

Syntheses and reactions of the carbyne complexes,  
 $M(\equiv CR)Cl(CO)(PPh_3)_2$  ( $M = Ru, Os$ ;  $R = 1\text{-naphthyl}, 2\text{-naphthyl}$ ). The  
 crystal structures of  $[Os(\equiv C\text{-}1\text{-naphthyl})(CO)_2(PPh_3)_2]ClO_4$ ,  
 $Os(=CH\text{-}2\text{-naphthyl})Cl_2(CO)(PPh_3)_2$ , and  
 $Os(2\text{-naphthyl})Cl(CO)_2(PPh_3)_2$ <sup>1</sup>

Lisa-Jane Baker, George R. Clark, Clifton E.F. Rickard, Warren R. Roper<sup>\*</sup>,  
 Scott D. Woodgate, L. James Wright<sup>2</sup>

*Department of Chemistry, The University of Auckland, Private Bag 92019, Auckland, New Zealand*

Received 7 May 1997; received in revised form 10 July 1997

### Abstract

Treatment of the dichlorocarbene-containing complex,  $Os(=CCl_2)Cl_2(CO)(PPh_3)_2$  with two equivalents of 1-naphthyllithium or two equivalents of 2-naphthyllithium in the presence of *N,N,N',N'*-tetramethylethylenediamine (tmeda) gives the corresponding carbyne-containing complexes  $Os(\equiv CR)Cl(CO)(PPh_3)_2$  ( $R = 1\text{-naphthyl}$  (**1**);  $R = 2\text{-naphthyl}$  (**2**)). Similar treatment of  $Ru(=CCl_2)Cl_2(CO)(PPh_3)_2$  with two equivalents of phenyllithium or 1-naphthyllithium yields  $Ru(\equiv CR)Cl(CO)(PPh_3)_2$  ( $R = Ph$  (**3**);  $R = 1\text{-naphthyl}$  (**4**)). When **1**, **2**, **3** and **4** are carbonylated in the presence of  $AgClO_4$  the corresponding carbyne-containing cations  $[M(\equiv CR)(CO)_2(PPh_3)_2]ClO_4$  are formed ( $M = Os$ ,  $R = 1\text{-naphthyl}$  (**5**);  $M = Os$ ,  $R = 2\text{-naphthyl}$  (**6**);  $M = Ru$ ,  $R = Ph$  (**7**);  $M = Ru$ ,  $R = 1\text{-naphthyl}$  (**8**)). When  $Ru(\equiv CPh)Cl(CO)(PPh_3)_2$  is added to an acetonitrile solution containing two equivalents of  $AgClO_4$  in the absence of CO the complex  $[Ru(\equiv CPh)(AgOCIO_3)(NCMe)(CO)(PPh_3)_2]ClO_4$  (**9**) can be isolated. Addition of LiCl to **9** yields the complex  $Ru(\equiv CPh)(AgCl)Cl(CO)(PPh_3)_2$  (**10**). The acids HX react with the neutral carbyne complexes **1**, **2**, **3** or **4** to form the corresponding carbene complexes  $M(=CHR)ClX(CO)(PPh_3)_2$  ( $M = Os$ ,  $R = 1\text{-naphthyl}$ ,  $X = Cl$  (**11**);  $M = Os$ ,  $R = 2\text{-naphthyl}$ ,  $X = Cl$  (**12**);  $M = Ru$ ,  $R = Ph$ ,  $X = Cl$  (**13**);  $M = Ru$ ,  $R = 1\text{-naphthyl}$ ,  $X = Cl$  (**14**);  $M = Os$ ,  $R = 1\text{-naphthyl}$ ,  $X = ClO_4$  (**15**);  $M = Os$ ,  $R = 1\text{-naphthyl}$ ,  $X = F$  (**16**)). Treatment of complexes **1** or **2** with  $PhCl_2$  leads to corresponding monochlorocarbene-containing complexes  $Os(=CClR)Cl_2(CO)(PPh_3)_2$  ( $R = 1\text{-naphthyl}$  (**17**);  $R = 2\text{-naphthyl}$  (**18**)) which subsequently rearrange on addition of aqueous base to give the  $\sigma$ -naphthyl, dicarbonyl complexes  $OsRCl(CO)_2(PPh_3)_2$  ( $R = 1\text{-naphthyl}$  (**19**);  $R = 2\text{-naphthyl}$  (**20**)). The single crystal X-ray structures of  $[Os(\equiv C\text{-}1\text{-naphthyl})(CO)_2(PPh_3)_2]ClO_4$ ,  $Os(=CH\text{-}2\text{-naphthyl})Cl_2(CO)(PPh_3)_2$ , and  $Os(2\text{-naphthyl})Cl(CO)_2(PPh_3)_2$  have been determined. © 1998 Elsevier Science S.A.

### 1. Introduction

In our previous reports of the reaction between  $M(=CCl_2)Cl_2(CO)(PPh_3)_2$  ( $M = Os, Ru$ ) and lithiated aryls to form carbyne complexes of the type  $M(\equiv CR)Cl(CO)(PPh_3)_2$ , the range of aryl substituents utilised is restricted to those containing six membered rings such as *p*-tolyl [1,2] phenyl [3] and *p*-N, N-di-

methylaminophenyl [4]. Given the highly reactive nature of these carbyne complexes it was of interest to explore the effect that larger, fused ring aryl substituents might have on the reactivity of complexes of this type. In this paper we describe the syntheses and some reactions of the 1- or 2-naphthyl substituted carbyne complexes  $M(\equiv CR)Cl(CO)(PPh_3)_2$ , and the crystal structures of  $[Os(\equiv C\text{-}1\text{-naphthyl})(CO)_2(PPh_3)_2]ClO_4$ ,  $Os(=CH\text{-}2\text{-naphthyl})Cl_2(CO)(PPh_3)_2$ , and  $Os(2\text{-naphthyl})Cl(CO)_2(PPh_3)_2$ . Details of the reaction chemistry of the phenylcarbyne complex of ruthenium,  $Ru(\equiv CPh)Cl(CO)(PPh_3)_2$  are also included.

