

Seven-coordinate dioxygen complexes from dioxygen addition to five-coordinate σ -phenyl, isocyanide-containing derivatives of ruthenium(II) and osmium(II). Crystal structures of $\text{Os}(\eta^2\text{-O}_2)(\eta^2\text{-CPh=NP-chlorophenyl})\text{Cl}(\text{PPh}_3)_2$ and $\text{Os}(\eta^2\text{-SO}_4)(\eta^2\text{-CPh=NP-chlorophenyl})\text{Cl}(\text{PPh}_3)_2$

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Abstract

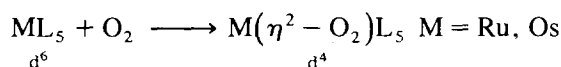
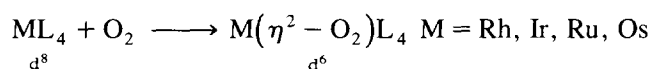
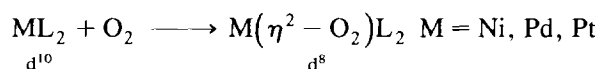
Reaction of the hydrido complexes $\text{MHCl}(\text{CNR})(\text{PPh}_3)_3$ (**1a**, M = Ru, R = *p*-tolyl; **1b**, M = Os, R = *p*-tolyl; **1c**, M = Os, R = *p*-chlorophenyl) with HgPh_2 results in formation of the five-coordinate σ -phenyl complexes $\text{MPhCl}(\text{CNR})(\text{PPh}_3)_2$ (**2a**, M = Ru, R = *p*-tolyl; **2b**, M = Os, R = *p*-tolyl; **2c**, M = Os, R = *p*-chlorophenyl). These five-coordinate complexes, upon contact with dioxygen, form seven-coordinate dioxygen complexes $\text{M}(\eta^2\text{-O}_2)(\eta^2\text{-CPh=NR})\text{Cl}(\text{PPh}_3)_2$ (**3a**, M = Ru, R = *p*-tolyl; **3b**, M = Os, R = *p*-tolyl; **3c**, M = Os, R = *p*-chlorophenyl) in which the phenyl group has migrated onto the isocyanide ligand to form a *dihapto*-iminoacyl ligand. The crystal structure of **3c** has been determined. The complex **3c** reacts with SO_2 to form the sulphate derivative $\text{Os}(\eta^2\text{-SO}_4)(\eta^2\text{-CPh=NP-chlorophenyl})\text{Cl}(\text{PPh}_3)_2$ (**4c**), the crystal structure of which has also been determined. Sodium acetate reacts with **2a** and **2b** to form $\text{MPh}(\eta^2\text{-O}_2\text{CCH}_3)(\text{CN}p\text{-tolyl})(\text{PPh}_3)_2$ (**5a**, M = Ru; **5b**, M = Os). CO reacts with $\text{OsPhCl}(\text{CN}p\text{-tolyl})(\text{PPh}_3)_2$ to form $\text{OsPhCl}(\text{CO})(\text{CN}p\text{-tolyl})(\text{PPh}_3)_2$ (**6b**) and with $\text{CN}p\text{-tolyl}$ to give $\text{OsPhCl}(\text{CN}p\text{-tolyl})_2(\text{PPh}_3)_2$ (**7b**). Reaction of **2a** with CO, and migration of the phenyl group, results in formation of the *dihapto*-iminoacyl complex $\text{Ru}(\eta^2\text{-CPh=NP-tolyl})\text{Cl}(\text{CO})(\text{PPh}_3)_2$ (**8a**). Treatment of **2a** with $\text{CN}p\text{-tolyl}$, followed by addition of HCl, gives the carbene complex $\text{RuCl}_2(\text{CPhNH}p\text{-tolyl})(\text{CN}p\text{-tolyl})(\text{PPh}_3)_2$ (**9a**). The hydrido complexes **1a–1c**, which are the immediate precursors of the five-coordinate σ -phenyl isocyanide complexes, are generated by reaction of the dihydrido complexes $\text{MH}_2(\text{CNR})(\text{PPh}_3)_3$ (**10a**, M = Ru, R = *p*-tolyl; **10b**, M = Os, R = *p*-tolyl; **10c**, M = Os, R = *p*-chlorophenyl) with HCl.

Keywords: Ruthenium; Osmium; Dioxygen complexes; Isocyanide complexes; Crystal structure

1. Introduction

The formation of η^2 -peroxo complexes, by direct reaction with dioxygen, is a feature of low oxidation state complexes of the platinum metals [1]. Typical examples include $\text{Pt}(\eta^2\text{-O}_2)(\text{PPh}_3)_2$ [2] from the parent $\text{Pt}(0), d^{10}$ complex, and likewise $\text{Ir}(\eta^2\text{-O}_2)\text{Cl}(\text{CO})(\text{PPh}_3)_2$ [3] from $\text{Ir}(I), d^8$. Directly comparable with the $\text{Ir}(I), d^8$ example are the dioxygen complexes $\text{Ru}(\eta^2\text{-O}_2)(\text{CO})_2(\text{PPh}_3)_2$ [4], $\text{Ru}(\eta^2\text{-O}_2)(\text{CO})(\text{CN}p\text{-tolyl})(\text{PPh}_3)_2$ [5], $\text{Ru}(\eta^2\text{-O}_2)\text{Cl}(\text{NO})(\text{PPh}_3)_2$ [6], and $\text{Os}(\eta^2\text{-O}_2)(\text{CO})_2(\text{PPh}_3)_2$ [4], derived from $\text{Ru}(0)$ and $\text{Os}(0), d^8$

parent compounds. An extension of this pattern suggests that suitably activated five-coordinate Ru^{II} and Os^{II} complexes will also react with dioxygen, forming seven-coordinate η^2 -peroxo complexes of Ru^{IV} and Os^{IV} respectively.



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The first example of this situation was provided in 1973 when $\text{Os}(\eta^2\text{-O}_2)\text{HX}(\text{CO})(\text{Pc-Hex}_3)_2$ ($\text{X} = \text{Cl}$ or Br) was reported [7]. The recent literature has provided several further examples, including two crystal structure determinations. Thus, $\text{Os}(\eta^2\text{-O}_2)\text{HCl}(\text{CO})(\text{Pi-Pr}_3)_2$ [8], $[\text{Ru}(\eta^2\text{-O}_2)\text{H}(\text{dippe})_2]^+$ (dippe = 1,2-bis(diiso-propylphosphino)ethane) [9], and $[\text{Os}(\eta^2\text{-O}_2)\text{H}(\text{dcpe})_2]^+$ (dcpe = 1,2-bis(dicyclo-hexylphosphino)ethane) [10], have all been described. It can be noted that reactivity towards dioxygen is always associated with the presence of good σ -donors as accompanying ligands. We describe herein results which reinforce this observation. Whereas the five-coordinate σ -aryl, carbonyl-containing complexes $\text{MArCl}(\text{CO})(\text{PPh}_3)_2$ ($\text{M} = \text{Ru}$ or Os) [11] show no reaction with dioxygen, the isocyanide-containing analogues $\text{MPhCl}(\text{CNR})(\text{PPh}_3)_2$ reported in this work react readily with dioxygen, and in the resulting seven-coordinate $\eta^2\text{-O}_2$ complexes a migration of the originally σ -bound phenyl group onto the isocyanide ligand occurs, forming an η^2 -iminoacyl ligand.

2. Results and discussion

2.1. Synthesis of $\text{MPhCl}(\text{CN}p\text{-tolyl})(\text{PPh}_3)_2$ and $\text{OsPhCl}(\text{CN}p\text{-chlorophenyl})(\text{PPh}_3)_2$

The carbonyl-containing complexes $\text{MPhCl}(\text{CO})(\text{PPh}_3)_2$ are synthesized by reaction of $\text{MHCl}(\text{CO})$

$(\text{PPh}_3)_3$ and HgPh_2 in toluene heated under reflux [11]. Formation of these five-coordinate complexes is characterised by the appearance of a red solution and the deposition of elemental mercury. Solutions of the complexes $\text{MPhCl}(\text{CO})(\text{PPh}_3)_2$ are stable in air. The analogous isocyanide complexes $\text{MPhCl}(\text{CNR})(\text{PPh}_3)_2$ (**2a**–**2c**) can be prepared in a similar manner by reaction of $\text{MHCl}(\text{CN}p\text{-tolyl})(\text{PPh}_3)_3$ (see below) and HgPh_2 . In marked contrast with the carbonyl complexes, neither $\text{OsPhCl}(\text{CN}p\text{-tolyl})(\text{PPh}_3)_2$ (**2b**) nor $\text{OsPhCl}(\text{CN}p\text{-chlorophenyl})(\text{PPh}_3)_2$ (**2c**) were successfully isolated as pure solids because of their extreme sensitivity to dioxygen. However, reaction of the ruthenium compound $\text{RuPhCl}(\text{CN}p\text{-tolyl})(\text{PPh}_3)_2$ (**2a**) with dioxygen is slower and it was possible to prepare an analytically pure sample of **2a** for spectroscopic characterisation (see Tables 1–3). Characterisation of **2b** and **2c** was by derivatisation (see below).

