i> (Å)	20.368(2)	11.966(1)
$\beta$ (°)	94.70(1)	
<i>V</i> (Å <sup>3</sup> )	3633.0	3667.3
<i>Z</i>	4	4
Molecular weight	780.2	780.2
$\rho$ (calc) (g cm <sup>-3</sup> )	1.42	1.41
Diffractometer	Hilger–Watts 7290	Nonius CAD-4
Radiation	Cu- $K_\alpha$ ( $\lambda$ 1.5418 Å)	Mo- $K_\alpha$ ( $\lambda$ 0.71069 Å)
Absorption coeff. (cm <sup>-1</sup> )	50.6	5.4
<i>F</i> (000)	1600	1600
Reflections ( $F^2 > 3\sigma(F^2)$ )	2789	1367
Least squares weight	0.221( $\sigma^2(F) + 0.007F^2$ )	0.089( $\sigma^2(F) + 0.11F^2$ )
<i>R</i>	0.045	0.069
<i>R<sub>w</sub></i>	0.048	0.073

Table 6

Atomic coordinates ( $\times 10^4 \text{ \AA}$ ) and isotropic thermal parameters ( $\times 10^3 \text{ \AA}^2$ ) for Ru(*p*-tolyl)Cl(CO)(PPh<sub>3</sub>)<sub>2</sub>

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i>
Ru	0	2794.6(3)	0	
P(1)	-941(4)	2690(3)	-1041(2)	
P(2)	928(4)	2690(3)	1066(2)	
CL(1)	-1720(7)	2563(6)	473(4)	44(2)
CL(2)	1725(10)	2573(9)	-440(6)	52(3)
O(1)	2016(21)	2689(18)	-462(12)	53(6)
O(2)	-1933(26)	2647(21)	544(15)	71(9)
C(1)	1082(25)	2677(23)	-345(15)	53(7)
C(2)	-1260(31)	2789(28)	251(19)	37(9)
C(3)	-16(10)	4284(2)	9(7)	43(1)
C(4)	588(10)	4781(2)	-417(7)	44(3)
C(5)	550(10)	5790(2)	-448(7)	61(4)
C(6)	-93(10)	6303(2)	-55(7)	58(2)
C(7)	-697(10)	5806(2)	370(7)	49(3)
C(8)	-659(10)	4797(2)	402(7)	58(4)
C(9)	-121(26)	7416(8)	-58(15)	89(3)
C(11)	-1386(8)	1434(5)	-1185(4)	40(3)
C(12)	-1395(8)	790(5)	-658(4)	48(4)
C(13)	-1748(8)	-156(5)	-764(4)	60(4)
C(14)	-2092(8)	-459(5)	-1398(4)	56(3)
C(15)	-2083(8)	185(5)	-1926(4)	61(3)
C(16)	-1730(8)	1132(5)	-1819(4)	61(4)
C(21)	-2131(6)	3427(6)	-1167(5)	45(4)
C(22)	-3118(6)	3048(6)	-1323(5)	47(3)
C(23)	-3973(6)	3664(6)	-1389(5)	54(3)
C(24)	-3840(6)	4660(6)	-1299(5)	69(4)
C(25)	-2853(6)	5039(6)	-1143(5)	53(3)
C(26)	-1999(6)	4422(6)	-1077(5)	46(4)
C(31)	-248(7)	2936(7)	-1795(4)	54(4)
C(32)	600(7)	2383(7)	-1949(4)	47(3)
C(33)	1082(7)	2575(7)	-2523(4)	61(3)
C(34)	717(7)	3319(7)	-2943(4)	55(3)
C(35)	-131(7)	3872(7)	-2789(4)	66(4)
C(36)	-614(7)	3681(7)	-2216(4)	52(3)
C(41)	2081(5)	3427(6)	1171(5)	39(3)
C(42)	3023(5)	3000(6)	1387(5)	50(3)
C(43)	3921(5)	3560(6)	1457(5)	68(4)
C(44)	3877(5)	4548(6)	1311(5)	58(4)
C(45)	2934(5)	4975(6)	1096(5)	58(4)
C(46)	2036(5)	4415(6)	1026(5)	55(5)
C(51)	1311(8)	1423(5)	1210(5)	44(3)
C(52)	1589(8)	1067(5)	1841(5)	49(3)
C(53)	1876(8)	98(5)	1927(5)	60(3)
C(54)	1885(8)	-515(5)	1383(5)	56(3)
C(55)	1608(8)	-159(5)	752(5)	56(4)
C(56)	1321(8)	810(5)	666(5)	51(4)
C(61)	268(6)	2937(7)	1787(4)	39(3)
C(62)	471(6)	3663(7)	2257(4)	56(3)
C(63)	-144(6)	3745(7)	2785(4)	53(3)
C(64)	-961(6)	3102(7)	2843(4)	64(3)
C(65)	-1163(6)	2376(7)	2374(4)	58(3)
C(66)	-549(6)	2294(7)	1846(4)	71(4)