<sup>\*</sup> Corresponding author.

<sup>1</sup> Dedicated to Professor Peter Maitlis, FRS, on the occasion of his 65th birthday.

<sup>2</sup> Also Corresponding author.

## 2. Results and discussion

### 2.1. Synthesis of osmium and ruthenium carbyne complexes 1–8

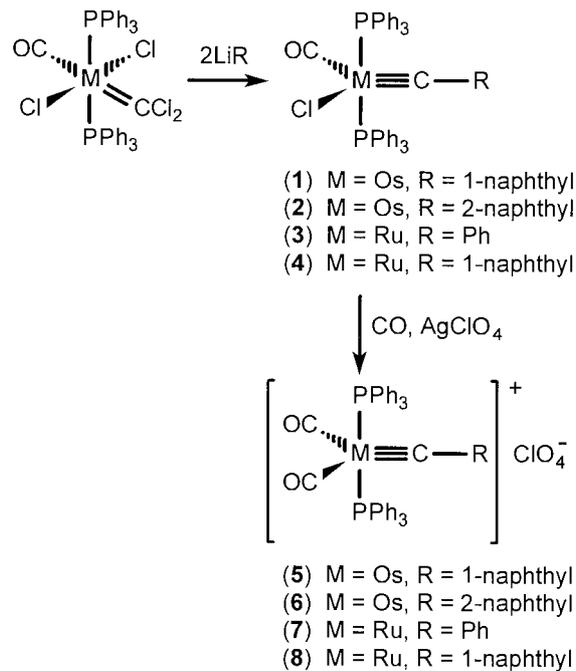
1-Bromonaphthalene was lithiated with  $n\text{BuLi}$  at room temperature until a white crystalline mass formed at which point the 1-naphthyllithium suspension was cooled to  $-40^\circ\text{C}$  and a tetrahydrofuran (thf) solution of  $\text{M}(\text{=CCl}_2)\text{Cl}_2(\text{CO})(\text{PPh}_3)_2$  ( $\text{M} = \text{Ru}, \text{Os}$ ) added rapidly. This mixture was warmed to room temperature and the green carbyne complexes **1** or **4** isolated (see Scheme 1). Crystalline samples of the ruthenium complex **4** were found to be very sensitive to oxygen and moisture and decomposed over a period of hours on exposure to the atmosphere.

Similarly, when a solution of  $\text{PhLi}$  was added to  $\text{Ru}(\text{=CCl}_2)\text{Cl}_2(\text{CO})(\text{PPh}_3)_2$  the dark green ruthenium phenyl carbyne complex **3** was isolated.

Attempts to prepare the osmium 2-naphthyl carbyne complex using similar conditions to those employed for the synthesis of **1**, **3** and **4** were not successful. The characteristic green colour of a carbyne-containing complex appeared in solution, but it was not possible to isolate a crystalline solid. However, addition of  $\text{N,N,N',N'}$ -tetramethylethylenediamine (tmeda) to the reaction mixture afforded high yields of **2**. Addition of tmeda to a variety of lithium reagents has been shown to reduce aggregation and increase the activity of the lithium reagents [5].

In the IR spectra of complexes **1**, **2**, **3** and **4**, low values are observed for  $\nu(\text{CO})$  at 1857, 1859, 1875 and  $1882\text{ cm}^{-1}$  respectively, as would be expected for complexes containing an electron rich carbyne fragment (see Table 1 for IR data of all the new complexes reported in this paper). Furthermore, all the carbyne complexes show absorptions close to  $1300\text{ cm}^{-1}$ . Bands in this region have been assigned previously to molecular vibrations arising from the metal-carbyne fragment [6]. Although all three complexes are extremely sensitive to hydrolysis when in solution,  $^{13}\text{C}$  NMR spectra of the less reactive osmium complexes **1** and **2** have been obtained (see Section 3). The carbyne carbon atoms give rise to triplet signals (due to coupling to the two mutually *trans* phosphorus atoms of the  $\text{PPh}_3$  ligands) at the extremely low field values of 321.6 ppm for **1** and 325.6 ppm for **2**. As expected, the resonances of the CO carbon atoms appear, also as triplets, in the 190 ppm region.

Upon addition of CO in the presence of  $\text{AgClO}_4$ , the complexes **1**, **2**, **3** and **4** rapidly lose chloride and the corresponding dicarbonyl, carbyne-containing complexes  $[\text{M}(\text{=CR})(\text{CO})_2(\text{PPh}_3)_2]\text{ClO}_4$  ( $\text{M} = \text{Os}, \text{R} = 1\text{-naphthyl}$  (**5**);  $\text{M} = \text{Os}, \text{R} = 2\text{-naphthyl}$  (**6**);  $\text{M} = \text{Ru}, \text{R} = 1\text{-naphthyl}$  (**7**); and  $\text{M} = \text{Ru}, \text{R} = \text{Ph}$  (**8**)) are formed. Unlike their neutral precursors, these com-



Scheme 1.

plexes are insensitive to air and moisture and fail to react with electrophiles such as  $\text{H}^+$  and  $\text{Ag}^+$ . Characteristic features in the IR spectra of each of these cationic complexes are the two  $\nu(\text{CO})$  bands, both of which are higher than the single  $\nu(\text{CO})$  band for the corresponding neutral precursor complex, and a band in the  $1300\text{ cm}^{-1}$  region which is in a similar position to that observed for the corresponding neutral complex. In the  $^{13}\text{C}$  NMR spectra the carbyne carbon resonances appear at the downfield positions of 327.8 ppm for **5** and 331.8 ppm for **6**.