2.2. Reaction of **2a**, **2b**, and **2c** with dioxygen

On exposure of solutions of either $\text{OsPhCl}(\text{CN}p\text{-tolyl})(\text{PPh}_3)_2$ (**2b**) or $\text{OsPhCl}(\text{CN}p\text{-chlorophenyl})(\text{PPh}_3)_2$ (**2c**) to air there is an immediate colour change of the solution to deep purple, and from these solutions compounds **3b** and **3c** are isolated (Scheme 1). Complete reaction of $\text{RuPhCl}(\text{CN}p\text{-tolyl})(\text{PPh}_3)_2$ requires dioxygen to be bubbled through the solution for about 30 s. The uptake of dioxygen is accompanied by migra-

Table 1
IR data^a for new complexes

Compound	$\nu(\text{C}\equiv\text{N})^b$ (cm^{-1})	Other bands (cm^{-1})
$\text{RuHCl}(\text{CN}p\text{-tolyl})(\text{PPh}_3)_3$ 1a	2068sh, 2031	1958m $\nu(\text{RuH})$, 838w $\delta(\text{RuH})$
$\text{OsHCl}(\text{CN}p\text{-tolyl})(\text{PPh}_3)_3$ 1b	2077mw, 2014, 1981sh	885w $\delta(\text{OsH})$
$\text{OsHCl}(\text{CN}p\text{-chlorophenyl})(\text{PPh}_3)_3$ 1c	1998	
$\text{RuPhCl}(\text{CN}p\text{-tolyl})(\text{PPh}_3)_2$ 2a	2070ms, 2039	1560m, 1016m (Ph)
$\text{Ru}(\eta^2\text{-O}_2)(\eta^2\text{-CPh}=\text{N}p\text{-tolyl})\text{Cl}(\text{PPh}_3)_2$ 3a	1734 ϵ ms	1242mw, 920m, 889m, 819m, 771w (CPh= <i>Np</i> -tolyl)
$\text{Os}(\eta^2\text{-O}_2)(\eta^2\text{-CPh}=\text{N}p\text{-tolyl})\text{Cl}(\text{PPh}_3)_2$ 3b	1709 ϵ ms	1248mw, 906w, 885m, 833w, 810m, 790w (CPh= <i>Np</i> -tolyl)
$\text{Os}(\eta^2\text{-O}_2)(\eta^2\text{-CPh}=\text{N}p\text{-chlorophenyl})\text{Cl}(\text{PPh}_3)_2$ 3c	1668 ϵ ms	1250m, 907mw, 891m, 832m, 809mw, 774w (CPh= <i>Np</i> -chlorophenyl)
$\text{Os}(\eta^2\text{-SO}_4)(\eta^2\text{-CPh}=\text{N}p\text{-chlorophenyl})\text{Cl}(\text{PPh}_3)_2$ 4c	1724 ϵ ms	1298m, 1175s, 665s (SO_4), 1236mw, 918m, 887m, 835mw, 799w (CPh= <i>Np</i> -chlorophenyl)
$\text{RuPh}(\eta^2\text{-O}_2\text{CCH}_3)(\text{CN}p\text{-tolyl})(\text{PPh}_3)_2$ 5a	2060mw, 1969sh, 1948	1566m, 1018 (Ph), 1533m, 1185mw, 940m, 732m (O_2CCH_3)
$\text{OsPh}(\eta^2\text{-O}_2\text{CCH}_3)(\text{CN}p\text{-tolyl})(\text{PPh}_3)_2$ 5b	1975sh, 1890	1570m (Ph), 1604mw, 1532mw, 947mw (O_2CCH_3)
$\text{OsPhCl}(\text{CO})(\text{CN}p\text{-tolyl})(\text{PPh}_3)_2$ 6b	2100	1944s $\nu(\text{CO})$, 1560mw, 1016mw (Ph)
$\text{OsPhCl}(\text{CN}p\text{-tolyl})_2(\text{PPh}_3)_2$ 7b	2117, 2070m, 2030	1567w (Ph)
$\text{Ru}(\eta^2\text{-CPh}=\text{N}p\text{-tolyl})\text{Cl}(\text{CO})(\text{PPh}_3)_2$ 8a	1636 ϵ m	1898 $\nu(\text{CO})$, 1223m, 907mw, 819mw (CPh= <i>Np</i> -tolyl)
$\text{RuCl}_2(\text{CPhNH}p\text{-tolyl})(\text{CN}p\text{-tolyl})(\text{PPh}_3)_2$ 9a	2108	1510m, 1260mw, 1025mw, 840w, 821m (carbene)
$\text{RuH}_2(\text{CN}p\text{-tolyl})(\text{PPh}_3)_3$ 10a	2058, 2038	1958mw $\nu(\text{RuH})$
$\text{OsH}_2(\text{CN}p\text{-tolyl})(\text{PPh}_3)_3$ 10b	2054m, 1994	802 $\delta(\text{OsH})$
$\text{OsH}_2(\text{CN}p\text{-chlorophenyl})(\text{PPh}_3)_3$ 10c	1977	

^a Spectra recorded as Nujol mulls between KBr plates. Intensity of IR bands described as: s, strong; ms, medium strong; m, medium; mw, medium weak; w, weak; sh shoulder.

^b All $\nu(\text{C}\equiv\text{N})$ bands are strong in intensity. CNR gives rise to two other bands at ca. 1504 and 817 cm^{-1} which are fairly invariant for all complexes.

^c $\nu(\text{C}\equiv\text{N})$.

tion of phenyl onto the isocyanide ligand. In the IR spectrum the band above 2000 cm^{-1} , which is due to a terminally-bound isocyanide ligand, is replaced by a band at about 1700 cm^{-1} , which is characteristic of a *dihapto*-iminoacyl ligand [12]. For example, in the IR

spectrum of **3c** a band due to the iminoacyl ligand appears at 1668 cm^{-1} ($\nu(\text{C}=\text{N})$), and there are other bands at 1250, 907, 891, 832, 809 and 704 cm^{-1} . No band could be unambiguously assigned to $\nu(\text{O}-\text{O})$, although there are several bands in the $800\text{--}900\text{ cm}^{-1}$

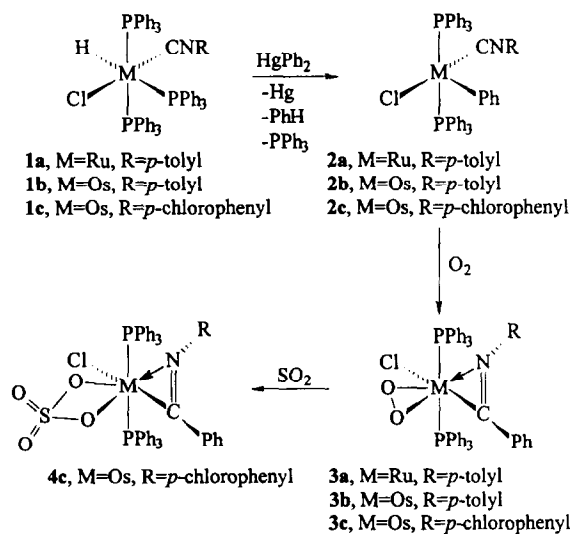
Table 2
 $^1\text{H-NMR}$ data ^a for new complexes

