

Cyclometallated complexes of ruthenium and osmium containing the *o*-C₆H₄PPh₂ ligand

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Received 13 December 1999; received in revised form 18 January 2000

Abstract

The reaction between [Hg(*o*-C₆H₄PPh₂)₂] and [MHCl(CO)(PPh₃)₃] gives the complexes [MCl(*o*-C₆H₄PPh₂)(CO)(PPh₃)₂] [M = Ru (**1**), Os (**2**)], which contain a four-membered cyclometallated ring. A single-crystal X-ray diffraction study of **2** shows the geometry about osmium to be distorted octahedral with the phosphorus atoms in a meridional arrangement. Both complexes react with CO, which displaces one of the triphenylphosphine ligands, the product from **2** being [OsCl(*o*-C₆H₄PPh₂)(CO)₂(PPh₃)]. In the case of **1**, there is an accompanying migratory insertion of coordinated CO into the Ru–C bond to give the five-membered cyclic acyl complex [RuCl(*o*-C(O)C₆H₄PPh₂)(CO)₂(PPh₃)]. Complex **2** reacts with AgSbF₆ in the presence of CO to give [Os(*o*-C₆H₄PPh₂)(CO)₂(PPh₃)₂]SbF₆. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Ruthenium; Osmium; Cyclometallation; CO insertion

1. Introduction

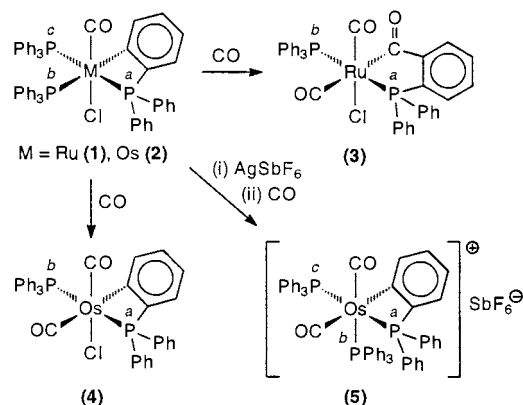
Since the discovery of the exchange of gaseous deuterium with the *ortho*-hydrogen atoms of the triphenylphosphine ligands of [RuHCl(PPh₃)₃] [1], which presumably proceeds via intermediate [Ru(*o*-C₆H₄PPh₂) species, numerous *ortho*-metallated complexes have been isolated starting from triphenylphosphine complexes of ruthenium(II) and, to a lesser extent, osmium(II). Sodium-amalgam reduction of [RuCl₂(PPh₃)_{*n*}] (*n* = 3, 4) in the presence of acetonitrile or pyridine generates [RuH(*o*-C₆H₄PPh₂)(L)(PPh₃)] (L = MeCN, C₅H₅N) [2] and similar treatment of [RuCl₂(PMe₃)₄] in the presence of PPh₃ gives [RuH(*o*-C₆H₄PPh₂)(PMe₃)₃] [3]. Hydrido complexes of ruthenium(II) have also been used as precursors to *ortho*-metallated complexes. The ethylene complex [RuH(*o*-C₆H₄PPh₂)(η²-C₂H₄)(PPh₃)₂] is formed from

[RuH₂(PPh₃)₄] and ethylene [4], and similar osmium compounds containing *ortho*-metallated tri-*p*-tolylphosphine have been obtained starting from [OsH₄{P(C₆H₄Me)₃}₃] [5]. The carbonyl complexes [MH(*o*-C₆H₄PPh₂)(CO)(PPh₃)₂] (M = Ru, Os) have been generated via intermediate hydrides by heating the (*o*-tolyl)formate complexes [M(η¹-C₆H₄Me-*o*)(η²O₂CH)(CO)(PPh₃)₂] [6] and [OsH(*o*-C₆H₄PPh₂)(CO)₂(PPh₃)] has been obtained by heating the adducts [Os(CO)₂(PPh₃)₂(L)] (L = CH₂O, C₂H₄) in alcoholic solvents [7]. The THF complex [RuH(*o*-C₆H₄PPh₂)(THF)(PPh₃)₂] is among the products of reaction of [RuHCl(PPh₃)₃] with alkylating agents [8]. Reaction of [RuHCl(PPh₃)₃] with alkynes gives [RuCl(*o*-C₆H₄PPh₂)(PPh₃)₂] [9], whereas maleic acid gives a dimer, [RuCl(*o*-C₆H₄PPh₂)(PPh₃)₂], which reacts with CO to give [RuCl(*o*-C₆H₄PPh₂)(CO)(PPh₃)] [10]. Finally, an anionic cycloruthenated complex, [RuH(*o*-C₆H₄PPh₂)(PPh₃)₂][−], is obtained as its potassium salt by the action of KC₁₀H₈ on [RuHCl(PPh₃)₃] [11].