A single crystal X-ray diffraction study of  $[\text{Os}(\text{=C-1-naphthyl})(\text{CO})_2(\text{PPh}_3)_2]\text{ClO}_4$  (**5**) shows that the structure about osmium can be described as a distorted trigonal bipyramid with two mutually *trans* triphenylphosphine ligands occupying the axial positions and the two *cis* carbonyl ligands and the carbyne fragment in the equatorial plane. The molecular structure is depicted in Fig. 1. Selected bond lengths and bond angles are listed in Table 2, and atomic coordinates are listed in Table 3.

The  $\text{Os}-\text{C}(\text{carbyne})$  carbon bond length,  $1.79(1)\text{ \AA}$ , is significantly shorter than the two  $\text{Os}-\text{C}(\text{CO})$  bonds of  $1.94(1)\text{ \AA}$  and  $1.96(1)\text{ \AA}$  in the same complex. The  $\text{Os}-\text{C}(\text{carbyne})$  distance in this complex is almost identical to that previously reported for the neutral carbyne complex  $\text{Os}(\text{=C-}i>p\text{-tolyl})\text{Cl}(\text{CO})(\text{PPh}_3)_2$  ( $1.78(2)\text{ \AA}$ ) [1] and the  $\text{Os}(\text{II})$  carbyne complexes  $[\text{Os}(\text{=C-C}_6\text{H}_4\text{NMe}_2)\text{Cl}_2(\text{CN-}i>p\text{-tolyl})(\text{PPh}_3)_2]^+$  ( $1.78(1)\text{ \AA}$ ) and  $\text{Os}(\text{=C-C}_6\text{H}_4\text{NMe}_2)\text{Cl}_2(\text{NCS})(\text{PPh}_3)_2$  ( $1.75(1)\text{ \AA}$ ) [4]. The  $\text{Os}-\text{C-1-naphthyl}$  angle is close to linear ( $177^\circ$ ), as expected for an *sp*-hybridised carbyne carbon atom, and

Table 1  
IR data for new complexes

Compound	$\nu(\text{CO})/\text{cm}^{-1\text{a}}$	Other bands/ $\text{cm}^{-1}$
$\text{Os}(\equiv\text{C-1-naphthyl})\text{Cl}(\text{CO})(\text{PPh}_3)_2$ ( <b>1</b> )	1857 s	1504 w, 1410 m, 1327 m $\nu(\text{Os}\equiv\text{C})$ , 1184 m, 779 m
$\text{Os}(\equiv\text{C-2-naphthyl})\text{Cl}(\text{CO})(\text{PPh}_3)_2$ ( <b>2</b> )	1859 s	1621 w, 1588 w, 1383 w $\nu(\text{Os}\equiv\text{C})$ , 1184 w
$\text{Ru}(\equiv\text{CPh})\text{Cl}(\text{CO})(\text{PPh}_3)_2$ ( <b>3</b> )	1875 s	1584 w, 1328 w, $\nu(\text{Ru}\equiv\text{C})$ , 927 w
$\text{Ru}(\equiv\text{C-1-naphthyl})\text{Cl}(\text{CO})(\text{PPh}_3)_2$ ( <b>4</b> )	1882 s	1589 w, 1563 w, 1311 m, $\nu(\text{Ru}\equiv\text{C})$ , 1243 m
$[\text{Os}(\equiv\text{C-1-naphthyl})(\text{CO})_2(\text{PPh}_3)_2]\text{ClO}_4$ ( <b>5</b> )	2023 s, 2002 s, 1953 s, 1936 s <sup>b</sup>	1558 m, 1506 s, 1417 s, 1352 s, 1323 s $\nu(\text{Os}\equiv\text{C})$ , 1249 m, 1091 s
$[\text{Os}(\equiv\text{C-2-naphthyl})(\text{CO})_2(\text{PPh}_3)_2]\text{ClO}_4$ ( <b>6</b> )	2023 s, 2009 s, 1957 s, 1944 s <sup>c</sup>	1618 m, 1587 m, 1556 w, 1388 w 1354 m $\nu(\text{Os}\equiv\text{C})$ , 1330 w, 1236 w, 1090 s, 877 w
$[\text{Ru}(\equiv\text{CPh})(\text{CO})_2(\text{PPh}_3)_2]\text{ClO}_4$ ( <b>7</b> )	2020 s, 1960 s	1585 w, 1370 m $\nu(\text{Ru}\equiv\text{C})$ , 1315 w, 1275 w, 1165 s, 960 w, 845 m, 1090 s <sup>c</sup> $\nu(\text{ClO}_4)$ , 620 s
$[\text{Ru}(\equiv\text{C-1-naphthyl})(\text{CO})_2(\text{PPh}_3)_2]\text{ClO}_4$ ( <b>8</b> )	2033 m, 2009 s, 1973 m, 1920 s <sup>d</sup>	1580 w, 1504 m, 1406 m, 1317 m $\nu(\text{Ru}\equiv\text{C})$ , 1247 w, 1093 s, 891 w
$[\text{Ru}(\text{CPh}\{\text{AgOClO}_3\})(\text{NCMe})(\text{CO})(\text{PPh}_3)_2]\text{ClO}_4$ ( <b>9</b> )	1965 s, 1953 s	1635 w, 1585 m, 1309 m, 1292 m, 1095 m <sup>e</sup> $\nu(\text{ClO}_4)$ , 763 s, 675 m, 624 m
$\text{Ru}(\text{CPh}\{\text{AgCl}\})\text{Cl}(\text{CO})(\text{PPh}_3)_2$ ( <b>10</b> )	1928 s	1585 w, 1284 m, 707 m, 680 w
$\text{Os}(\equiv\text{CH-1-naphthyl})\text{Cl}_2(\text{CO})(\text{PPh}_3)_2$ ( <b>11</b> )	1952 s	1622 w, 1586 m, 1508 w, 1300 w, 1226 m
$\text{Os}(\equiv\text{CH-2-naphthyl})\text{Cl}_2(\text{CO})(\text{PPh}_3)_2$ ( <b>12</b> )	1950 s	1620 m, 1589 w, 1280 w
$\text{Ru}(\equiv\text{CHPh})\text{Cl}_2(\text{CO})(\text{PPh}_3)_2$ ( <b>13</b> )	1965 s	1590 w, 1370 w, 1265 w, 1160 w, 840 w
$\text{Ru}(\equiv\text{CH-1-naphthyl})\text{Cl}_2(\text{CO})(\text{PPh}_3)_2$ ( <b>14</b> )	1975 s	1582 m, 1506 w, 1296 w
$\text{Os}(\equiv\text{CH-1-naphthyl})\text{Cl}(\text{OCIO}_3)(\text{CO})(\text{PPh}_3)_2$ ( <b>15</b> )	1939 s	1093 s
$\text{Os}(\equiv\text{CH-1-naphthyl})\text{Cl}(\text{F})(\text{CO})(\text{PPh}_3)_2$ ( <b>16</b> )	1952 s	1564 m, 1226 m
$\text{Os}(\equiv\text{CCl-1-naphthyl})\text{Cl}_2(\text{CO})(\text{PPh}_3)_2$ ( <b>17</b> )	1988 s	1222 w, 1210 w
$\text{Os}(\equiv\text{CCl-2-naphthyl})\text{Cl}_2(\text{CO})(\text{PPh}_3)_2$ ( <b>18</b> )	1980 s	1622 w, 1586 w
$\text{Os}(\text{1-naphthyl})\text{Cl}(\text{CO})_2(\text{PPh}_3)_2$ ( <b>19</b> )	2025 s, 1940 s	782 w
$\text{Os}(\text{2-naphthyl})\text{Cl}(\text{CO})_2(\text{PPh}_3)_2$ ( <b>20</b> )	2017 s, 1948 s	1580 w, 782 w