Compound	Chemical shift (ppm)
$\text{RuHCl}(\text{CN-}p\text{-tolyl})(\text{PPh}_3)_3$ 1a	–7.64 (dt, 1H, Ru–H, $J(\text{HP}_{\text{trans}}) = 100.0$, $J(\text{HP}_{\text{cis}}) = 25.4$); 2.25 (s, 3H, $\text{CNC}_6\text{H}_4\text{CH}_3$); 6.01 (d, 2H, $\text{CNC}_6\text{H}_4\text{CH}_3$, $J(\text{HH}) = 8.2$); 6.82 (d, 2H, $\text{CNC}_6\text{H}_4\text{CH}_3$, $J(\text{HH}) = 8.2$); 7.00–7.74 (m, 45H, PPh_3).
$\text{OsHCl}(\text{CN-}p\text{-tolyl})(\text{PPh}_3)_3$ 1b	–7.44 (dt, 1H, Os–H, $J(\text{HP}_{\text{trans}}) = 86.2$, $J(\text{HP}_{\text{cis}}) = 25.2$); 2.21 (s, 3H, $\text{CNC}_6\text{H}_4\text{CH}_3$); 5.95 (d, 2H, $\text{CNC}_6\text{H}_4\text{CH}_3$, $J(\text{HH}) = 8.3$); 6.77 (d, 2H, $\text{CNC}_6\text{H}_4\text{CH}_3$, $J(\text{HH}) = 8.2$); 6.85–7.35 (m, 45H, PPh_3).
$\text{OsHCl}(\text{CN-}p\text{-chlorophenyl})(\text{PPh}_3)_3$ 1c	–7.19 (dt, 1H, Os–H, $J(\text{HP}_{\text{trans}}) = 86.1$, $J(\text{HP}_{\text{cis}}) = 25.4$); 5.95 (d, 2H, $\text{CNC}_6\text{H}_4\text{CH}_3$, $J(\text{HH}) = 8.5$); 6.83–7.36 (m, 47H, PPh_3 , $\text{CNC}_6\text{H}_4\text{Cl}$).
$\text{RuPhCl}(\text{CN-}p\text{-tolyl})(\text{PPh}_3)_2$ 2a	2.21 (s, 3H, $\text{CNC}_6\text{H}_4\text{CH}_3$); 5.99 (d, 2H, $\text{CNC}_6\text{H}_4\text{CH}_3$, $J(\text{HH}) = 8.2$); 6.50 (m, 2H, C_6H_5); 6.77 (d, 2H, $\text{CNC}_6\text{H}_4\text{CH}_3$, $J(\text{HH}) = 8.7$); 7.01–7.46 (m, 33H, PPh_3 , C_6H_5).
$\text{Ru}(\eta^2\text{-O}_2)(\eta^2\text{-CPh}=\text{N-}p\text{-tolyl})\text{Cl}(\text{PPh}_3)_2$ 3a	2.29 (s, 3H, $\text{CPh}=\text{NC}_6\text{H}_4\text{CH}_3$); 6.79 (m, 4H, $\text{CPh}=\text{NC}_6\text{H}_4\text{CH}_3$); 7.02–7.72 (m, 35H, PPh_3 , $\text{CPh}=\text{NC}_6\text{H}_4\text{CH}_3$).
$\text{Os}(\eta^2\text{-O}_2)(\eta^2\text{-CPh}=\text{N-}p\text{-tolyl})\text{Cl}(\text{PPh}_3)_2$ 3b	2.30 (s, 3H, $\text{CPh}=\text{NC}_6\text{H}_4\text{CH}_3$); 6.79 (m, 4H, $\text{CPh}=\text{NC}_6\text{H}_4\text{CH}_3$); 7.03–7.49 (m, 35H, PPh_3 , $\text{CPh}=\text{NC}_6\text{H}_4\text{CH}_3$).
$\text{Os}(\eta^2\text{-O}_2)(\eta^2\text{-CPh}=\text{N-}p\text{-chlorophenyl})\text{Cl}(\text{PPh}_3)_2$ 3c	6.67 (d, 2H, $\text{CPh}=\text{NC}_6\text{H}_4\text{Cl}$, $J(\text{HH}) = 8.7$); 6.89 (d, 2H, $\text{CPh}=\text{NC}_6\text{H}_4\text{Cl}$, $J(\text{HH}) = 8.7$); 7.05–7.51 (m, 35H, PPh_3 , $\text{CPh}=\text{NC}_6\text{H}_4\text{CH}_3$).
$\text{Os}(\eta^2\text{-SO}_4)(\eta^2\text{-CPh}=\text{N-}p\text{-chlorophenyl})\text{Cl}(\text{PPh}_3)_2$ 4c	6.39 (d, 2H, $\text{CPh}=\text{NC}_6\text{H}_4\text{Cl}$, $J(\text{HH}) = 8.8$); 6.80 (d, 2H, $\text{CPh}=\text{NC}_6\text{H}_4\text{Cl}$, $J(\text{HH}) = 8.9$); 7.08–7.63 (m, 33H, PPh_3 , $\text{CPh}=\text{NC}_6\text{H}_4\text{CH}_3$); 7.83 (d, 2H, $\text{CPh}=\text{NC}_6\text{H}_4\text{CH}_3$, $J(\text{HH}) = 7.4$).
$\text{RuPh}(\eta^2\text{-O}_2\text{CCH}_3)(\text{CN-}p\text{-tolyl})(\text{PPh}_3)_2$ 5a	0.74 (s, 3H, O_2CCCH_3); 2.21 (s, 3H, $\text{CNC}_6\text{H}_4\text{CH}_3$); 6.04 (d, 2H, $\text{CNC}_6\text{H}_4\text{CH}_3$, $J(\text{HH}) = 8.1$); 6.38 (m, 3H, C_6H_5); 6.79 (d, 2H, $\text{CNC}_6\text{H}_4\text{CH}_3$, $J(\text{HH}) = 8.1$); 7.14–7.45 (m, 32H, PPh_3 , C_6H_5).
$\text{OsPh}(\eta^2\text{-O}_2\text{CCH}_3)(\text{CN-}p\text{-tolyl})(\text{PPh}_3)_2$ 5b	0.68 (s, 3H, O_2CCCH_3); 2.21 (s, 3H, $\text{CNC}_6\text{H}_4\text{CH}_3$); 6.05 (d, 2H, $\text{CNC}_6\text{H}_4\text{CH}_3$, $J(\text{HH}) = 8.3$); 6.32 (m, 3H, C_6H_5); 6.74 (d, 2H, $\text{CNC}_6\text{H}_4\text{CH}_3$, $J(\text{HH}) = 8.3$); 7.03 (d, 2H, C_6H_5 , $J(\text{HH}) = 7.6$); 7.23–7.42 (m, 30H, PPh_3).
$\text{OsPhCl}(\text{CO})(\text{CN-}p\text{-tolyl})(\text{PPh}_3)_2$ 6b	2.28 (s, 3H, $\text{CNC}_6\text{H}_4\text{CH}_3$); 6.27 (d, 2H, $\text{CNC}_6\text{H}_4\text{CH}_3$, $J(\text{HH}) = 8.3$); 6.68 (t, 2H, C_6H_5 , $J(\text{HH}) = 7.3$); 6.79 (t, 1H, C_6H_5 , $J(\text{HH}) = 7.0$ Hz); 6.90 (d, 2H, $\text{CNC}_6\text{H}_4\text{CH}_3$, $J(\text{HH}) = 8.3$); 7.12–7.40 (m, 32H, PPh_3 , C_6H_5).
$\text{OsPhCl}(\text{CN-}p\text{-tolyl})_2(\text{PPh}_3)_2$ 7b	2.23 (s, 3H, $\text{CNC}_6\text{H}_4\text{CH}_3$); 2.28 (s, 3H, $\text{CNC}_6\text{H}_4\text{CH}_3$); 6.00 (d, 2H, $\text{CNC}_6\text{H}_4\text{CH}_3$, $J(\text{HH}) = 8.1$); 6.17 (d, 2H, $\text{CNC}_6\text{H}_4\text{CH}_3$, $J(\text{HH}) = 8.1$); 6.79 (m, 5H, C_6H_5 , $\text{CNC}_6\text{H}_4\text{CH}_3$); 7.12–7.46 (m, 34H, PPh_3 , C_6H_5 , $\text{CNC}_6\text{H}_4\text{CH}_3$).
$\text{Ru}(\eta^2\text{-CPh}=\text{N-}p\text{-tolyl})\text{Cl}(\text{CO})(\text{PPh}_3)_2$ 8a	2.24 (s, 3H, $\text{CPh}=\text{NC}_6\text{H}_4\text{CH}_3$); 6.25 (d, 2H, $\text{CPh}=\text{NC}_6\text{H}_4\text{CH}_3$, $J(\text{HH}) = 8.3$); 6.77 (m, 7H, $\text{CPh}=\text{NC}_6\text{H}_4\text{CH}_3$); 7.05–7.71 (m, 30H, PPh_3).
$\text{RuCl}_2(\text{CPhNH-}p\text{-tolyl})(\text{CN-}p\text{-tolyl})(\text{PPh}_3)_2$ 9a	2.16 ^b (s, 3H); 2.26 ^b (s, 3H); 5.77 (d, 2H, $\text{CPhNHC}_6\text{H}_4\text{CH}_3$, $J(\text{HH}) = 7.4$); 6.06 ^c (d, 2H, $J(\text{HH}) = 8.4$); 6.14 ^c (d, 2H, $J(\text{HH}) = 8.3$); 6.71 ^c (d, 2H, $J(\text{HH}) = 8.3$); 6.78 ^c (d, 2H, $J(\text{HH}) = 8.2$); 6.89–7.81 (m, 33H, PPh_3 , $\text{CPhNHC}_6\text{H}_4\text{CH}_3$); 12.31 (s, 1H, N–H).
$\text{RuH}_2(\text{CN-}p\text{-tolyl})(\text{PPh}_3)_3$ 10a	–8.69 (ddt, 1H, Ru–H, $J(\text{HH}) = 6.1$, $J(\text{HP}_{\text{trans}}) = 73.0$, $J(\text{HP}_{\text{cis}}) = 28.4$); –7.77 (ddt, 1H, Ru–H, $J(\text{HH}) = 6.1$, $J(\text{HP}_{\text{trans}}) = 15.8$, $J(\text{HP}_{\text{cis}}) = 30.0$); 6.47 (d, 2H, $\text{CNC}_6\text{H}_4\text{CH}_3$, $J(\text{HH}) = 8.3$); 6.83–7.36 (m, 47H, PPh_3 , $\text{CNC}_6\text{H}_4\text{CH}_3$).
$\text{OsH}_2(\text{CN-}p\text{-tolyl})(\text{PPh}_3)_3$ 10b	–9.54 (oddt, 1H, Os–H, $J(\text{HH}) = 4.6$, $J(\text{HP}_{\text{trans}}) = 58.9$, $J(\text{HP}_{\text{cis}}) = 29.5$); –8.48 (ddt, 1H, Os–H, $J(\text{HH}) = 4.4$, $J(\text{HP}_{\text{trans}}) = 28.2$); 6.36 (d, 2H, $\text{CNC}_6\text{H}_4\text{CH}_3$, $J(\text{HH}) = 8.2$); 6.82–7.36 (m, 47H, PPh_3 , $\text{CNC}_6\text{H}_4\text{CH}_3$).
$\text{OsH}_2(\text{CN-}p\text{-chlorophenyl})(\text{PPh}_3)_3$ 10c	–9.43 (oddt, 1H, Os–H, $J(\text{HH}) = 4.5$, $J(\text{HP}_{\text{trans}}) = 26.2$, $J(\text{HP}_{\text{cis}}) = 17.5$); –8.83 (oddt, 1H, Os–H, $J(\text{HH}) = 4.5$, $J(\text{HP}_{\text{trans}}) = 59.0$, $J(\text{HP}_{\text{cis}}) = 28.6$); 6.24 (d, 2H, $\text{CNC}_6\text{H}_4\text{Cl}$); 6.83–7.33 (m, 47H, PPh_3 , $\text{CNC}_6\text{H}_4\text{Cl}$).

^a Spectra recorded in CDCl_3 at 25°C . Chemical shifts (δ) are given in ppm and are referenced to $(\text{CH}_3)_4\text{Si}$ ($\delta = 0.00$). Coupling constants J are in Hz. Splitting patterns are indicated thus: s, singlet; d, doublet; triplet; m, multiplet; ddt, doubled doublet of triplets; oddt, overlapping doubled doublet of triplets.

^b Methyl signals of either $\text{CPhNH-}p\text{-tolyl}$ or $\text{CN-}p\text{-tolyl}$.

^c Aromatic protons of either $\text{CPhNH-}p\text{-tolyl}$ or $\text{CN-}p\text{-tolyl}$.



Scheme 1.

region which is the position expected for $\nu(\text{O}-\text{O})$ [1]. Complete spectral data for all the new compounds are presented in Tables 1, 2 and 3. Confirmation of the

presence of both the dioxygen ligand and the iminoacyl ligand in compound **3c** was provided by a single crystal X-ray structure determination (see Section 2.4).

2.3. Reaction of **3c** with sulphur dioxide

Only one reaction of the dioxygen complexes described here has been investigated in detail. $\text{Os}(\eta^2\text{-O}_2)(\eta^2\text{-CPh}=\text{N}p\text{-chlorophenyl})\text{Cl}(\text{PPh}_3)_2$ (**3c**) reacts with SO_2 to give the *dihapto*-sulphato derivative $\text{Os}(\eta^2\text{-SO}_4)(\eta^2\text{-CPh}=\text{N}p\text{-chlorophenyl})\text{Cl}(\text{PPh}_3)_2$ (**4c**) (Scheme 1). This is not a new type of reaction, other transition metal dioxygen complexes have been reported to react with SO_2 to give *dihapto*-sulphate complexes [1]. In the IR spectrum of **4c**, bands due to the *dihapto*-sulphato group appear at 1298, 1175 and 665 cm^{-1} . The *dihapto*-sulphato formulation has been confirmed by crystal structure determination (see Section 2.4).