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Although C–H activation of coordinated triphenylphosphine is the most commonly used method for generating $M(o-C_6H_4PPh_2)$ complexes, other procedures have been developed. Derivatives of rhodium(III) and palladium(II) have been obtained by oxidative addition of the carbon–halogen bonds of $o-XC_6H_4PPh_2$ ($X = Cl, Br$) to rhodium(I) and palladium(0) precursors



Scheme 1.

Table 1
 $^{31}P\{^1H\}$ -NMR spectroscopic data for cyclometallated complexes **1–5**

Complex	$^{31}P\{^1H\}$ -NMR		
	δ (ppm)		$[^2J]$ (Hz)
$[RuCl(o-C_6H_4PPh_2)(CO)(PPh_3)_2]$ (1) ^a	P_a	–52.2 (dd)	$^2J_{P_a-P_c} = 311$
	P_b	12.6 (dd)	$^2J_{P_a-P_b} = 20$
	P_c	33.2 (dd)	$^2J_{P_b-P_c} = 13$
$[OsCl(o-C_6H_4PPh_2)(CO)(PPh_3)_2]$ (2) ^a	P_a	–82.4 (dd)	$^2J_{P_a-P_c} = 285$
	P_b	–12.1 (dd)	$^2J_{P_a-P_b} = 17$
	P_c	–2.4 (dd)	$^2J_{P_b-P_c} = 7$
$[RuCl(o-C_6H_4PPh_2)(CO)_2(PPh_3)]$ (3) ^b	P_a	55.6 (d)	$^2J_{P_a-P_b} = 264$
	P_b	22.4 (d)	
$[RuCl(o-C(O)C_6H_4PPh_2)(^{13}CO)_2(PPh_3)]$ (3a) ^c	P_a	55.6 (dd)	$^2J_{P_a-P_b} = 264$
	P_b	22.4 (dd)	$^2J_{P_C} = 11.5, 7.0$ $^2J_{P_C} = 10.4, 7.6$
$[OsCl(o-C_6H_4PPh_2)(CO)_2(PPh_3)]$ (4) ^a	P_a	–64.6 (d)	$^2J_{P_a-P_b} = 268$
	P_b	–1.5 (d)	
$[OsCl(o-C_6H_4PPh_2)(CO)_2(PPh_3)_2]SbF_6$ (5) ^a	P_a	–86.5 (dd)	$^2J_{P_a-P_c} = 166$
	P_b	–11.4 (dd)	$^2J_{P_b-P_c} = 15$
	P_c	–6.7 (dd)	$^2J_{P_a-P_b} = 6$

^a Spectra recorded in $CDCl_3$ at 25°C (external reference 85% H_3PO_4).

^b Spectrum recorded in C_6D_6 (external reference 85% H_3PO_4).

^c Spectrum of the product from the reaction of **1** and ^{13}CO , recorded in C_6D_6 (external reference 85% H_3PO_4).

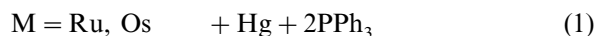
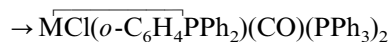
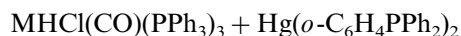
[12,13] and transmetalation of $o-LiC_6H_4PPh_2$ has been used to prepare *ortho*-metallated complexes of platinum(II) and gold(I) [14,15]. The reaction of $o-LiC_6H_4PPh_2$ with $HgCl_2$ gives the organomercury compound $[Hg(o-C_6H_4PPh_2)_2]$, which can function both as a bidentate P-donor ligand and as a transfer agent for the $C_6H_4PPh_2$ group to d^8 metal complexes [16].

The reaction between bis(aryl)mercury compounds $[HgAr_2]$ and $[MHCl(CO)(PPh_3)_3]$ ($M = Ru, Os$) has been used to prepare a wide range of five-coordinate arylmetal complexes of ruthenium and osmium of general formula $[M(Ar)Cl(CO)(PPh_3)_2]$ [17]. In this paper, we show that this chemistry can be extended to $[Hg(o-C_6H_4PPh_2)_2]$, thus providing an alternative route to *ortho*-metallated complexes of ruthenium and osmium.