<sup>a</sup>Unless otherwise stated all IR spectra were recorded as Nujol mulls.

<sup>b</sup>Solid state splitting, solution IR in dichloromethane shows  $\nu(\text{CO})$  2025, 1963  $\text{cm}^{-1}$ .

<sup>c</sup>Solid state splitting, solution IR in dichloromethane shows  $\nu(\text{CO})$  2035, 1978  $\text{cm}^{-1}$ .

<sup>d</sup>Solid state splitting, solution IR in dichloromethane shows  $\nu(\text{CO})$  2036, 1980  $\text{cm}^{-1}$ .

<sup>e</sup>Broad structured band.

the naphthyl ring, which shows no significant distortions from planarity, lies in the equatorial plane. The  $\text{ClO}_4^-$  anion is distinct from the osmium complex and shows no close contacts. The angles between the ligands in the equatorial plane are distorted from the  $120^\circ$

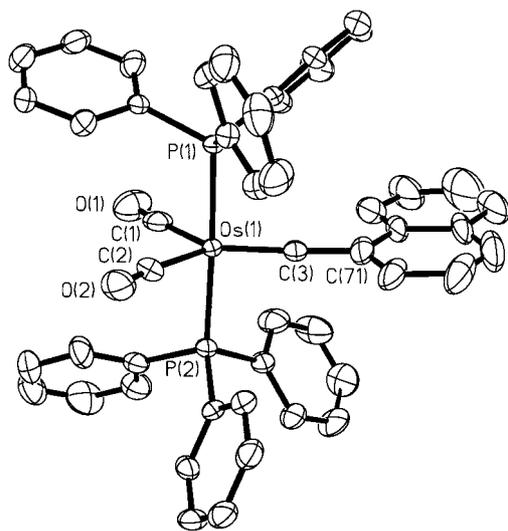


Fig. 1. The molecular structure of  $[\text{Os}(\equiv\text{C-1-naphthyl})(\text{CO})_2(\text{PPh}_3)_2]\text{ClO}_4$  (**5**).

expected for a regular trigonal bipyramid. The two CO ligands are bent away from the carbyne carbon atom with the angles  $\text{C}(1)\text{-Os}(1)\text{-C}(2) = 100.1(4)^\circ$ ,  $\text{C}(3)\text{-}$