2.4. Crystal structures of **3c** and **4c**

The molecular geometries of **3c** and **4c** are depicted in Figs. 1 and 2 respectively. Bond length and bond

Table 3
 ^{13}C -NMR data ^a for selected new complexes

Compound	Chemical shift (ppm)
$\text{Os}(\eta^2\text{-O}_2)(\eta^2\text{-CPh}=\text{N}p\text{-chlorophenyl})\text{Cl}(\text{PPh}_3)_2$ 3c	165.61 (t, CPhNR, $J(\text{CP}) = 5.6$); 134.20 (t, $\text{PPh}_3\text{-}o$, $J(\text{CP}) = 5.7$); 133.52 (s ^b); 131.87 (s ^b); 130.88 (t, $\text{PPh}_3\text{-}i$, $J(\text{CP}) = 23.6$); 130.08 (s ^b); 129.91 (s ^b); 129.50 (s, $\text{PPh}_3\text{-}p$); 128.64 (s ^b); 128.49 (s ^b); 127.50 (t, $\text{PPh}_3\text{-}m$, $J(\text{CP}) = 4.7$).
$\text{Os}(\eta^2\text{-SO}_4)(\eta^2\text{-CPh}=\text{N}p\text{-chlorophenyl})\text{Cl}(\text{PPh}_3)_2$ 4c	154.14 (t, CPhNR, $J(\text{CP}) = 5.5$); 134.81 (t, $\text{PPh}_3\text{-}o$, $J(\text{CP}) = 5.2$); 134.27 (s ^b); 133.49 (s ^b); 130.10 (s, $\text{PPh}_3\text{-}p$); 130.07 (t, $\text{PPh}_3\text{-}i$, $J(\text{CP}) = 26.7$); 129.55 (s ^b); 129.01 (s ^b); 128.72 (s ^b); 127.70 (t, $\text{PPh}_3\text{-}m$, $J(\text{CP}) = 4.5$).
$\text{RuPh}(\eta^2\text{-O}_2\text{CCH})(\text{CN}p\text{-tolyl})(\text{PPh}_3)_2$ 5a	182.89 (t, CNR, $J(\text{CP}) = 17.1$); 181.59 (s, O_2CCH_3); 160.33 (t, $\text{C}_6\text{H}_5\text{-}i$, $J(\text{CP}) = 10.1$); 134.45 (t, $\text{PPh}_3\text{-}o$, $J(\text{CP}) = 5.5$); 132.49 (t, $\text{PPh}_3\text{-}i$, $J(\text{CP}) = 20.1$); 130.44 (s ^b); 129.15 (s, $\text{PPh}_3\text{-}p$); 127.65 (t, $\text{PPh}_3\text{-}m$, $J(\text{CP}) = 4.4$); 124.63 (s ^b); 124.06 (s ^b); 118.71 (s ^b); 22.43 (s, O_2CCH_3); 20.89 (s, $\text{CNC}_6\text{H}_4\text{CH}_3$).
$\text{OsPh}(\eta^2\text{-O}_2\text{CCH})(\text{CN}p\text{-tolyl})(\text{PPh}_3)_2$ 5b	183.36 (s, O_2CCH_3); 173.46 (t, CNR, $J(\text{CP}) = 11.6$); 138.52 (t, $\text{C}_6\text{H}_5\text{-}i$, $J(\text{CP}) = 6.5$); 134.51 (t, $\text{PPh}_3\text{-}o$, $J(\text{CP}) = 5.6$); 132.68 (s ^b); 132.52 (s ^b); 131.86 (t, $\text{PPh}_3\text{-}i$, $J(\text{CP}) = 23.6$); 129.32 (s, $\text{PPh}_3\text{-}p$); 128.92 (s ^b); 127.66 (t, $\text{PPh}_3\text{-}m$, $J(\text{CP}) = 4.8$); 124.70 (s ^b); 123.82 (s ^b); 118.40 (s ^b); 23.52 (s, O_2CCH_3); 20.89 (s, $\text{CNC}_6\text{H}_4\text{CH}_3$).
$\text{OsPhCl}(\text{CO})(\text{CN}p\text{-tolyl})(\text{PPh}_3)_2$ 6b	184.11 (t, CO, $J(\text{CP}) = 7.2$); 149.31 (t, CNR, $J(\text{CP}) = 11.2$); 145.32 (t, $\text{C}_6\text{H}_5\text{-}i$, $J(\text{CP}) = 8.8$); 142.37 (s ^b); 136.85 (s ^b); 134.62 (t, $\text{PPh}_3\text{-}o$, $J(\text{CP}) = 4.9$); 132.18 (t, $\text{PPh}_3\text{-}i$, $J(\text{CP}) = 25.1$); 129.50 (s, $\text{PPh}_3\text{-}p$); 129.13 (s ^b); 129.13 (s ^b); 127.41 (t, $\text{PPh}_3\text{-}m$, $J(\text{CP}) = 4.9$); 126.61 (s ^b); 125.17 (s ^b); 122.16 (s ^b); 21.13 (s, $\text{CNC}_6\text{H}_4\text{CH}_3$).
$\text{OsPhCl}(\text{CN}p\text{-tolyl})_2(\text{PPh}_3)_2$ 7b	151.76 (t, CNR, $J(\text{CP}) = 9.9$); 150.33 (t, CNR, $J(\text{CP}) = 10.8$); 143.04 (s, $\text{C}_6\text{H}_5\text{-}i$); 137.08 (s ^b); 135.26 (s ^b); 134.82 (t, $\text{PPh}_3\text{-}o$, $J(\text{CP}) = 4.9$); 133.25 (t, $\text{PPh}_3\text{-}i$, $J(\text{CP}) = 24.0$); 128.98 (s, $\text{PPh}_3\text{-}p$); 128.92 (s ^b); 127.27 (t, $\text{PPh}_3\text{-}m$, $J(\text{CP}) = 4.6$); 126.34 (s ^b); 125.77 (s ^b); 125.06 (s ^b); 121.14 (s ^b); 21.15 (s, $\text{CNC}_6\text{H}_4\text{CH}_3$); 21.03 (s, $\text{CNC}_6\text{H}_4\text{CH}_3$).
$\text{RuCl}_2(\text{CPhNH}p\text{-tolyl})(\text{CN}p\text{-tolyl})(\text{PPh}_3)_2$ 9a	252.94 (t, =C, $J(\text{CP}) = 9.6$); 171.82 (t, $\text{PPh}_3\text{-}o$, $J(\text{CP}) = 13.9$); 148.45 (s ^b); 136.99 (s ^b); 135.93 (s ^b); 134.76 (t, $\text{PPh}_3\text{-}o$, $J(\text{CP}) = 5.1$); 133.51 (t, $\text{PPh}_3\text{-}i$, $J(\text{CP}) = 20.6$); 128.82 (s, $\text{PPh}_3\text{-}p$); 128.41 (s ^b); 128.41 (s ^b); 128.19 (s ^b); 127.45 (t, $\text{PPh}_3\text{-}m$, $J(\text{CP}) = 4.5$); 127.16 (s ^b); 125.59 (s ^b); 124.36 (s ^b); 21.16 ^c (s), 20.84 ^c (s).

^a Spectra recorded in CDCl_3 at 25°C . Chemical shifts (δ) are given in ppm and are referenced to CDCl_3 ($\delta = 77.00$). Coupling constants J are in Hz. Splitting patterns are indicated thus: s, singlet; t, triplet. Positions on the phenyl rings of the triphenylphosphine ligands are denoted: *o*, ortho; *m*, meta; *p*, para; *i*, ipso.

^b Signals are due to aromatic carbons of either the phenyl group or the isocyanide.

^c Methyl signals of either $\text{CPhNH}p\text{-tolyl}$ or $\text{CN}p\text{-tolyl}$.

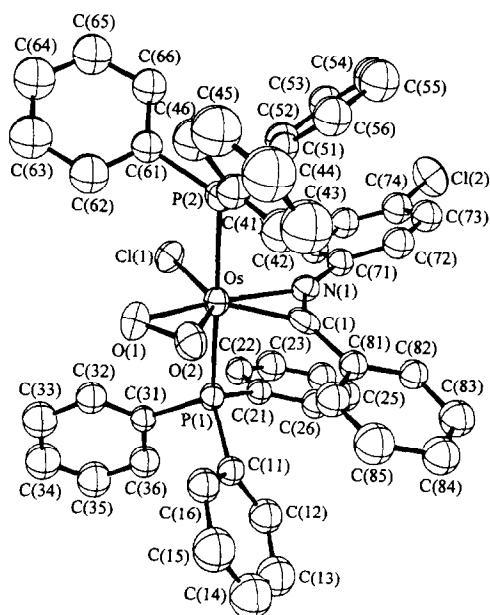


Fig. 1. The molecular structure of $\text{Os}(\eta^2\text{-O}_2)(\eta^2\text{-CPh=N-}p\text{-chlorophenyl})\text{Cl}(\text{PPh}_3)_2$ (**3c**).

angle data for **3c** are given in Tables 4 and 5 and for **4c** in Tables 6 and 7. In both complexes the geometry at osmium can be considered as pentagonal bipyramidal with the triphenylphosphine ligands in mutually *trans* sites. The chloride, iminoacyl, and dioxygen or sulphato ligands are in the equatorial plane. In **3c**, the O(1)–O(2) bond length of 1.451(11) Å is in the middle of the range observed for η^2 -dioxygen ligands (1.40–1.49 Å [1]). It is very similar to that observed (1.45(1) Å) in the first structurally characterised osmium dioxygen complex $[\text{OsH}(\eta^2\text{-O}_2)(\text{dcpe})_2]\text{BPh}_4$ (dcpe = 1,2-bis(di*cyclo*-

Table 4
Selected bond lengths (Å) for $\text{Os}(\eta^2\text{-O}_2)(\eta^2\text{-CPh=N-}p\text{-chlorophenyl})\text{Cl}(\text{PPh}_3)_2$ (**3c**)

Os–C(1)	1.978(10)
Os–O(2)	2.003(7)
Os–O(1)	2.029(7)
Os–N(1)	2.151(8)
Os–Cl(1)	2.385(3)
Os–P(2)	2.399(2)
Os–P(1)	2.414(2)
P(1)–C(11)	1.818(11)
P(1)–C(31)	1.825(9)
P(1)–C(21)	1.822(9)
P(2)–C(51)	1.823(9)
P(2)–C(61)	1.836(11)
P(2)–C(41)	1.843(11)
O(1)–O(2)	1.452(10)
N(1)–C(1)	1.250(14)
N(1)–C(71)	1.409(13)
C(1)–C(81)	1.51(2)

hexylphosphino)ethane), which was reported recently [10]. The C(1)–N bond lengths of 1.25(2) Å in **3c** and 1.258(12) Å in **4c** are in the range observed for other iminoacyl complexes (1.24–1.29 Å [12]). Formation of the sulphate ligand causes the angle O(1)–Os–O(2) to increase from 42.2(3)° in **3c** to 66.6(3)° in **4c** and the Os–O bond lengths in **4c** of 2.090(6) and 2.114(6) Å

Table 5
Selected bond angles (°) for $\text{Os}(\eta^2\text{-O}_2)(\eta^2\text{-CPh=N-}p\text{-chlorophenyl})\text{Cl}(\text{PPh}_3)_2$ (**3c**)