2. Results and discussion

2.1. Formation of $[MCl(o-C_6H_4PPh_2)(CO)(PPh_3)_2]$ [$M = Ru$ (**1**), Os (**2**)]

The complexes $[MHCl(CO)(PPh_3)_3]$ react readily with $[Hg(o-C_6H_4PPh_2)_2]$ in refluxing toluene to give colourless compounds of formula $[MCl(o-C_6H_4PPh_2)(CO)(PPh_3)_2]$ [$M = Ru$ (**1**), Os (**2**)] in high yield, together with triphenylphosphine and metallic mercury (Eq. (1) and Scheme 1).



Roper et al. [17] have suggested, as one possibility, that the reaction between bis(aryl)mercury(II) compounds and $[MHCl(CO)(PPh_3)_3]$ proceeds by oxidative addition of the fragments $HgAr$ and Ar to a coordinatively unsaturated intermediate generated by dissociation of PPh_3 from the ruthenium or osmium center. Elimination of ArH and Hg from the adduct completes the reaction. We assume that our reactions proceed similarly, so that half the liberated PPh_3 is derived from the hydrido complex and half from the mercury compound.

The $\nu(MH)$ bands in the IR spectra of the starting hydrido complexes at 2014 (Ru) and 2097 cm^{-1} (Os) are absent from the spectra of **1** and **2**; there are new bands in the regions 1560 and 730 cm^{-1} that can be attributed to C–C stretching and C–H out-of-plane deformation modes of *ortho*-metallated triphenylphosphine [8,14,18] and strong $\nu(CO)$ bands at 1930 cm^{-1} (**1**) and 1917 cm^{-1} (**2**). The $^{31}P\{^1H\}$ -NMR spectra of complexes **1** and **2** (Table 1) show three doublets of

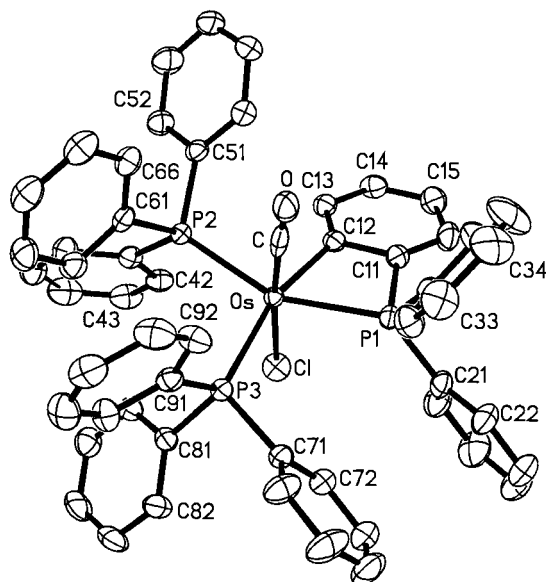


Fig. 1. X-ray structure (ORTEP) of $[\text{OsCl}(o\text{-C}_6\text{H}_4\text{PPh}_2)(\text{CO})(\text{PPh}_3)_2]$ (**2**) with atom labelling and 50% probability ellipsoids.

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

<i>Bond lengths</i>			
Os–C	1.889(3)	Os–C(12)	2.135(3)
Os–P(2)	2.3847(9)	Os–P(1)	2.4250(9)
Os–P(3)	2.4368(9)	Os–Cl	2.4645(11)
O–C	1.068(3)		
<i>Bond angles</i>			
C–Os–P(2)	83.89(11)	C1–Os–P(2)	93.39(10)
C–Os–P(1)	85.42(11)	C(12)–Os–P(1)	66.05(10)
P(2)–Os–P(1)	155.77(3)	C–Os–P(3)	95.83(12)
C(12)–Os–P(3)	163.17(10)	P(2)–Os–P(3)	100.22(3)
P(1)–Os–P(3)	102.46(3)	C–Os–Cl	174.97(11)
C(12)–Os–Cl	83.36(10)	P(2)–Os–Cl	101.04(3)
P(1)–Os–Cl	89.63(3)	P(3)–Os–Cl	84.35(3)
C–Os–C(12)	95.42(15)		

doublets of equal intensity arising from inequivalent phosphorus atoms. One of the resonances is highly shielded [$\delta_{\text{P}} - 52.2$ (**1**), -82.4 (**2**)], suggestive of the presence of the four-membered chelate ring $\overline{\text{M}(o\text{-C}_6\text{H}_4\text{PPh}_2)}$ [19]. In each case, this resonance, due to P_a , is strongly coupled (J ca. 300 Hz) to the less shielded of the remaining phosphorus atoms (P_c), indicating that P_a and P_c are mutually *trans* in an octahedral arrangement; the other P–P coupling constants are less than 20 Hz, as expected for mutually *cis*-phosphorus atoms. The structure for **1** and **2** shown in Scheme 1 is consistent with the spectroscopic data and has been confirmed in the case of **2** by a single-crystal X-ray diffraction study.