Table 7

Atomic coordinates ( $\times 10^4 \text{ \AA}$ ) and isotropic thermal parameters ( $\times 10^3 \text{ \AA}^2$ ) for  $\text{Ru}(o\text{-tolyl})\text{Cl}(\text{CO})(\text{PPh}_3)_2$ 

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i>
Ru	1200(1)	1354(2)	2500(0)	
P(1)	1015(3)	1434(8)	563(6)	
P(2)	1377(3)	1331(9)	4449(6)	
Cl	595(3)	-200(10)	2802(6)	
C	1758(14)	962(41)	2192(26)	
O	2083(10)	502(32)	2051(19)	
C(1)	1307(11)	3317(28)	2420(44)	39(10)
C(2)	1759(11)	3929(33)	2189(26)	93(10)
C(3)	1840(12)	5174(33)	2093(26)	95(9)
C(4)	1496(14)	5729(38)	2334(38)	101(12)
C(5)	1020(10)	5558(28)	2588(37)	109(8)
C(6)	1032(10)	4172(30)	2622(36)	65(9)
C(7)	600(11)	3642(33)	2911(27)	101(9)
C(11)	918(11)	-140(29)	-131(23)	47(7)
C(12)	1043(10)	-1308(31)	374(25)	56(7)
C(13)	963(13)	-2461(36)	-136(33)	69(11)
C(14)	753(12)	-2495(33)	-1199(30)	62(9)
C(15)	586(13)	-1409(39)	-1574(31)	77(10)
C(16)	638(12)	-191(34)	-1084(28)	57(9)
C(21)	495(10)	2351(31)	342(28)	43(8)
C(22)	97(11)	1622(29)	419(28)	62(9)
C(23)	-306(12)	2396(38)	400(32)	67(10)
C(24)	-321(13)	3699(42)	194(33)	72(10)
C(25)	97(17)	4351(42)	120(37)	96(13)
C(26)	502(13)	3242(38)	144(30)	69(10)
C(31)	1447(10)	2184(30)	-368(24)	45(7)
C(32)	1526(13)	3530(43)	-344(36)	86(11)
C(33)	1889(14)	3938(39)	-1131(36)	88(11)
C(34)	2112(16)	3080(46)	-1786(41)	96(14)
C(35)	2022(13)	1736(34)	-1790(32)	76(11)
C(36)	1672(14)	1318(44)	-1071(37)	84(11)
C(41)	972(8)	1957(24)	5439(21)	26(6)
C(42)	509(11)	1604(29)	5283(27)	25(8)
C(43)	207(10)	1986(31)	6060(24)	57(7)
C(44)	309(11)	2768(34)	6893(26)	55(8)
C(45)	743(11)	3263(29)	7086(26)	53(9)
C(46)	1075(11)	2837(33)	6276(27)	58(9)
C(51)	1890(8)	2217(26)	4755(21)	29(6)
C(52)	1932(9)	3494(27)	4770(22)	36(6)
C(53)	2319(12)	4198(31)	4950(26)	53(8)
C(54)	2709(12)	3471(37)	5004(30)	66(10)
C(55)	2702(11)	2170(36)	5029(26)	64(9)
C(56)	2293(12)	1475(34)	4841(28)	56(9)
C(61)	1484(10)	-257(27)	5058(22)	38(7)
C(62)	1489(15)	-444(44)	6209(37)	91(13)
C(63)	1559(15)	-1635(41)	6691(37)	86(13)
C(64)	1656(14)	-2618(42)	5939(42)	88(12)
C(65)	1653(14)	-2526(41)	4929(39)	90(13)
C(66)	1537(11)	-1387(37)	4434(28)	64(8)