C(1)–Os–O(2)	92.5(4)
C(1)–Os–O(1)	134.4(4)
O(2)–Os–O(1)	42.2(3)
C(1)–Os–N(1)	34.9(4)
O(2)–Os–N(1)	127.1(3)
O(1)–Os–N(1)	169.3(3)
C(1)–Os–Cl(1)	130.3(3)
O(2)–Os–Cl(1)	137.1(2)
O(1)–Os–Cl(1)	95.0(2)
N(1)–Os–Cl(1)	95.7(2)
C(1)–Os–P(2)	95.1(3)
O(2)–Os–P(2)	87.3(2)
O(1)–Os–P(2)	88.5(2)
N(1)–Os–P(2)	91.4(2)
Cl(1)–Os–P(2)	89.89(10)
C(1)–Os–P(1)	86.1(3)
O(2)–Os–P(1)	94.5(2)
O(1)–Os–P(1)	92.0(2)
N(1)–Os–P(1)	88.5(2)
Cl(1)–Os–P(1)	87.94(9)
P(2)–Os–P(1)	177.81(9)
O(2)–O(1)–Os	67.9(4)
O(1)–O(2)–Os	69.9(4)
C(1)–N(1)–C(71)	144.6(9)
C(1)–N(1)–Os	64.9(6)
C(71)–N(1)–Os	149.6(6)
N(1)–C(1)–C(81)	137.1(9)
N(1)–C(1)–Os	80.1(7)
C(81)–C(1)–Os	142.1(8)

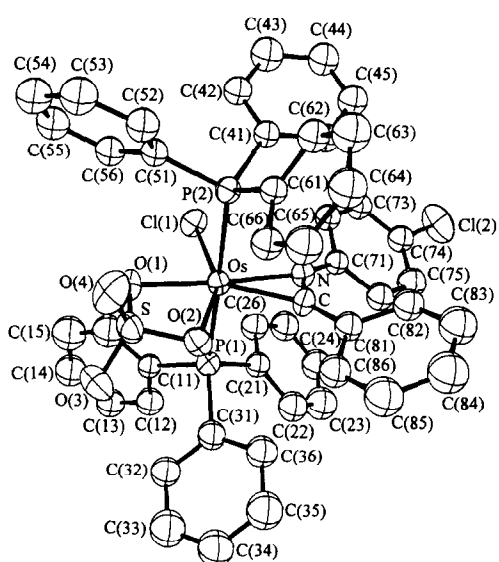


Fig. 2. The molecular structure of $\text{Os}(\eta^2\text{-SO}_4)(\eta^2\text{-CPh=N-}p\text{-chlorophenyl})\text{Cl}(\text{PPh}_3)_2$ (**4c**).

Table 6

Selected bond lengths (Å) for Os(η^2 -SO₄)(η^2 -CPh=N-*p*-chlorophenyl)Cl(PPh₃)₂ (**4c**)

Os–C	2.049(9)
Os–O(1)	2.090(6)
Os–O(2)	2.114(6)
Os–N	2.127(8)
Os–Cl(1)	2.359(2)
Os–P(1)	2.426(3)
Os–P(2)	2.445(2)
Os–S	2.751(3)
P(1)–C(11)	1.839(9)
P(1)–C(31)	1.832(10)
P(1)–C(21)	1.851(10)
P(2)–C(41)	1.829(9)
P(2)–C(61)	1.829(9)
P(2)–C(51)	1.840(10)
Cl(2)–C(74)	1.731(10)
S–O(3)	1.420(8)
S–O(4)	1.441(8)
S–O(2)	1.523(7)
S–O(1)	1.526(7)
C–N	1.258(12)
C–C(81)	1.449(13)
N–C(71)	1.395(12)

are significantly longer than those observed in **3c** (2.030(7) and 2.003(8) Å), but otherwise there is very little difference in the overall coordination geometry between **3c** and **4c**.

2.5. Synthesis of the precursor complexes MHCl(CNR)(PPh₃)₃ and MH₂(CNR)(PPh₃)₃

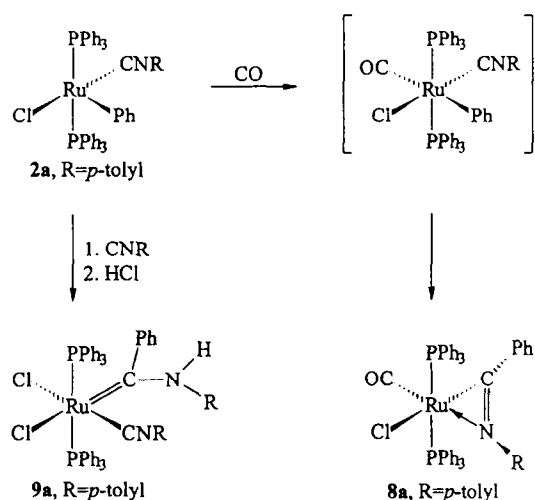
The carbonyl-containing complexes MHCl(CO)(PPh₃)₃ (M = Ru, Os) have proved to be useful starting materials for the syntheses of many other derivatives because they contain both labile phosphine and chloride ligands as well as a potentially acidic M–H bond. These complexes have been known for some time and are available in high-yield, one-pot syntheses, from RuCl₃ or (NH₄)₂OsCl₆. A route to the isocyanide analogue OsHCl(CNPh)(PMe₂Ph)₃, from reaction of OsCl₂(CNPh)(PMe₂Ph)₃ and NaBH₄, was reported some time ago [13]. This has not, however, been used generally as a route to ruthenium and osmium complexes of formula MHCl(CNR)L₃ (L = tertiaryphosphine). The dihydride complexes MH₂(CN*p*-tolyl)(PPh₃)₃ (**10a**, M = Ru; **10b**, M = Os) have been synthesized previously in this laboratory by treatment of OsH₄(PPh₃)₃ or RuH₂(PPh₃)₄ with excess *p*-tolyl isocyanide, heated in benzene or ethanol under reflux respectively. OsH₂(CN*p*-chlorophenyl)(PPh₃)₃ (**10c**) was generated in a similar reaction from OsH₄(PPh₃)₃ and *p*-chlorophenyl isocyanide. It should be noted that in all these reactions with isocyanide, substitution of one phosphine only occurs and no bis-isocyanide complexes were ob-

served. These resulting dihydride complexes, **10a–10c**, proved to be ideal precursors to the complexes MHCl(CNR)(PPh₃)₃, requiring substitution of one hydride for chloride. This was achieved by reaction with 1.1 mol equiv. HCl (conveniently provided by the hydrolysis of 1.1 mol equiv. trimethylsilyl chloride) carried out in an ethanolic suspension to give **1a–1c** (Scheme 2). In the ¹H-NMR spectra of **1a–1c** the resonance for the hydride ligand appears at high-field as a doublet of triplets through coupling to two equivalent and one inequivalent phosphine ligand. The size of these coupling constants indicates that the geometry of

Table 7

Selected bond angles (°) for Os(η^2 -SO₄)(η^2 -CPh=N-*p*-chlorophenyl)Cl(PPh₃)₂ (**4c**)

C–Os–O(1)	150.7(3)
C–Os–O(2)	84.6(3)
O(1)–Os–O(2)	66.6(3)
C–Os–N	35.0(3)
O(1)–Os–N	174.1(3)
O(2)–Os–N	119.3(3)
C–Os–Cl(1)	122.8(3)
O(1)–Os–Cl(1)	86.0(2)
O(2)–Os–Cl(1)	152.5(2)
N–Os–Cl(1)	88.2(2)
C–Os–P(1)	94.1(3)
O(1)–Os–P(1)	90.8(2)
O(2)–Os–P(1)	88.4(2)
N–Os–P(1)	90.1(2)
Cl(1)–Os–P(1)	90.68(9)
C–Os–P(2)	87.5(3)
O(1)–Os–P(2)	88.4(2)
O(2)–Os–P(2)	93.0(2)
N–Os–P(2)	90.5(2)
Cl(1)–Os–P(2)	87.36(9)
P(1)–Os–P(2)	177.92(10)
C–Os–S	117.5(3)
O(1)–Os–S	33.3(2)
O(2)–Os–S	33.3(2)
N–Os–S	152.5(2)
Cl(1)–Os–S	119.29(9)
P(1)–Os–S	91.34(8)
P(2)–Os–S	89.00(8)
O(3)–S–O(4)	116.1(6)
O(3)–S–O(2)	109.7(5)
O(4)–S–O(2)	109.5(5)
O(3)–S–O(1)	110.8(5)
O(4)–S–O(1)	110.9(4)
O(2)–S–O(1)	98.4(4)
O(3)–S–Os	125.2(5)
O(4)–S–Os	118.6(4)
O(2)–S–Os	49.7(2)
O(1)–S–Os	48.8(2)
S–O(1)–Os	97.9(3)
S–O(2)–Os	96.9(3)
N–C–C(81)	138.0(9)
N–C–Os	75.9(6)
C(81)–C–Os	145.5(7)
C–N–C(71)	140.4(9)
C–N–Os	69.1(5)
C(71)–N–Os	148.8(7)



Scheme 5.

($R = p\text{-tolyl}$) [14], i.e. the iminoacyl carbon is adjacent to the carbonyl group.

Treatment of a solution of $\text{RuPhCl}(\text{CN}p\text{-tolyl})(\text{PPh}_3)_2$ (**2a**) with $\text{CN}p\text{-tolyl}$ results in a lightening of the colour of the solution but no tractable compound could be isolated. However if, after adding $\text{CN}p\text{-tolyl}$ to the solution of **2a**, 1.1 mol equiv. HCl are added, the carbene complex $\text{RuCl}_2(\text{CPhNH}p\text{-tolyl})(\text{CN}p\text{-tolyl})(\text{PPh}_3)_2$ (**9a**) can be isolated (Scheme 5). In the IR spectrum the band at 1510 cm^{-1} can be assigned to $\nu(\text{CN})$. No band appeared which could be assigned to $\nu(\text{N-H})$. The N-H proton is observed in the $^1\text{H-NMR}$ spectrum as a singlet at 12.31 ppm. The carbene ligand is formed by protonation of the iminoacyl compound $\text{Ru}(\eta^2\text{-CPh}=\text{N}p\text{-tolyl})\text{Cl}(\text{CN}p\text{-tolyl})(\text{PPh}_3)_2$. Presumably migratory insertion of the mutually *cis* Ph and $\text{CN}p\text{-tolyl}$ ligands occurred rapidly after addition of $\text{CN}p\text{-tolyl}$ to **2a**. Protonation of the N atom of the resulting η^2 -iminoacyl-containing complex $\text{Ru}(\eta^2\text{-CPh}=\text{N}p\text{-tolyl})\text{Cl}(\text{CN}p\text{-tolyl})(\text{PPh}_3)_2$ then occurred on addition of HCl . Similar reactions of η^2 -iminoacyl ligands with HCl have been observed previously [14].

2.9. Conclusion

Replacement of the CO ligand in $\text{MArCl}(\text{CO})(\text{PPh}_3)_2$ ($M = \text{Ru}, \text{Os}$) by an isocyanide ligand specifically activates these complexes towards the coordination of dioxygen. This dioxygen coordination induces a very rapid migration of the aryl group onto the isocyanide ligand, so forming a *dihapto*-iminoacyl ligand. The five-coordinate complexes $\text{MArCl}(\text{CNR})(\text{PPh}_3)_2$ also add CO or CNR to become six-coordinate. This does not promote aryl migration to isocyanide in the osmium derivatives, although such a reaction is observed for the ruthenium derivatives.