The structure of **2** is shown in Fig. 1; selected bond distances and angles are in Table 2. The osmium atom has a distorted octahedral coordination geometry in

which the three phosphorus atoms adopt the sterically favoured meridional arrangement. Phosphorus atoms P(2) and P(3) are, respectively, *trans* and *cis* to phosphorus atom P(1) of the four-membered ring, the Os–P distances being in the usual range of 2.38–2.44 Å. Surprisingly, the Os–P distance *trans* to the η^1 -aryl group, Os–P(3), is not the largest of the three, even though η^1 -aryls are expected to have a high *trans*-bond weakening influence. The angle subtended at the metal atom in the four-membered ring is 66° (*cf.* 68° in *cis*- $[\text{Pt}(o\text{-C}_6\text{H}_4\text{PPh}_2)_2]$ [14]), i.e. much smaller than the angle of 90° for a regular octahedron. Correspondingly, the angle of 100° subtended at the metal atom by the two PPh_3 ligands opposite the four-membered ring, P(2)–Os–P(3), is significantly greater than 90° . The Os–C(aryl) bond length of 2.135(3) Å in **2** is somewhat greater than that in $[\text{OsI}(8\text{-quinoyl})(\text{CO})(\text{PPh}_3)_2]$ [2.096(9) Å], which also contains a cyclometallated group in a four-membered ring [20].

2.2. Reactions of $[\overline{\text{MCl}(o\text{-C}_6\text{H}_4\text{PPh}_2)(\text{CO})(\text{PPh}_3)_2}]$ [$\text{M} = \text{Ru}$ (**1**), Os (**2**)] with CO

A colourless solution of complex **1** in toluene immediately turns yellow on reaction with CO. The pale yellow solid isolated from the solution shows a pair of doublets at δ 55.6 and 22.4 ($^2J_{\text{PP}} = 264$ Hz) in its $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum, indicative of mutually *trans*-phosphorus atoms. The fact that neither resonance is highly shielded shows that the four-membered chelate ring is no longer present. The IR spectrum in Nujol shows a pair of intense bands at 2039 and 1987 cm^{-1} assigned to mutually *cis*, terminal CO groups and a strong band at 1619 cm^{-1} due to an acyl group; the last two absorptions also show weak shoulders at 1945 and 1574 cm^{-1} , respectively. The $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum contains a pair of triplets at δ 196.1 and 195.5 ($^2J_{\text{CP}} = 10.5, 7.5$ Hz) that are assigned to inequivalent terminal CO groups; the peak due to the acyl carbon atom could not be located. The spectroscopic data are consistent with the formulation $[\overline{\text{RuCl}(o\text{-C}(\text{O})\text{C}_6\text{H}_4\text{PPh}_2)(\text{CO})_2}(\text{PPh}_3)]$ (**3**) containing a five-membered chelate acyl group derived from insertion of CO into the four-membered ring of **1**. A similar insertion of CO has been observed in the cases of the *ortho*-metallated complexes $[\overline{\text{Rh}(o\text{-C}_6\text{H}_4\text{PPh}_2)(\text{PPh}_3)_2}]$ [21] and $[\overline{\text{Mn}(o\text{-C}_6\text{H}_4\text{PPh}_2)(\text{CO})_4}]$ [22].

Spectroscopic data for compound **3a** prepared by the reaction of ^{13}CO with complex **1** support the assignment. The resonances in the $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum now appear as two doublets of doublets at δ 55.6 ($^2J_{\text{PC}} = 11.5, 7.0$ Hz) and 22.4 ($^2J_{\text{PC}} = 10.4, 7.6$ Hz) owing to coupling of the inequivalent phosphorus atoms with inequivalent ^{13}C nuclei. In the carbonyl region of the $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum a weak signal can be observed at δ 202, which is probably due to the

acyl carbon that has been slightly enriched. The signals due to the terminal CO groups at δ 196.1 and 195.8 are highly enhanced and appear as triplets of doublets with two P–C couplings each of ca. 11 Hz on the first resonance and ca. 7.5 Hz on the second resonance, together with a superimposed ^{13}C – ^{13}C coupling of 3.5 Hz. The IR spectrum of **3a** shows that the bands due to terminal CO are shifted, as expected, by ca. 40 cm^{-1} to a lower wavenumber than their positions in the spectrum of **3**, whereas the acyl $\nu(\text{C}=\text{O})$ absorptions at $1620(\text{s})$ and $1573(\text{w})\text{ cm}^{-1}$ are unshifted. These observations establish that in the conversion of **1** into **3** it is predominantly the initially coordinated CO that is incorporated into the acyl group. The reaction probably proceeds by the cooperative migration mechanism common to most CO insertions into transition metal–carbon σ -bonds [23–25].