(i)  $\text{Ru}(p\text{-tolyl})\text{Br}(\text{CO})(\text{PPh}_3)_2$ .  $\text{Ru}(p\text{-tolyl})\text{Cl}(\text{CO})(\text{PPh}_3)_2$  (0.300 g), silver perchlorate (0.079 g) and sodium bromide (0.045 g) were treated as in (h) to produce deep red crystals (0.295 g, 93%). M.p. 234–237 °C. Anal. Found: C, 63.69; H, 4.47; P, 7.42.  $\text{C}_{44}\text{H}_{37}\text{BrOP}_2\text{Ru}$  calcd.: C, 64.08; H, 4.52; P, 7.51%.

(j)  $Ru(o\text{-tolyl})I(CO)(PPh_3)_2$ .  $Ru(o\text{-tolyl})Cl(CO)(PPh_3)_2$  (0.500 g), silver perchlorate (0.120 g) and sodium iodide (0.100 g) were treated as in (h) to produce dark orange needles (0.510 g, 91%). M.p. 228–230°C. Anal. Found: C, 61.01; H, 4.17.  $C_{44}H_{37}IO_2P_2Ru$  calcd.: C, 60.63; H, 4.28%.

(k)  $Ru(trans\text{-}\beta\text{-styryl})I(H_2O)(CO)(PPh_3)_2$ .  $Ru(trans\text{-}\beta\text{-styryl})Cl(CO)(PPh_3)_2$  (0.500 g), silver perchlorate (0.120 g) and sodium iodide (0.100 g) were treated as in (h) to produce pale yellow needles (0.500 g, 88%). M.p. 158–161°C. Anal. Found: C, 59.77; H, 4.42.  $C_{45}H_{39}IO_2P_2Ru$  calcd.: C, 59.94; H, 4.36%.

(l)  $Ru(trans\text{-}\beta\text{-styryl})I(DMF)(CO)(PPh_3)_2$ . To a solution of  $Ru(trans\text{-}\beta\text{-styryl})I(H_2O)(CO)(PPh_3)_2$  (0.300 g) in dichloromethane (40 ml) was added DMF (0.25 ml). The mixture was stirred for a few minutes and methanol (40 ml) then added and the solvent volume reduced under reduced pressure. Yellow crystals of the aquo solvate  $Ru(trans\text{-}\beta\text{-styryl})I(DMF)(CO)(PPh_3)_2 \cdot (H_2O)_{0.5}$  were filtered off and washed with ethanol (0.280 g, 87%). ( $^1H$  NMR shows a signal at 1.47 ppm, s, 1H,  $H_2O$ ). M.p. 150–158°C. Anal. Found: C, 59.22; H, 4.48; N, 1.55.  $C_{48}H_{44}IO_2NP_2Ru \cdot (H_2O)_{0.5}$  calcd.: C, 59.69; H, 4.70; N, 1.45%.

### Crystal structure determinations

Crystal data are summarised in Table 5. Cell parameters were obtained by least squares fit to the four circle angles of a series of reflections spread through space. Intensity data were recorded by the  $\omega/2\theta$  scan technique. The intensity of each of three standard reflections was monitored throughout data collection as a check on crystal decomposition, no systematic variation being apparent. Data were corrected for Lorentz and polarization effects and analytical absorption corrections applied [46].