3. Experimental details

Reactions were carried out in round-bottomed flasks under oxygen-free nitrogen using solvents which had been deoxygenated by bubbling a stream of nitrogen through the refluxing solvent. Reactions which were carried out in a Schlenk tube were deoxygenated by several cycles of freeze–evacuate–thaw. The compounds $\text{RuH}_2(\text{PPh}_3)_4$ [15] and $\text{OsH}_4(\text{PPh}_3)_3$ [16] and the ligands *p*-tolyl isocyanide and *p*-chlorophenyl isocyanide [17] were prepared by standard literature procedures.

Analytical data were obtained from the Microanalytical Laboratory, University of Otago. IR spectra ($4000\text{--}400\text{ cm}^{-1}$) were recorded on a Digilab FTS-7 spectrophotometer as Nujol mulls between KBr plates. ^1H - and ^{13}C -NMR spectra were recorded on a Bruker AC 200 in CDCl_3 and were referenced to either tetramethylsilane (0.00 ppm) or residual CHCl_3 (7.25 ppm). Melting points (uncorrected) were recorded on a Reichert hot-stage microscope.

3.1. $\text{RuHCl}(\text{CN}p\text{-tolyl})(\text{PPh}_3)_3$ (**1a**)

To a suspension of $\text{RuH}_2(\text{CN}p\text{-tolyl})(\text{PPh}_3)_3$ (1.00 g, 0.993 mmol) in ethanol (50 ml) containing dissolved triphenylphosphine (1.302 g, 4.964 mmol) was added, dropwise with stirring, trimethylsilyl chloride (0.118 g, 1.09 mmol). The suspension was stirred for 1 h and then the product was removed by filtration and washed well with ethanol and hexane to give crude **1a** (1.00 g, 97%). A sample of analytical quality was obtained by recrystallization from benzene/ethanol to which a small quantity of triphenylphosphine had been added, m.p. $131.5\text{--}133^\circ\text{C}$. Anal. Found: C, 71.69; H, 5.11; N, 1.33. $\text{C}_{62}\text{H}_{53}\text{ClNP}_3\text{Ru}$. Calc.: C, 71.50; H, 5.13; N, 1.34%.

3.2. $\text{OsHCl}(\text{CN}p\text{-tolyl})(\text{PPh}_3)_3$ (**1b**)

To a suspension of $\text{OsH}_2(\text{CN}p\text{-tolyl})(\text{PPh}_3)_3$ (1.00 g, 0.912 mmol) in ethanol (25 ml) was added, dropwise with stirring, trimethylsilyl chloride (0.109 g, 1.00 mmol). The suspension was stirred for 1 h. The product was removed by filtration and washed with ethanol, then recrystallized from benzene/ethanol containing a small quantity of triphenylphosphine to give pure **1b** (0.901 g, 87%), m.p. $158\text{--}160^\circ\text{C}$. Anal. Found: C, 65.99; H, 4.69; N, 1.19. $\text{C}_{62}\text{H}_{53}\text{ClNP}_3\text{Os}$. Calc.: C, 65.86; H, 4.72; N, 1.24%.

3.3. $\text{OsHCl}(\text{CN}p\text{-chlorophenyl})(\text{PPh}_3)_3$ (**1c**)

$\text{OsH}_2(\text{CN}p\text{-chlorophenyl})(\text{PPh}_3)_3$ (1.00 g, 0.870 mmol) was treated as in Section 3.2. The product was

recrystallized from benzene/ethanol/triphenylphosphine to give pure **1c** (0.922 g, 89%), m.p. 149–151.5°C. Anal. Found; C, 63.68; H, 4.28; N, 1.16. $C_{61}H_{50}Cl_2NP_3Os$. Calc.: C, 63.65; H, 4.38; N, 1.22%.

3.4. $RuPhCl(CNp\text{-tolyl})(PPh_3)_2$ (**2a**)

$RuHCl(CNp\text{-tolyl})(PPh_3)_3$ (0.150 g, 0.144 mmol) and $HgPh_2$ (0.061 g, 0.17 mmol) were added to rigorously deoxygenated benzene (10 ml) in a Schlenk tube. The solution was heated at 80°C for 1 h, during which time it turned red and elemental mercury was deposited. The solution was cooled to room temperature and then filtered by canula to another Schlenk tube to remove mercury. The volume was reduced to approximately 2 ml in vacuo and deoxygenated ethanol was gradually added to effect crystallization. The product was left to stir for 30 min to maximise precipitation. Crude **2a** was obtained as an orange product after filtration (0.075 g, 61%). A sample of analytical quality was obtained by recrystallization under nitrogen from benzene/ethanol after filtration through Celite, m.p. 126–129°C. Anal. Found: C, 69.73; H, 4.74; N, 1.62. $C_{50}H_{42}ClNP_2Ru$. Calc.: C, 70.21; H, 4.95; N, 1.64%.

3.5. $Ru(\eta^2\text{-}O_2)(\eta^2\text{-}CPhNp\text{-tolyl})Cl(PPh_3)_2$ (**3a**)

$RuHCl(CNp\text{-tolyl})(PPh_3)_3$ (0.200 g, 0.192 mmol) and $HgPh_2$ (0.075 g, 0.21 mmol) were heated in rigorously deoxygenated benzene (10 ml) in a Schlenk tube at 78°C for 1 h. The solution turned red and elemental mercury was deposited. The solution was cooled to room temperature and oxygen was bubbled through it for 20 s. The solution turned a deeper red. It was then filtered through Celite to remove mercury and the volume decreased under reduced pressure to approximately 3 ml. Ethanol was added to precipitate the red product. Recrystallization from dichloromethane/ethanol gave pure **3a** (0.060 g, 35%), m.p. 125–126°C. Anal. Found: C, 67.50; H, 4.64; N, 1.60. $C_{50}H_{42}ClNO_2P_2Ru$. Calc.: C, 67.68; H, 4.77; N, 1.58%.

3.6. $Os(\eta^2\text{-}O_2)(\eta^2\text{-}CPh=Np\text{-tolyl})Cl(PPh_3)_2$ (**3b**)

$OsHCl(CNp\text{-tolyl})(PPh_3)_3$ (0.150 g, 0.133 mmol) and $HgPh_2$ (0.070 g, 0.20 mmol) were heated in rigorously deoxygenated benzene (10 ml) in a Schlenk tube at 80°C for 3 h. The solution turned deep red and elemental mercury was deposited. The solution was cooled to room temperature and filtered through Celite in air. During filtration the solution turned purple as it reacted with atmospheric oxygen. The solvent volume was reduced to approximately 3 ml and ethanol was added to precipitate the purple/black product. Recrystallization from dichloromethane/ethanol gave pure **3b** (0.090 g, 60%), m.p. 105–106°C. Anal. Found: C, 60.27; H, 4.34;

N, 1.38. $C_{50}H_{42}ClNO_2P_2Os \cdot 0.33(CH_2Cl_2)$. Calc.: C, 60.16; H, 4.28; N, 1.39%.

3.7. $Os(\eta^2\text{-}O_2)(\eta^2\text{-}CPh=Np\text{-chlorophenyl})Cl(PPh_3)_2$ (**3c**)

$OsHCl(CNp\text{-chlorophenyl})(PPh_3)_3$ (0.200 g, 0.174 mmol) and $HgPh_2$ (0.080 g, 0.23 mmol) were heated in rigorously deoxygenated benzene (12 ml) at 80°C in a Schlenk tube for 3 h. The solution was then treated as in Section 3.6. Recrystallization from dichloromethane/ethanol afforded purple/black crystals of pure **3c** (0.126 g, 73%), m.p. 111–113°C. Anal. Found: C, 58.97, H, 3.89, N, 1.52. $C_{49}H_{39}Cl_2NO_2P_2Os$. Calc.: C, 59.04, H, 3.94; N, 1.40%.

3.8. $Os(\eta^2\text{-}SO_4)(\eta^2\text{-}CPh=Np\text{-chlorophenyl})Cl(PPh_3)_2$ (**4c**)

$Os(\eta^2\text{-}O_2)(\eta^2\text{-}CPh=Np\text{-chlorophenyl})Cl(PPh_3)_2$ (0.100 g, 0.105 mmol) was dissolved in dichloromethane (6 ml) which had been stood over and then distilled from CaH_2 . SO_2 was bubbled through the solution for 1 min. The reaction vessel was sealed and the solution left to stir for 2 h. The purple solution gradually turned brown. Reduction of the solvent volume in vacuo followed by the addition of ethanol gave brown microcrystals. Recrystallization from dichloromethane/ethanol gave pure **4c** (0.066 g, 55%), m.p. 199–200.5°C. Anal. Found: C, 55.81, H, 4.04, N, 1.02. $C_{49}H_{39}Cl_2NO_4Os$. Calc.: C, 55.47, H, 3.71; N, 1.32%.

3.9. $Ru(Ph)(\eta^2\text{-}O_2CCH_3)(CNp\text{-tolyl})(PPh_3)_2$ (**5a**)

$RuHCl(CNp\text{-tolyl})(PPh_3)_3$ (0.090 g, 0.086 mmol) and $HgPh_2$ (0.036 g, 0.10 mmol) were added to deoxygenated benzene (8 ml). The solution was heated at 80°C for 1 h. After cooling to room temperature a deoxygenated solution of CH_3COONa (0.040 g, 0.49 mmol) in water (0.5 ml) and ethanol (10 ml) was added. The colour of the solution turned to pale yellow, and after filtration through Celite the volume was reduced in vacuo. On addition of further ethanol a pale yellow crystalline precipitate formed. This was collected and upon recrystallization from dichloromethane/ethanol gave pure **5a** (0.054 g, 71%), m.p. 210–213°C. Anal. Found: C, 70.83, H, 5.10; N, 1.45. $C_{52}H_{45}NO_2P_2Ru$. Calc.: C, 71.01; H, 5.16; N, 1.59%.