Complex **2** reacts more slowly than **1** with CO at room temperature to give $[\text{OsCl}(\text{o-}C_6H_4PPh_2)(\text{CO})_2(\text{PPh}_3)]$ (**4**) as a colourless solid whose $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum consists of two doublets at δ -64.6 and -1.5 ($^2J_{\text{PP}} = 268$ Hz). These data show that one of the PPh_3 ligands of **2** has been replaced by CO but that the four-membered ring has been retained. The IR spectrum of **4** shows strong terminal $\nu(\text{CO})$ bands at 2017, 1948 cm^{-1} (Nujol) [2023, 1954 cm^{-1} (CH_2Cl_2)] suggestive of a *cis*-dicarbonyl arrangement. There is also a weak absorption of unknown origin at ca. 1895 cm^{-1} in both Nujol and CH_2Cl_2 . There is no acyl band in the region of 1620 cm^{-1} , again consistent with the presence of the cyclometallated ring.

In an unsuccessful effort to induce CO insertion into the osmacyclic unit of **2**, we treated the complex with AgSbF_6 in the presence of CO. The product is the salt $[\text{Os}(\text{o-}C_6H_4PPh_2)(\text{CO})_2(\text{PPh}_3)_2]\text{SbF}_6$ (**5**) in which the four-membered ring is retained. The IR spectrum shows two strong $\nu(\text{CO})$ bands in the 2000 cm^{-1} region due to a *cis*-dicarbonyl arrangement, hence the entering CO does not occupy the position vacated by the leaving chloride ion; there are no bands in the region of 1620 cm^{-1} due to acyl C=O groups. The $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum of **5** contains three doublets of doublets whose chemical shifts and coupling constants are similar to those of the precursor complex **2**. The spectroscopic data for **4** and **5** are consistent with the structures shown in Scheme 1.

3. Conclusions

The reaction between bis(aryl)mercury compounds and $[\text{MHCl}(\text{CO})(\text{PPh}_3)_3]$ ($\text{M} = \text{Ru}, \text{Os}$) to give σ -aryls of ruthenium and osmium has proved to be remarkably general and has already been used to prepare functionalized 2-pyrrolyl and 8-quinolyl derivatives in which the metal achieves six-coordination by interaction with a

suitably placed donor on the aromatic ring [20,26]. We have shown here that a *o*- $C_6H_4PPh_2$ group can be transferred similarly to give new six-coordinate *ortho*-metallated complexes of ruthenium and osmium. It may be possible to extend this methodology to other hydrido complexes, thus providing a general route to *o*- $C_6H_4PPh_2$ complexes of other transition elements [16].

4. Experimental

All manipulations were performed under a nitrogen atmosphere using standard Schlenk-tube techniques and all solvents were dried and degassed before use. NMR spectra were recorded on a Varian Gemini-300 BB spectrometer [^1H - (300 MHz), ^{13}C - (75.43 MHz) and ^{31}P -NMR (121.4 MHz)] with tetramethylsilane and H_3PO_4 as references. The $^{31}\text{P}\{^1\text{H}\}$ -NMR spectra are shown in Table 1. Infrared spectra were measured on Perkin–Elmer Paragon 1000 series FTIR or 1800 FTIR spectrometers as Nujol mulls between KBr plates. Elemental analyses were performed by the Microanalytical Laboratories of the Research School of Chemistry, ANU and of the University of Otago. Mass spectra (FAB, nitrobenzyl alcohol as matrix) were obtained on a Fisons Instruments VG Autospec spectrometer.

The compounds $[\text{Hg}(\text{o-}C_6H_4PPh_2)_2]$ [16], $[\text{RuHCl}(\text{CO})(\text{PPh}_3)_3]$ [27] and $[\text{OsHCl}(\text{CO})(\text{PPh}_3)_3]$ [28] were prepared by literature methods.