The structures were solved by conventional Patterson and Fourier techniques and refined by full matrix least squares, minimising  $\sum w(|F_o| - |F_c|)^2$ . For I the Cl and CO ligands are disordered and are randomly distributed over two sites, and hence their coordinates and bond lengths are subject to large errors. After the initial isotropic refinement, the ruthenium and phosphorus atoms, and chlorine and carbonyl for II, were allowed to assume anisotropic motion. Scattering curves were for neutral atoms and final least-squares weights and residuals are given in Table 5. Programs used were FORDAP and CUCLS for I and SHELX-76 FOR II<sup>47</sup>.

Atomic coordinates are given in Tables 6 and 7, and important bond distances and angles are in Tables 3 and 4. The numbering schemes are given in Figs. 1 and 2 which depict the molecular geometry. Tables of anisotropic thermal parameters, complete lists of bond lengths and angles, and lists of  $F_o$  and  $F_c$  values are available from the authors.

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### References

- 1 J.L. Wardell, G. Wilkinson, F.G.A. Stone, and E. Abel, (Eds.), in *Comprehensive Organometallic Chemistry*, Pergamon Press, Oxford, 1982, Vol. 2, p. 961.
- 2 D. Seyferth, *J. Organomet. Chem.*, 203 (1980) 183.