Table 2  
Bond lengths (Å) and angles ( $^\circ$ ) for **5**

$\text{Os}(1)\text{-C}(3)$	1.792(10)
$\text{Os}(1)\text{-C}(2)$	1.944(10)
$\text{Os}(1)\text{-C}(1)$	1.961(11)
$\text{Os}(1)\text{-P}(1)$	2.386(2)
$\text{Os}(1)\text{-P}(2)$	2.390(2)
$\text{O}(1)\text{-C}(1)$	1.142(13)
$\text{O}(2)\text{-C}(2)$	1.136(12)
$\text{C}(3)\text{-C}(71)$	1.44(2)
$\text{C}(3)\text{-Os}(1)\text{-C}(2)$	127.8(5)
$\text{C}(3)\text{-Os}(1)\text{-C}(1)$	132.1(5)
$\text{C}(2)\text{-Os}(1)\text{-C}(1)$	100.1(4)
$\text{C}(3)\text{-Os}(1)\text{-P}(1)$	89.8(3)
$\text{C}(2)\text{-Os}(1)\text{-P}(1)$	88.0(3)
$\text{C}(1)\text{-Os}(1)\text{-P}(1)$	90.1(3)
$\text{C}(3)\text{-Os}(1)\text{-P}(2)$	92.4(3)
$\text{C}(2)\text{-Os}(1)\text{-P}(2)$	89.9(3)
$\text{C}(1)\text{-Os}(1)\text{-P}(2)$	89.1(3)
$\text{P}(1)\text{-Os}(1)\text{-P}(2)$	177.62(8)
$\text{O}(1)\text{-C}(1)\text{-Os}(1)$	173.6(10)
$\text{O}(2)\text{-C}(2)\text{-Os}(1)$	171.5(9)
$\text{C}(71)\text{-C}(3)\text{-Os}(1)$	177.2(8)

Table 3

Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for **5**.  $U(\text{eq})$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor

	<i>x</i>	<i>y</i>	<i>z</i>	$U(\text{eq})$
Os(1)	1956(1)	3773(1)	2995(1)	26(1)
P(1)	8(2)	4162(2)	2646(1)	26(1)
P(2)	3865(2)	3397(2)	3400(1)	27(1)
Cl(1)	3524(3)	-417(2)	2418(2)	58(1)
Cl(2)	313(10)	7804(9)	3652(7)	91(3)
Cl(2')	625(14)	7867(11)	3232(10)	121(4)
Cl(3)	-266(21)	10,042(17)	2609(13)	179(7)
Cl(3')	-929(13)	9923(10)	2866(8)	108(3)
Cl(4)	176(13)	9643(11)	4195(8)	120(4)
Cl(4')	-467(19)	9220(16)	4369(13)	176(7)
Cl(5)	7133(19)	108(16)	107(13)	340(9)
Cl(6)	7728(19)	1955(18)	-790(13)	353(10)
Cl(7)	9665(45)	149(37)	-424(24)	619(26)
O(1)	1742(9)	1577(7)	4065(6)	64(2)
O(2)	708(7)	5408(7)	4113(5)	51(2)
O(3)	3153(18)	612(15)	2622(14)	58(5)
O(3')	3209(21)	687(18)	2216(15)	70(6)
O(4)	2861(13)	-608(13)	1951(8)	113(5)
O(5)	4805(11)	-847(11)	2145(9)	101(4)
O(6)	3229(15)	-1008(11)	3233(8)	112(5)
C(1)	1787(9)	2412(9)	3710(7)	38(2)
C(2)	1147(9)	4744(8)	3750(6)	34(2)
C(3)	2604(9)	4104(10)	1938(6)	41(2)
C(11)	68(8)	3604(8)	1792(6)	32(2)
C(12)	785(10)	2525(10)	1769(7)	46(3)
C(13)	840(11)	2090(12)	1148(8)	57(3)
C(14)	239(11)	2720(12)	494(7)	54(3)
C(15)	-441(11)	3773(11)	502(7)	47(3)
C(16)	-520(9)	4224(9)	1141(6)	35(2)
C(21)	-1032(8)	3602(8)	3494(5)	28(2)
C(22)	-1279(9)	2682(8)	3515(6)	37(2)
C(23)	-1962(9)	2228(9)	4212(7)	42(2)
C(24)	-2393(10)	2677(9)	4881(7)	43(2)
C(25)	-2140(9)	3623(9)	4863(6)	37(2)
C(26)	-1481(9)	4090(9)	4178(6)	37(2)
C(31)	-812(9)	5597(8)	2381(6)	31(2)
C(32)	-187(10)	6336(9)	2113(7)	42(2)
C(33)	-790(12)	7410(10)	1857(8)	52(3)
C(34)	-2072(12)	7764(10)	1885(7)	51(3)
C(35)	-2694(11)	7023(9)	2158(7)	46(3)
C(36)	-2090(9)	5929(9)	2414(7)	41(2)
C(41)	4192(8)	4599(8)	3410(6)	29(2)
C(42)	3663(9)	5588(8)	2943(6)	35(2)
C(43)	3911(10)	6502(9)	2960(7)	40(2)
C(44)	4688(9)	6445(9)	3452(7)	41(2)
C(45)	5232(9)	5450(10)	3918(7)	43(3)
C(46)	4977(8)	4536(9)	3913(6)	34(2)
C(51)	5192(8)	2663(9)	2759(6)	35(2)
C(52)	6288(9)	2947(10)	2506(7)	42(2)
C(53)	7277(10)	2347(10)	2001(8)	53(3)
C(54)	7186(11)	1511(12)	1767(9)	65(4)
C(55)	6131(12)	1215(11)	2022(9)	63(4)
C(56)	5138(10)	1803(10)	2521(8)	48(3)
C(61)	3952(10)	2599(9)	4427(6)	37(2)
C(62)	4963(12)	1698(10)	4597(8)	52(3)
C(63)	5012(15)	1141(11)	5395(9)	68(4)
C(64)	4100(15)	1451(12)	6018(8)	63(4)
C(65)	3102(14)	2357(14)	5847(7)	66(4)
C(66)	3017(11)	2911(12)	5062(7)	55(3)
C(71)	3066(10)	4389(14)	1078(7)	66(4)