4.1. Preparation of $[\text{RuCl}(\text{o-}C_6H_4PPh_2)(\text{CO})(\text{PPh}_3)_2]$ (**1**)

To $[\text{RuHCl}(\text{CO})(\text{PPh}_3)_3]$ (0.457 g, 0.50 mmol) in toluene (20 ml) was added $[\text{Hg}(\text{o-}C_6H_4PPh_2)_2]$ (0.434 g, 0.60 mmol). After heating at reflux for 30 min, the solution was cooled and filtered through Celite in order to remove the metallic mercury formed during the reaction. The resulting pale yellow solution was concentrated in vacuo to ca. 3 ml, and *n*-hexane (30 ml) was added to precipitate **1** as an off-white solid (0.390 g, 82%). The analytical sample was purified by recrystallization from dichloromethane–ether. ^1H -NMR (CD_2Cl_2): δ 6.80–7.40 (overlapping multiplets due to aromatic protons). $^{13}\text{C}\{^1\text{H}\}$ -NMR (CD_2Cl_2): δ 138–124 (overlapping resonances due to aromatic carbons). IR $\nu(\text{CO}) = 1930\text{ cm}^{-1}$. Anal. Found: C, 69.33; H, 4.71. Calc. for $\text{C}_{55}\text{H}_{44}\text{ClOP}_3\text{Ru}$: C, 69.51; H, 4.67%. FABMS: $m/z = 950$, 8%, $[\text{M}^+]$ 660, 84% $[\text{M}^+ - (\text{PPh}_3) - (\text{CO})]$.

4.2. Preparation of $[\text{OsCl}(\text{o-}C_6H_4PPh_2)(\text{CO})(\text{PPh}_3)_2]$ (**2**)

To $[\text{OsHCl}(\text{CO})(\text{PPh}_3)_3]$ (0.260 g, 0.25 mmol) in toluene (20 ml) was added $[\text{Hg}(\text{o-}C_6H_4PPh_2)_2]$ (0.217 g, 0.30 mmol). After heating at reflux for 30 min, the

solution was cooled and filtered through Celite. The almost colourless solution was concentrated in vacuo to ca. 5 ml, and *n*-hexane (30 ml) was added to give **2** as a white solid (0.150 g, 58%). The analytical sample was purified by recrystallization from dichloromethane–ether. Crystals of **2** suitable for an X-ray diffraction study were obtained by slowly evaporating a solution in dichloromethane–ethanol. ¹H-NMR (CDCl₃): δ 6.50–7.70 (overlapping multiplets due to aromatic protons). ¹³C{¹H}-NMR (CDCl₃): δ 184 (s), 157 (s), 138–124 (overlapping aromatic resonances). IR: ν(CO) = 1917 cm⁻¹. Anal. Found: C, 63.72; H, 4.35. Calc. for C₅₅H₄₄ClO₃OsP₃: C, 63.55; H, 4.27%. FABMS: *m/z* = 1040, 10%, [M⁺], 750, 100% [M⁺ – (PPh₃) – (CO)]⁺.

4.3. Preparation of [RuCl(o-C(O)C₆H₄PPh₂)(CO)₂(PPh₃)₂] (**3**)

Carbon monoxide was bubbled through a solution of **1** (0.096 g, 0.10 mmol) in toluene (10 ml) for 10 min. The resulting bright yellow solution was concentrated in vacuo to ca. 1 ml and *n*-hexane (10 ml) was added to give **3** as a pale yellow solid (0.051 g, 69%). ¹H-NMR (C₆D₆): δ 6.50–8.40 (multiplets due to aromatic protons). ¹³C{¹H}-NMR (C₆D₆): δ 196.0 (t, ²J_{PC} = 10.5 Hz, CO), 195.5 (t, ²J_{PC} = 7.5 Hz, CO), 158.0 (d, ²J_{PC} = 37 Hz), 138–124 (aromatic carbons and signals of deuterated solvent). IR (cm⁻¹, Nujol): ν(CO) = 2039 (s), 1987 (s), 1945 (w); ν(acyl C=O) = 1619 (s), 1574 (w). Anal. Found: C, 63.81; H, 4.21. Calc. for C₃₉H₂₉ClO₃P₂Ru: C, 62.95; H, 3.93%. FABMS: *m/z* = 716, 10% [M⁺ – CO], 651, 62% [M⁺ – CO – Cl].

Complex **3a** was prepared similarly from **1** and ¹³CO. ¹³C{¹H}-NMR (C₆D₆): δ 202 (m, acyl C=O), 196.1 (ddd, ²J_{PC} = 11.0, 10.8), 10.8 Hz, ²J_{CC} = 3.5 Hz, CO), 195.5 (ddd, ²J_{PC} = 7.5, 7.1 Hz, ²J_{CC} = 3.5 Hz, CO), 138–124 (aromatic carbons and deuterated solvent). IR (cm⁻¹, Nujol): ν(CO) = 1992 (s), 1934 (s), 1907 (w); ν(acyl C=O) = 1620 (s), 1573 (w).