3.10. $Os(Ph)(\eta^2\text{-}O_2CCH_3)(CNp\text{-tolyl})(PPh_3)_2$ (**5b**)

$OsHCl(CNp\text{-tolyl})(PPh_3)_3$ (0.090 g, 0.080 mmol) and $HgPh_2$ (0.037 g, 0.11 mmol) were heated in deoxygenated benzene at 80°C for 2 h in a Schlenk tube. The solution was cooled to room temperature and a solution of CH_3COONa (0.016 g, 0.20 mmol) in deoxygenated

water (0.5 ml) and ethanol (10 ml) was added. The solution changed colour to very pale yellow/brown. The benzene was removed in vacuo, and the residue was extracted into dichloromethane and filtered through Celite. On reduction of the solvent volume and then addition of ethanol, a pale yellow precipitate formed. This was collected and upon recrystallization from dichloromethane/ethanol gave pure **5b** (0.061 g, 78%), m.p. 229–232°C. Anal. Found: C, 64.32; H, 4.90; N, 1.09. $C_{52}H_{45}NO_2P_2Os$. Calc.: C, 64.51; H, 4.68; N, 1.45%.

3.11. $OsPhCl(CO)(CNp\text{-tolyl})(PPh_3)_2$ (**6b**)

$OsHCl(CNp\text{-tolyl})(PPh_3)_3$ (0.080 g, 0.071 mmol) and $HgPh_2$ (0.038 g, 0.11 mmol) were added to rigorously deoxygenated benzene (6 ml) in a Schlenk tube. The solution was heated at 80°C for 90 min and during this time it turned red and mercury was deposited. CO was bubbled slowly through the solution, causing the colour to change to pink/brown. The solution was filtered through Celite and the benzene was removed in vacuo.

The residue was dissolved in dichloromethane and chromatographed on a silica gel column ($1 \times 7 \text{ cm}^2$) using dichloromethane as eluent. The colourless fraction which eluted immediately after the solvent front was collected. The volume was reduced and ethanol was added to effect crystallization of the colourless product. Recrystallization from dichloromethane/ethanol gave pure **6b** (0.040 g, 58%), m.p. 174–175°C. Anal. Found: C, 62.99; H, 4.36; N, 1.49. $C_{51}H_{42}ClNO_2Os$. Calc.: C, 62.99; N, 4.35; H, 1.44%.

3.12. $OsPhCl(CNp\text{-tolyl})_2(PPh_3)_2$ (**7b**)

$OsHCl(CNp\text{-tolyl})(PPh_3)_3$ (0.200 g, 0.177 mmol) and $HgPh_2$ (0.096 g, 0.27 mmol) were added to rigorously deoxygenated benzene (8 ml) in a Schlenk tube. As the solution was heated at 80°C for 1 h 30 min it turned red and elemental mercury was deposited. The solution was cooled to room temperature and to it was added a solution of *p*-tolyl isocyanide (0.017 g, 0.145 mmol) in deoxygenated dichloromethane (10 ml). The deep red solution turned a very pale purple/brown. This was

Table 8

Crystal data for $Os(\eta^2\text{-O}_2)(\eta^2\text{-CPh=N-}p\text{-chlorophenyl)Cl(PPh}_3)_2$ (**3c**) and $Os(\eta^2\text{-SO}_4)(\eta^2\text{-CPh=N-}p\text{-chlorophenyl)Cl(PPh}_3)_2$ (**4c**)

	3c	4c
Formula	$C_{49}H_{39}Cl_2NO_2OsP_2$	$C_{49}H_{39}Cl_2NO_4OsP_2S$
Molecular weight	996.85	1060.91
Crystal system	Orthorhombic	Triclinic
Space group	<i>Pbca</i>	$P\bar{1}$
<i>a</i> (Å)	17.329(5)	10.619(5)
<i>b</i> (Å)	23.824(3)	11.886(3)
<i>c</i> (Å)	20.355(6)	18.818(3)
α (°)	90.0	83.95(10)
β (°)	90.0	79.88(2)
γ (°)	90.0	83.31(3)
<i>V</i> (Å ³)	8404(8)	2313.5(13)
<i>Z</i>	8	2
<i>d</i> (calc) (g cm ⁻³)	1.576	1.523
<i>F</i> (000)	3968	1056
μ (mm ⁻¹)	3.28	3.03
Radiation Mo <i>K</i> α (monochromatic) λ (Å)	0.71069	0.71069
Temperature (K)	293	294
Diffractometer	Nonius CAD-4	Nonius CAD-4
Scan technique	$\omega/2\theta$	$\omega/2\theta$
2θ (min–max) (°)	2–50	2–50
No. of reflections	4994	8136
No. of observed reflections $I > 2\sigma(I)$	3383	5742
Crystal size (mm ³)	0.18 × 0.12 × 0.10	0.28 × 0.18 × 0.15
Λ (min–max)	0.89–1.00	0.75–0.99
Least squares weights <i>a</i> , <i>b</i>	0.078, 10.83	0.086, 0.00
Goodness of fit on F^2	1.046	1.047
Function minimised	$\sum w(F_o^2 - F_c^2)^2$	$\sum w(F_o^2 - F_c^2)^2$
<i>R</i> , <i>wR</i> ₂	0.042, 0.106	0.047, 0.128
$R = \sum F_o - F_c / \sum F_o $ $wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$ $w = 1.0 / [\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2) / 3$		

then filtered through Celite and all the solvent was removed in vacuo. The residue was chromatographed on a silica gel column ($1.5 \times 5 \text{ cm}^2$) with dichloromethane as eluent. The colourless fraction which eluted immediately after the solvent front was collected. The volume was reduced in vacuo and on the addition of hexane and iso-propanol a white precipitate formed slowly. Recrystallization from dichloromethane/hexane gave pure **7b** (0.113 g, 60%), m.p. 176–178.5°C. Anal. Found: C, 65.50; H, 4.77; N, 2.58. $\text{C}_{58}\text{H}_{49}\text{ClN}_2\text{P}_2\text{Os}$. Calc.: C, 65.62; H, 4.65; N, 2.64%.

3.13. $\text{Ru}(\eta^2\text{-CPh}=\text{Np-tolyl})\text{Cl}(\text{CO})(\text{PPh}_3)_2$ (**8a**)

$\text{RuHCl}(\text{CNp-tolyl})(\text{PPh}_3)_3$ (0.100 g, 0.096 mmol) and Ph_2Hg (0.044 g, 0.12 mmol) were added to rigorously degassed benzene (10 ml) in a Schlenk tube and heated at 80°C for 1 h. The solution turned red and elemental mercury was deposited. CO was bubbled through the solution until it turned pale yellow in colour. It was then immediately frozen in liquid nitrogen and the excess CO was removed under vacuum. The solution was heated to 80°C for five min and then the benzene was removed in vacuo. Dichloromethane (10 ml) was added and the solution was filtered through Celite to remove mercury. Ethanol was added and on reduction of the solvent volume a yellow solid precipitated. This was recrystallized from dichloromethane/ethanol to give pure **8a** (0.060 g, 64%), m.p. 193–196°C. Anal. Found: C, 67.75; H, 4.71; N, 1.68. $\text{C}_{51}\text{H}_{42}\text{ClN}_2\text{OP}_2\text{Ru} \cdot 0.25(\text{CH}_2\text{Cl}_2)$. Calc.: C, 68.05; H, 4.74; N, 1.55%.

3.14. $\text{RuCl}_2(\text{CPhNHp-tolyl})(\text{CNp-tolyl})(\text{PPh}_3)_2$ (**9a**)

$\text{RuHCl}(\text{CNp-tolyl})(\text{PPh}_3)_3$ (0.300 g, 0.288 mmol) and HgPh_2 (0.153 g, 0.432 mmol) were added to rigorously deoxygenated benzene (15 ml) in a Schlenk tube. The solution was frozen and evacuated completely. The Schlenk tube was then sealed and heated at 80°C (oil bath) for 3 h. The solution was cooled to room temperature and to it was added a solution of *p*-tolyl isocyanide (0.034 g, 0.29 mmol) in degassed dichloromethane (10 ml). The red solution turned light orange. It was then heated at 50°C for 10 min, during which time the orange colour became deeper. After cooling to room temperature trimethylsilyl chloride (0.032 g, 0.29 mmol) was added. The solution became slightly lighter in colour. It was then filtered through Celite and the benzene was removed in vacuo. Equal volumes of dichloromethane and ethanol were added and on slow reduction of the solvent volume a light yellow precipitate formed. Recrystallization from dichloromethane/ethanol gave pure **9a** (0.110 g, 38%), m.p. 208–210°C. Anal. Found: C, 69.00; H, 4.96; N, 2.61. $\text{C}_{58}\text{H}_{50}\text{Cl}_2\text{N}_2\text{P}_2\text{Ru}$. Calc.: C, 69.04; H, 5.00; N, 2.78%.

Table 9

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{Os}(\eta^2\text{-O}_2\text{X}\eta^2\text{-CPh}=\text{N-}p\text{-chlorophenyl})\text{-Cl}(\text{PPh}_3)_2$ (**3c**)

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Os	4704(1)	5531(1)	1981(1)	37(1)
P(1)–4832(1)	4525(1)	2056(1)	39(1)	
P(2)	4574(1)	6529(1)	1861(1)	46(1)
Cl(1)	4445(2)	5416(1)	837(1)	55(1)
Cl(2)	8564(2)	6028(2)	128(2)	96(1)
O(1)	3580(4)	5501(3)	2258(4)	53(2)
O(2)	4091(4)	5601(3)	2811(4)	53(2)
N(1)	5937(5)	5585(3)	1879(4)	38(2)
C(1)	5697(6)	5568(4)	458(6)	46(3)
C(11)	4875(5)	4220(4)	2873(5)	45(3)
C(12)	5379(6)	3794(5)	3066(7)	64(3)
C(13)	5333(8)	3561(6)	3675(6)	76(4)
C(14)	4796(9)	3744(6)	4109(7)	87(4)
C(15)	4302(8)	4169(6)	3936(7)	75(4)
C(16)	4330(6)	4404(5)	3318(5)	51(3)
C(21)	5702(5)	4286(4)	1637(5)	42(2)
C(22)	5669(6)	4136(4)	974(6)	50(3)
C(23)	6348(8)	3991(5)	652(6)	67(3)
C(24)	7044(6)	3995(5)	949(7)	65(3)
C(25)	7084(6)	4156(5)	1597(7)	63(3)
C(26)	6424(6)	4306(4)	1943(6)	50(3)
C(31)	4054(5)	4088(4)	731(5)	44(2)
C(32)	337(6)	4305(4)	1646(6)	60(3)
C(33)	2722(7)	953(6)	1468(7)	76(4)
C(34)	828(7)	3393(6)	1397(8)	84(4)
C(35)	3558(8)	3170(5)	1461(8)	87(4)
C(36)	176(7)	3505(5)	1655(7)	67(3)
C(41)	387(6)	6918(4)	2627(6)	55(3)
C(42)	4790(8)	6802(5)	3152(6)	66(3)
C(43)	4719(11)	7112(7)	3743(8)	98(5)
C(44)	187(11)	7544(6)	3757(9)	97(6)
C(45)	3799(9)	665(5)	240(8)	83(4)
C(46)	839(7)	7358(5)	2644(7)	74(4)
C(51)	5430(6)	6884(4)	1547(6)	53(3)
C(52)	5696(7)	6729(5)	934(6)	62(3)
C(53)	6350(8)	7011(5)	663(7)	75(4)
C(54)	6711(7)	7403(6)	1022(7)	77(4)
C(55)	6461(8)	7561(6)	1619(8)	86(4)
C(56)	5807(7)	7312(5)	1889(7)	71(3)
C(61)	3785(6)	6758(4)	1323(6)	53(3)
C(62)	3879(7)	7125(4)	810(5)	58(3)
C(63)	3231(9)	7290(5)	439(7)	77(4)
C(64)	2519(8)	7087(6)	579(7)	78(4)
C(65)	427(8)	6729(5)	1079(10)	101(6)
C(66)	3070(6)	6550(5)	1455(8)	75(4)
C(71)	6590(5)	675(4)	1480(5)	44(2)
C(72)	6551(5)	5493(4)	842(6)	50(3)
C(73)	7163(6)	5600(4)	412(6)	60(3)
C(74)	7791(7)	5890(5)	663(7)	67(3)
C(75)	838(6)	6078(5)	1281(6)	57(3)
C(76)	7225(6)	5980(4)	1712(6)	54(3)
C(81)	6041(5)	5508(4)	133(5)	2(2)
C(82)	6830(5)	5434(4)	238(5)	43(2)
C(83)	7091(6)	5357(5)	3860(6)	57(3)
C(84)	594(7)	5362(5)	4389(6)	63(3)
C(85)	5791(8)	5433(5)	4282(6)	67(3)
C(86)	5538(6)	5504(4)	3664(5)	52(3)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