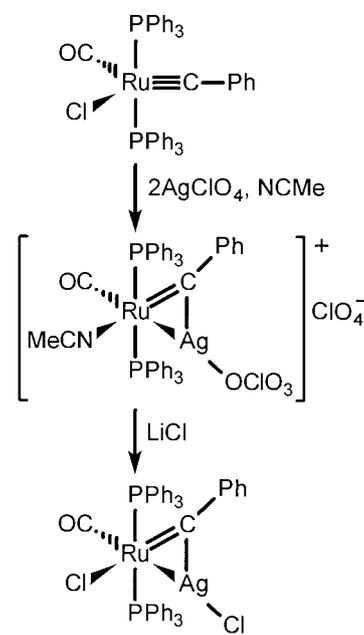
Table 3 (continued)

	<i>x</i>	<i>y</i>	<i>z</i>	$U(\text{eq})$
C(72)	3011(12)	5491(15)	762(8)	74(5)
C(73)	3430(16)	5806(22)	-76(12)	122(11)
C(74)	3851(15)	5119(25)	-574(10)	113(10)
C(75)	3916(13)	4020(25)	-288(8)	111(9)
C(76)	3540(11)	3617(19)	562(7)	79(6)
C(77)	3642(13)	2556(17)	846(9)	74(5)
C(78)	4115(15)	1881(21)	304(10)	104(7)
C(79)	4480(24)	2159(29)	-489(16)	138(12)
C(80)	4397(17)	3218(29)	-801(11)	127(12)
C(81)	400(19)	9090(16)	3341(13)	95(6)
C(82)	8256(44)	726(37)	-626(26)	201(16)

Os(1)–C(1) = 132.0(5)°, and C(3)–Os(1)–C(2) = 127.8(5)°.

## 2.2. Addition of $\text{AgClO}_4$ to the ruthenium carbyne-containing complex **3** to form **9**, and formation of **10** from **9** through treatment with lithium chloride

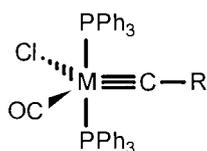
Addition of CO and  $\text{AgClO}_4$  to  $\text{Ru}(\equiv\text{CPh})\text{Cl}(\text{CO})(\text{PPh}_3)_2$  (**3**) yields the cationic complex  $[\text{Ru}(\equiv\text{CPh})(\text{CO})_2(\text{PPh}_3)_2]\text{ClO}_4$ . Treatment of  $\text{Ru}(\equiv\text{CPh})\text{Cl}(\text{CO})(\text{PPh}_3)_2$  (**3**) with two equivalents of  $\text{AgClO}_4$  in the presence of acetonitrile only yields the purple complex  $[\text{Ru}(\equiv\text{CPh}\{\text{AgOClO}_3\})(\text{NCMe})(\text{CO})(\text{PPh}_3)_2]\text{ClO}_4$  (**9**) (CAUTION, see Section 3) as depicted in Scheme 2. In contrast, the ruthenium 1-naphthyl carbyne derivative (**4**) failed to give a tractable complex upon the addition of  $\text{AgClO}_4$  under the same conditions. Treatment of **9** with LiCl gives the olive green complex



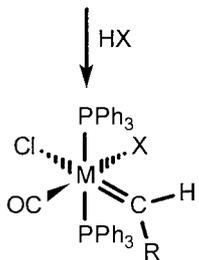
$\text{Ru}(\equiv\text{CPh}\{\text{AgCl}\})\text{Cl}(\text{CO})(\text{PPh}_3)_2$  (**10**). Similar reactivity has been observed on treatment of  $\text{Os}(\equiv\text{CR})\text{Cl}(\text{CO})(\text{PPh}_3)_2$  ( $\text{R} = \text{Ph}$ , *p*-tolyl) with  $\text{AgClO}_4$  and then with  $\text{LiCl}$  [7].

### 2.3. Electrophilic addition of HX to the neutral carbyne-containing complexes 1–4 to form 11–16

Whereas the carbyne carbon atoms in the cationic complexes **5**, **6**, **7**, and **8** are not susceptible to electrophilic attack, the neutral carbyne complexes **1**, **2**, **3** and **4** are readily protonated at the carbyne carbon atom to form the corresponding carbene-containing complexes (see Scheme 3).  $^1\text{H}$  NMR spectroscopy proved to be a valuable technique in characterising the complexes **11**–**16**. The resonance of the hydrogen attached to the carbene carbon appears between 17–19 ppm for each of these complexes. These chemical shift positions are significantly downfield from the triphenylphosphine and naphthyl proton envelope which is recorded between 7–8 ppm in each case. The hydrogen attached to the carbene carbon appears as a triplet signal, through coupling to the two triphenylphosphine phosphorus atoms. The  $^{13}\text{C}$  NMR spectra of these complexes shows the carbene carbon atoms as triplet signals in the region 283–291 ppm. In each case the carbene carbon resonances appear further upfield than the resonances of the corresponding carbyne carbon atoms in the precursor carbyne complexes although they are still significantly further downfield than the resonances of the CO ligands



- (1)  $\text{M} = \text{Os}$ ,  $\text{R} = 1\text{-naphthyl}$   
 (2)  $\text{M} = \text{Os}$ ,  $\text{R} = 2\text{-naphthyl}$   
 (3)  $\text{M} = \text{Ru}$ ,  $\text{R} = \text{Ph}$   
 (4)  $\text{M} = \text{Ru}$ ,  $\text{R} = 1\text{-naphthyl}$