4.4. Preparation of [OsCl(o-C₆H₄PPh₂)(CO)₂(PPh₃)] (**4**)

A solution of **2** (0.065 g, 0.063 mmol) in toluene (11 ml) was saturated with carbon monoxide and left in a sealed flask under atmospheric pressure overnight. Removal of the toluene in vacuo to ca. 1 ml and addition of *n*-hexane (10 ml) afforded crude **4** as a white solid (0.030 g, 59%). It was purified by column chromatography on silica gel using dichloromethane as the eluent and crystallized from ether–*n*-hexane. ¹³C{¹H}-NMR (CDCl₃): δ 138–124 ppm (aromatic carbons). IR: ν(CO) = 2017 (s), 1948 (s) cm⁻¹. Anal. Found: C, 56.22; H, 3.88. Calc. for C₃₈H₂₉ClO₂OsP₂: C, 56.68; H, 3.64%.

4.5. Preparation of [Os(o-C₆H₄PPh₂)(CO)₂(PPh₃)₂]SbF₆ (**5**)

A solution of **2** (0.100 g, 0.097 mmol) in dichloromethane (10 ml) was treated with AgSbF₆ (0.050 g, 0.15 mmol) in water (1 ml). Ethanol (5 ml) was added to ensure mixing of the two phases. The mixture was stirred for 1 h while carbon monoxide was bubbled through slowly; a pale yellow colour developed. The solution was filtered to remove the AgCl precipitate, washed with water to remove the aqueous phase, and filtered again. Hexane was added and the solution evaporated to dryness in vacuo to give **5** as an off-white solid. ¹H-NMR (CDCl₃): δ 6.60–7.80 (multiplets due to aromatic protons). ¹³C{¹H}-NMR (CDCl₃): δ 186.1 (m, CO) 186.0 (m, CO), 139–126 (aromatic carbons). IR (cm⁻¹, Nujol): ν(CO) = 2041 (s), 1984 (s); ν(SbF₆) = 657 cm⁻¹. Anal. Found: C, 51.79; H, 3.46. Calc. for C₅₆H₄₄F₆O₂OsP₃Sb. 0.5 CH₂Cl₂: C, 51.75; H, 3.88%.

4.6. Crystallography

Measurements were made on a Siemens SMART CCD diffractometer using graphite-monochromated Mo–K_α radiation, λ = 0.71073 Å. Data collection covered a nominal sphere of reciprocal space by a series of three sets of exposures each covering 0.3° in ω. Crystal decay was monitored by repeating the initial frames at the end of the data collection and analyzing duplicate reflections. Unit cell parameters were obtained by a least-squares fit to all data with *I* > 10σ(*I*). Lorentz and polarization corrections were applied and absorption corrections made by analyzing equivalent reflections [29].

The structures were solved by Patterson and difference Fourier methods using SHELXS-97 [30] and refined on *F*² using all data by full-matrix least squares with the program SHELXL-97 [31]. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included in calculated positions with a thermal parameter 20% greater than that of the carrier atom. The unit cell contained one molecule of water. Details of crystal data and structure refinement are listed in Table 3.

5. Supplementary material

Crystallographic data for the structural analysis of **2** have been deposited with the Cambridge Crystallography Data Centre, CCDC no. 137156. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2

Table 3
Crystal data and structure refinement for complex 2

Empirical formula	C ₅₅ H ₄₄ ClO ₆ P ₃ H ₂ O
Formula weight	1057.48
Temperature (K)	203(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> (Å)	12.9777(1)
<i>b</i> (Å)	19.0472(2)
<i>c</i> (Å)	18.9796(2)
β (°)	100.259(1)
<i>V</i> (Å ³)	4616.54(8)
<i>Z</i>	4
<i>D</i> _{calc} (g cm ⁻³)	1.519
Absorption coefficient (mm ⁻¹)	2.966
<i>F</i> (000)	2112
Crystal size (mm)	0.32 × 0.31 × 0.19
θ Range for data collection (°)	1.53 to 27.48
Reflections collected	28 109
Independent reflections	10 145 [<i>R</i> _{int} = 0.0160]
Max., min. transmission	0.6026, 0.4504
Data/restraints/parameters	10 145/0/559
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0278, <i>wR</i> ₂ = 0.0865
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.311, <i>wR</i> ₂ = 0.0892
Goodness-of-fit on <i>F</i> ₂	1.095
Largest diff. peak and hole (e Å ⁻³)	2.794, -0.925

1EZ UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www:http://www.ccdc.cam.ac.uk).

Acknowledgements

We thank the Universidad Pública de Navarra (Spain) for a postdoctoral grant to M.C. and the Marsden Fund, administered by the Royal Society of New Zealand, for the award of a Ph.D. scholarship to A.C. We also thank Mr A.G. Oliver for assistance with the crystallography.