- 3 W.H. Ilsley, *J. Organomet. Chem.*, 337 (1987) 1.
- 4 V.I. Sokolov and O.A. Reutov, *Coord. Chem. Rev.*, 27 (1978) 89.
- 5 W.R. Roper and L.J. Wright, *J. Organomet. Chem.*, 142 (1977) C1.
- 6 R.S. Nyholm and K. Vrieze, *J. Chem. Soc.*, (1965) 5331; R.S. Nyholm and K. Vrieze, *ibid.*, (1965) 5337.
- 7 B. Bell, J. Chatt and G.J. Leigh, *J. Chem. Soc., Dalton Trans.*, (1973) 997.
- 8 N.G. Connelly, J.A.K. Howard, J.L. Spencer and P.K. Woodley *J. Chem. Soc., Dalton Trans.*, (1984) 2003.
- 9 R. Fahmy, K. King, E. Rosenberg, A. Tiripicchio, and M. Tiripicchio Camellini, *J. Am. Chem. Soc.*, 102 (1980) 3626.
- 10 G. Predieri, A. Tiripicchio, C. Vignali, E. Sappa and P. Braunstein, *J. Chem. Soc., Dalton Trans.*, (1986) 1135.
- 11 B.S. McGilligan, L.M. Venanzi and M. Wolfer, *Organometallics*, 6 (1987) 946.
- 12 L.J. Johnston and M.C. Baird, *Organometallics*, 7 (1988) 2469.
- 13 J.R. Norton, *Acc. Chem. Res.*, 12 (1979) 139.
- 14 W.R. Roper, G.E. Taylor, J.M. Waters and L.J. Wright, *J. Organomet. Chem.*, 182 (1979) C46.
- 15 W.R. Roper, G.E. Taylor, J.M. Waters and L.J. Wright, *J. Organomet. Chem.*, 157 (1978) C27.
- 16 W.R. Roper and L.J. Wright, *J. Organomet. Chem.*, 234 (1982) C5.
- 17 M. Kubota and D.M. Blake, *J. Am. Chem. Soc.*, 93 (1971) 1368.
- 18 R. Mason and A.D.C. Towl, *J. Chem. Soc. A*, (1970) 1601.1
- 19 G.R. Clark, T.J. Collins, K. Marsden and W.R. Roper, *J. Organomet. Chem.*, 157 (1978) C23.
- 20 W.R. Roper and K.G. Town, unpublished work.
- 21 G.R. Clark, K. Marsden, W.R. Roper and L.J. Wright, *J. Am. Chem. Soc.*, 102 (1980) 1206.
- 22 W.R. Roper, *J. Organomet. Chem.*, 300 (1986) 167.
- 23 G.R. Clark, C.E.F. Rickard, W.R. Roper, D.M. Salter and L.J. Wright, *Pure Appl. Chem.*, 62 (1990) 1039.
- 24 S.J. La Placa and J.A. Ibers, *Inorg. Chem.*, 4 (1965) 778.
- 25 A.C. Skapski and P.G.H. Troughton, *Chem. Comm.*, (1968) 1230.
- 26 P.G.H. Troughton and A.C. Skapski, *Chem. Comm.*, (1968) 575.
- 27 C. Masters, W.S. McDonald, G. Raper and B.L. Shaw, *J. Chem. Soc. Chem. Comm.*, (1971) 210.
- 28 K.W. Muir and J.A. Ibers, *Inorg. Chem.*, 9 (1970) 440.
- 29 H. Werner, M.A. Esteruelas and H. Otto, *Organometallics*, 5 (1986) 2295.
- 30 R.G. Pearson, *J. Am. Chem. Soc.*, 91 (1969) 4947.
- 31 P.R. Hoffman and K.G. Caulton, *J. Am. Chem. Soc.*, 97 (1975) 4221.
- 32 P.B. Hitchcock, M.F. Lappert and P.L. Pye, *J. Chem. Soc., Chem. Comm.*, (1977) 196.
- 33 M.I. Bruce, R.C.F. Gardner, B.L. Goodall, F.G.A. Stone, R.J. Doedens, and J.A. Moreland, *J. Chem. Soc., Chem. Comm.*, (1974) 185.
- 34 M.R. Torres, A. Vegas, A. Santos and J. Ros, *J. Organomet. Chem.*, 309 (1986) 169.
- 35 R.-M. Catala, D. Cruz-Garritz, P. Terreros, H. Torrens, A. Hills, D.L. Hughes and R.L. Richards, *J. Organomet. Chem.*, 328 (1987) C37.
- 36 J.M. Williams, R.K. Brown, A.J. Schultz, G.D. Stucky and S.D. Ittel, *J. Am. Chem. Soc.*, 100 (1978) 7407.
- 37 F.A. Cotton, T. LaCour, and A.G. Stanislawski, *J. Am. Chem. Soc.*, 96 (1974) 754.
- 38 C.E.F. Rickard, W.R. Roper, L.J. Wright, and L. Young, *J. Organomet. Chem.*, 364 (1989) 391.
- 39 G.R. Clark, K.R. Grundy, R.O. Harris, S.M. James and W.R. Roper, *J. Organomet. Chem.*, 90 (1975) C37.
- 40 L. Vaska, *J. Am. Chem. Soc.*, 86 (1964) 1943.
- 41 L. Vaska, and J.W. DiLuzio, *J. Am. Chem. Soc.*, 83 (1961) 1262.
- 42 F.C. Whitmore, F.H. Hamilton, and N. Thurman, *Org. Synth.* 1941, Coll. vol. 1, 519.
- 43 J.L. Maynard, *J. Am. Chem. Soc.*, 46 (1924) 1510.
- 44 L.G. Makarova, and A.N. Nesmeyanov, in A.N. Nesmeyanov and K.A. Kocheshkov (Eds.), *Methods of Elemento-Organic Chemistry: The Organic Compounds of Mercury*, North Holland, Amsterdam, 1967, Vol. 4, p. 236.
- 45 G.F. Wright, *J. Org. Chem.*, 1 (1936) 457.
- 46 D.S. Bohle, G.R. Clark, C.E.F. Rickard, W.R. Roper and L.J. Wright. *J. Organomet. Chem.*, 358 (1988) 411.
- 47 FORDAP, A. Zalkin; CUCLS, R.J. Dellaca, University of Canterbury, N.Z.; SHELX-76, G.M. Sheldrick, University Chemical Laboratory, Cambridge.