- (11)  $\text{M} = \text{Os}$ ,  $\text{X} = \text{Cl}$ ,  $\text{R} = 1\text{-naphthyl}$   
 (12)  $\text{M} = \text{Os}$ ,  $\text{X} = \text{Cl}$ ,  $\text{R} = 2\text{-naphthyl}$   
 (13)  $\text{M} = \text{Ru}$ ,  $\text{X} = \text{Cl}$ ,  $\text{R} = \text{Ph}$   
 (14)  $\text{M} = \text{Ru}$ ,  $\text{X} = \text{Cl}$ ,  $\text{R} = 1\text{-naphthyl}$   
 (15)  $\text{M} = \text{Os}$ ,  $\text{X} = \text{ClO}_4$ ,  $\text{R} = 1\text{-naphthyl}$   
 (16)  $\text{M} = \text{Os}$ ,  $\text{X} = \text{F}$ ,  $\text{R} = 1\text{-naphthyl}$

Scheme 3.

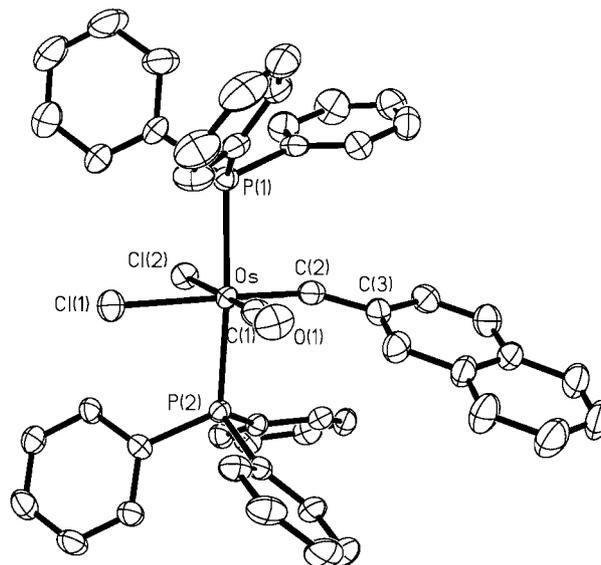


Fig. 2. The molecular structure of  $\text{Os}(\text{=CH-2-naphthyl})\text{Cl}_2(\text{CO})(\text{PPh}_3)_2$  (**12**).

in the same molecules.  $\text{FAB}^+$  mass spectra of these complexes showed a parent peak corresponding to loss of the X group in each instance rather than a molecular ion peak. The reaction of HX with these naphthyl complexes proceeds in a similar manner to that previously observed for the corresponding *p*-tolyl complexes. The single crystal X-ray structure of  $\text{Os}(\text{=CH-2-naphthyl})\text{Cl}_2(\text{CO})(\text{PPh}_3)_2$  was determined and this shows an octahedral geometry about the osmium centre (see Fig. 2). The metal–C(carbene) distance is 1.930(7) Å and the naphthyl ring is 22 degrees out of the plane formed by the other equatorial ligands of the metal complex. The Os–Cl(1) distance (2.503(2) Å) is almost 0.05 Å longer than the Os–Cl(2) distance (2.458(2) Å), and this reflects the larger *trans*-influence of the carbene ligand. The structural parameters of this complex compare favourably with those previously reported for  $\text{Os}(\text{=CHPh})\text{Cl}_2(\text{CO})(\text{PPh}_3)_2$  which has a metal–C(carbene) distance of 1.94(1) Å [3]. The molecular structure of  $\text{Os}(\text{=CH-2-naphthyl})\text{Cl}_2(\text{CO})(\text{PPh}_3)_2$  is depicted in Fig. 2 while selected bond lengths and bond angles are listed in Table 4, and atomic coordinates are listed in Table 5.

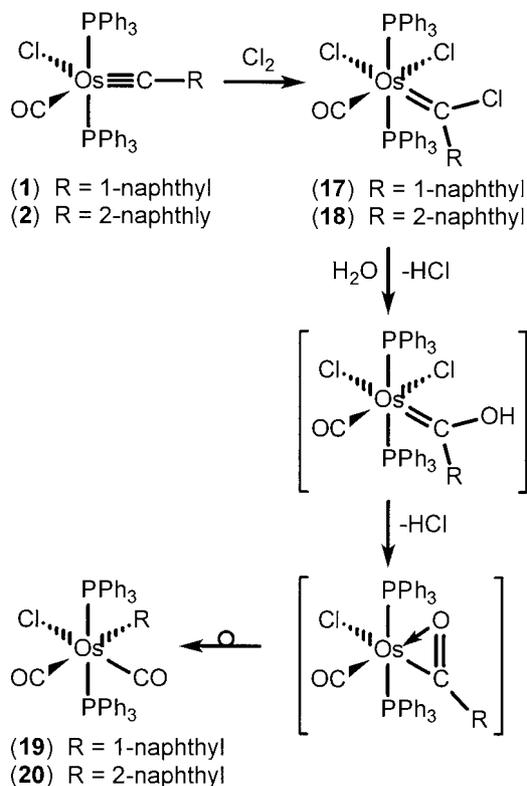
### 2.4. Addition of chlorine to the neutral carbyne-containing complexes 1 and 2 to form the chloro-substituted carbene-containing complexes 17 and 18. Formation of the $\sigma$ -naphthyl complexes 19 and 20 via hydrolysis and rearrangement of 17 and 18