References

- [1] G.W. Parshall, W.H. Knoth, R.A. Schunn, *J. Am. Chem. Soc.* 91 (1969) 4990.
- [2] D.J. Cole-Hamilton, G. Wilkinson, *J. Chem. Soc. Dalton Trans.* (1979) 1283.
- [3] H. Werner, J. Gotzig, *J. Organomet. Chem.* 284 (1985) 73.
- [4] D.J. Cole-Hamilton, G. Wilkinson, *Nouv. J. Chim.* 1 (1977) 141.
- [5] P.J. Desrosiers, L. Cai, J. Halpern, *J. Am. Chem. Soc.* 111 (1989) 8513.
- [6] W.R. Roper, L.J. Wright, *J. Organomet. Chem.* 234 (1982) C5.
- [7] G.R. Clark, C.E.L. Headford, K. Marsden, W.R. Roper, *J. Organomet. Chem.* 231 (1982) 335.
- [8] D.J. Cole-Hamilton, G. Wilkinson, *J. Chem. Soc. Dalton Trans.* (1977) 797.
- [9] A.M. Stolzenberg, E.L. Muetterties, *Organometallics* 4 (1985) 1739.
- [10] B.R. James, L.D. Markham, D.K.W. Wang, *J. Chem. Soc. Chem. Commun.* (1974) 439.
- [11] G.P. Pez, R.A. Grey, J. Corsi, *J. Am. Chem. Soc.* 103 (1981) 7528.
- [12] P. Lahuerta, J. Latorre, R. Martínez-Máñez, F. Sanz, *J. Organomet. Chem.* 356 (1988) 355.
- [13] A.M. Arif, F. Estevan, A. García-Bernabé, P. Lahuerta, M. Sanaú, M.A. Ubeda, *Inorg. Chem.* 36 (1997) 6472.
- [14] M.A. Bennett, D.E. Berry, S.K. Bhargava, E.J. Ditzel, G.B. Robertson, A.C. Willis, *J. Chem. Soc. Chem. Commun.* (1987) 1613.
- [15] (a) M.A. Bennett, S.K. Bhargava, K.D. Griffiths, G.B. Robertson, W.A. Wickramasinghe, A.C. Willis, *Angew. Chem. Int. Ed. Engl.* 26 (1987) 258. (b) M.A. Bennett, S.K. Bhargava, D.C.R. Hockless, L.L. Welling, A.C. Willis, *J. Am. Chem. Soc.* 118 (1996) 10469.
- [16] M.A. Bennett, M. Contel, D.C.R. Hockless, L.L. Welling, *Chem. Commun.* (Cambridge) (1998) 2401.
- [17] (a) W.R. Roper, L.J. Wright, *J. Organomet. Chem.* 142 (1977) C1. (b) C.E.F. Rickard, W.R. Roper, G.E. Taylor, J.M. Waters, L.J. Wright, *J. Organomet. Chem.* 389 (1990) 375.
- [18] (a) M.A. Bennett, D.L. Milner, *J. Am. Chem. Soc.* 91 (1969) 6983. (b) J.S. Valentine, *J. Chem. Soc. Chem. Commun.* (1973) 857.
- [19] P.E. Garrou, *Chem. Rev.* 81 (1981) 229.
- [20] A.M. Clark, C.E.F. Rickard, W.R. Roper, L.J. Wright, *J. Organomet. Chem.* 546 (1997) 619.
- [21] W. Keim, *J. Organomet. Chem.* 19 (1969) 161.
- [22] R.J. McKinney, R. Hoxmeier, H.D. Kaesz, *J. Am. Chem. Soc.* 97 (1975) 3059.
- [23] A. Wojcicki, *Adv. Organomet. Chem.* 11 (1973) 87.
- [24] A. Yamamoto, *Organotransition Metal Chemistry: Fundamental Concepts and Applications*, Wiley, New York, 1986, p. 246.
- [25] J.P. Collman, L.S. Hegedus, J.R. Norton, R.G. Finke, *Principles and Applications of Organotransition Metal Chemistry*, University Science Books, Mill Valley, CA, 1987, p. 355.
- [26] G.R. Clark, M.M.P. Ng, W.R. Roper, L.J. Wright, *J. Organomet. Chem.* 491 (1995) 219.
- [27] L. Vaska, J.W. diLuzio, *J. Am. Chem. Soc.* 83 (1961) 1262.
- [28] L. Vaska, *J. Am. Chem. Soc.* 86 (1964) 1943.
- [29] L.H. Blessing, *Acta Crystallogr. Sect. A* 51 (1995) 33.
- [30] G.M. Sheldrick, *Acta Crystallogr. Sect. A* 46 (1990) 467.
- [31] G.M. Sheldrick, *SHELXL-97*, Program for the Refinement of Crystal Structures, University of Göttingen, Germany, 1997.