3.15. $RuH_2(CNp\text{-tolyl})(PPh_3)_3$ (**10a**)

$RuH_2(PPh_3)_4$ (1.00 g, 0.868 mmol) and *p*-tolyl isocyanide (0.15 g, 1.2 mmol) in ethanol (25 ml) were heated gently under reflux for 5 min. The yellow sus-

Table 10

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $Os(\eta^2\text{-SO}_4)(\eta^2\text{-CPh=N-}p\text{-chlorophenyl)Cl(PPh}_3)_2$ (**4c**)

	x	y	z	U_{eq}
Os	150(1)	2979(1)	2432(1)	30(1)
P(1)	230(2)	958(2)	2313(1)	35(1)
P(2)	126(2)	5022(2)	2511(1)	33(1)
Cl(1)	945(2)	3312(2)	1185(1)	42(1)
Cl(2)	-5320(4)	3389(3)	105(2)	82(1)
S	1852(2)	2593(2)	3399(1)	44(1)
O(1)	2074(6)	2794(6)	2574(4)	40(2)
O(2)	397(6)	2576(5)	3524(3)	38(2)
O(3)	2440(8)	1510(8)	3624(5)	81(3)
O(4)	2172(8)	3548(7)	3719(4)	65(2)
C	-1772(9)	3145(8)	2849(5)	36(2)
N	-1740(7)	3225(6)	2175(4)	36(2)
C(11)	1696(9)	241(8)	1813(5)	37(2)
C(12)	2781(12)	780(10)	1575(8)	68(4)
C(13)	3836(13)	214(12)	1161(9)	90(5)
C(14)	3818(13)	-897(11)	1025(8)	76(4)
C(15)	2728(12)	-1438(10)	1249(7)	61(3)
C(16)	1679(11)	-873(9)	1639(6)	53(3)
C(21)	-960(10)	581(8)	1791(6)	40(2)
C(22)	-1919(11)	-96(10)	2091(7)	61(3)
C(23)	-2700(14)	-407(13)	1626(9)	84(5)
C(24)	-2533(13)	-41(11)	914(8)	70(4)
C(25)	-1596(12)	627(11)	625(7)	64(3)
C(26)	-798(12)	927(9)	1069(6)	55(3)
C(31)	-57(11)	124(9)	3191(5)	45(2)
C(32)	06(12)	663(9)	3417(6)	53(3)
C(33)	702(16)	-1230(11)	4092(8)	74(4)
C(34)	-415(16)	-1021(11)	4552(7)	73(4)
C(35)	-1403(15)	-230(11)	4337(7)	74(4)
C(36)	-1218(12)	352(9)	3638(6)	56(3)
C(41)	559(9)	5839(8)	1766(5)	37(2)
C(42)	195(10)	6324(9)	1170(5)	46(3)
C(43)	-357(13)	6907(11)	611(6)	64(3)
C(44)	-1680(12)	7023(10)	638(6)	58(3)
C(45)	-2431(11)	6528(9)	1233(6)	53(3)
C(46)	-1869(10)	5955(8)	1782(6)	42(2)
C(51)	1719(9)	5523(8)	2453(5)	39(2)
C(52)	1882(11)	6280(9)	2935(6)	50(3)
C(53)	3110(11)	6631(11)	2915(7)	63(3)
C(54)	4139(11)	6240(10)	2418(7)	59(3)
C(55)	3950(11)	5507(9)	1930(7)	54(3)
C(56)	2749(10)	5127(8)	1964(6)	46(3)
C(61)	-811(9)	5649(8)	3310(5)	35(2)
C(62)	-1465(10)	6723(8)	3260(6)	46(3)
C(63)	-2100(13)	7215(11)	3865(7)	67(4)
C(64)	-2104(11)	6645(10)	4538(6)	59(3)
C(65)	-1441(11)	5579(10)	4596(6)	55(3)
C(66)	-786(10)	5081(9)	3971(5)	44(2)
C(71)	-2549(9)	3213(8)	1667(5)	37(2)
C(72)	-2263(10)	3733(9)	986(5)	45(2)
C(73)	-3088(11)	3790(9)	493(6)	50(3)
C(74)	-4243(11)	3294(9)	706(6)	49(3)
C(75)	-4527(11)	2758(10)	1377(7)	57(3)
C(76)	-3682(10)	2701(9)	1863(6)	47(3)

pension turned colourless. Recrystallization from benzene/ethanol gave pure **10a** (0.70 g, 80%), m.p. 148–149°C. Anal. Found: C, 73.44, H, 5.37; N, 1.27. $C_{62}H_{54}NP_3Ru$. Calc.: C, 73.96; H, 5.41; N, 1.39%.

3.16. $OsH_2(CNp\text{-tolyl})(PPh_3)_3$ (**10b**)

A suspension of $OsH_4(PPh_3)_3$ (1.10 g, 1.12 mmol) and *p*-tolyl isocyanide (0.27 g, 2.3 mmol) in benzene (60 ml) was heated under reflux for 4 h. The resulting brown solution was reduced to 10 ml and chromatographed on a Florisil column ($2.5 \times 12 \text{ cm}^2$) using benzene as eluent. The very pale yellow band was collected, the solvent volume reduced and ethanol was added to effect crystallization of crude **10b** (1.08 g, 88%). A sample of analytical purity was recrystallized from benzene/petroleum spirit, m.p. 184–187°C. Anal. Found: C, 68.01; H, 5.33; N, 1.38. $C_{62}H_{54}NOsP_3$. Calc.: C, 67.93; H, 5.96; N, 1.28%.

3.17. $OsH_2(CNp\text{-chlorophenyl})(PPh_3)_3$ (**10c**)

$OsH_4(PPh_3)_3$ (1.000 g, 1.019 mmol) and *p*-chlorophenyl isocyanide (0.276 g, 2.04 mmol) were heated under reflux in benzene (60 ml) for 4 h. The resulting brown solution was reduced to 10 ml by distillation of the excess benzene and then chromatographed on a Florisil column ($2.5 \times 10 \text{ cm}^2$) using benzene as eluent. The pale yellow band which eluted immediately after the solvent front was collected. The volume was reduced to 10 ml and iso-propanol added to effect crystallization. The very pale yellow product was collected and recrystallized from benzene/iso-propanol to give pure **10c** (0.91 g, 80%), m.p. 185–186.5°C. Anal. Found: C, 65.52; H, 4.36; N, 1.50. $C_{61}H_{51}ClNP_3Os$. Calc.: C, 65.61; H, 4.60; N, 1.25%.

3.18. X-ray diffraction studies of $Os(\eta^2\text{-O}_2)(\eta^2\text{-CPh=N-}p\text{-chlorophenyl)Cl(PPh}_3)_2$ (**3c**) and $Os(\eta^2\text{-SO}_4)(\eta^2\text{-CPh=N-}p\text{-chlorophenyl)Cl(PPh}_3)_2$ (**4c**)

Crystal data

Details of crystal data and intensity collection parameters are given in Table 8. Unit cell parameters were obtained from a least-squares fit to the four circle coordinates of 25 reflections determined on a Nonius CAD-4 diffractometer. Intensity data collection, using graphite monochromated Mo K α radiation, employed

Table 10 (continued)

	x	y	z	U_{eq}
C(81)	-2721(9)	3282(8)	3496(5)	39(2)
C(82)	-3941(10)	3838(9)	3427(6)	48(3)
C(83)	-4836(11)	4013(11)	4009(7)	62(3)
C(84)	-4590(12)	3633(12)	4681(8)	74(4)
C(85)	-3384(13)	3082(12)	4775(7)	70(4)
C(86)	-2455(10)	2906(10)	4176(5)	48(3)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

ω - 2θ scans with peak-to-background count time of 2:1 and ω scan angle $0.80 + 0.347 \tan \theta$. Reflections were counted until $\sigma(I)/I$ was 0.02 or for a maximum of 60 s. Three reflections were monitored throughout data collection as checks on crystal alignment and decomposition. Intensities of the standards showed only statistical variation for **4c**, but those for **3c** declined steadily with time. Once the standards for **3c** had declined to $\approx 60\%$ of their initial value a second crystal was used to complete the data collection. The raw intensities were scaled and separate scale factors were subsequently refined for the two crystals. The data sets were corrected for Lorentz, polarisation and absorption [18] using locally written programs.

The structures were solved by Patterson [19] and Fourier techniques and refined by full-matrix least-squares on F^2 [20]. Atomic scattering factors were for neutral atoms [21]. Hydrogen atoms were included in calculated positions and allowed to ride on the atom to which they were attached with 20% greater thermal parameter. All non-hydrogen atoms were allowed to assume anisotropic thermal motion. Final refinement details are given in Table 8. Atomic coordinates of **3c** and **4c** are given in Tables 9 and 10 respectively. Supplementary data available from the authors (CEFR) comprise full tables of interatomic distances and angles, anisotropic thermal parameters, hydrogen atom positions and observed and calculated structure factors.

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