The neutral carbyne-containing complexes **1** and **2** also add chlorine across the  $\text{Os}\equiv\text{CR}$  bond on treatment with  $\text{PhICl}_2$ , to form the carbene-containing complexes **17** and **18**. Subsequent attack at the carbene carbon by

Table 4  
Selected bond lengths (Å) and angles (°) for **12**

Os–C(1)	1.856(7)
Os–C(2)	1.930(7)
Os–P(1)	2.437(2)
Os–P(2)	2.442(2)
Os–Cl(2)	2.458(2)
Os–Cl(1)	2.503(2)
O(1)–C(1)	1.154(8)
C(2)–C(3)	1.477(9)
C(1)–Os–C(2)	95.9(3)
C(1)–Os–P(1)	91.1(2)
C(2)–Os–P(1)	91.0(2)
C(1)–Os–P(2)	95.1(2)
C(2)–Os–P(2)	90.3(2)
P(1)–Os–P(2)	173.46(5)
C(1)–Os–Cl(2)	176.5(2)
C(2)–Os–Cl(2)	87.3(2)
P(1)–Os–Cl(2)	87.48(5)
P(2)–Os–Cl(2)	86.18(5)
C(1)–Os–Cl(1)	85.4(2)
C(2)–Os–Cl(1)	178.3(2)
P(1)–Os–Cl(1)	90.17(6)
P(2)–Os–Cl(1)	88.37(5)
O(1)–C(1)–Os	176.0(6)
C(3)–C(2)–Os	135.0(5)

water results in hydrolysis of the C–Cl bond and after loss of HCl and rearrangement, the corresponding dicarbonyl,  $\sigma$ -bound naphthyl complexes **19** and **20** are



Scheme 4.

Table 5  
Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for **12**.  $U(\text{eq})$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor

	<i>x</i>	<i>y</i>	<i>z</i>	$U(\text{eq})$
Os	7211(1)	8147(1)	1112(1)	22(1)
Cl(1)	8999(1)	8256(1)	1338(1)	35(1)
Cl(2)	7590(1)	7272(1)	649(1)	32(1)
P(1)	6936(1)	7488(1)	1760(1)	27(1)
P(2)	7576(1)	8712(1)	418(1)	23(1)
O(1)	6904(4)	9193(2)	1727(2)	46(1)
C(1)	6992(5)	8798(3)	1482(2)	36(2)
C(2)	5844(5)	8058(3)	919(2)	32(2)
C(3)	4949(5)	8435(3)	928(2)	33(2)
C(4)	4956(5)	9018(3)	1063(2)	38(2)
C(5)	4098(5)	9377(3)	1016(2)	40(2)
C(6)	4131(6)	9983(3)	1139(3)	53(2)
C(7)	3296(7)	10,323(4)	1088(3)	63(2)
C(8)	2406(6)	10,079(4)	917(3)	60(2)
C(9)	2357(6)	9499(4)	793(3)	53(2)
C(10)	3196(5)	9129(3)	836(3)	42(2)
C(11)	3212(6)	8539(4)	703(3)	48(2)
C(12)	4045(5)	8195(3)	749(3)	41(2)
C(21)	6904(5)	7838(3)	2328(2)	30(2)
C(22)	7659(6)	8242(3)	2432(2)	46(2)
C(23)	7673(7)	8507(4)	2866(3)	57(2)
C(24)	6967(8)	8374(4)	3189(3)	59(3)
C(25)	6255(7)	7962(4)	3093(3)	53(2)
C(26)	6222(5)	7689(3)	2667(2)	41(2)
C(31)	5722(5)	7137(3)	1694(2)	30(1)
C(32)	5666(6)	6589(3)	1479(3)	43(2)
C(33)	4748(6)	6328(3)	1405(3)	55(2)
C(34)	3897(6)	6605(4)	1538(3)	51(2)
C(35)	3932(6)	7149(3)	1738(3)	46(2)
C(36)	4843(5)	7415(3)	1809(2)	38(2)
C(41)	7795(5)	6874(3)	1870(2)	31(1)
C(42)	8697(5)	6820(3)	1646(3)	45(2)
C(43)	9343(7)	6366(4)	1768(3)	61(2)
C(44)	9099(7)	5968(4)	2104(3)	63(3)
C(45)	8193(7)	6011(4)	2324(3)	61(2)
C(46)	7539(7)	6466(3)	2211(3)	52(2)
C(51)	8865(4)	8736(3)	211(2)	24(1)
C(52)	9204(5)	9238(3)	–17(2)	32(2)
C(53)	10,144(5)	9239(3)	–219(3)	40(2)
C(54)	10,745(5)	8750(3)	–188(3)	40(2)
C(55)	10,420(5)	8257(3)	38(2)	33(2)
C(56)	9478(5)	8244(3)	239(2)	30(1)
C(61)	6898(4)	8451(3)	–89(2)	25(1)
C(62)	7395(5)	8159(3)	–445(2)	31(1)
C(63)	6860(5)	7909(3)	–809(2)	37(2)
C(64)	5836(6)	7951(3)	–815(3)	40(2)
C(65)	5331(5)	8247(3)	–472(2)	35(2)
C(66)	5869(5)	8491(3)	–115(2)	28(1)
C(71)	7262(5)	9488(3)	490(2)	28(1)
C(72)	6584(5)	9795(3)	226(2)	34(2)
C(73)	6362(6)	10,379(3)	326(3)	47(2)
C(74)	6810(6)	10,653(3)	691(3)	48(2)
C(75)	7506(6)	10,354(3)	955(3)	42(2)
C(76)	7735(5)	9774(3)	851(2)	35(2)
C(79)	9694(7)	9482(4)	2056(3)	68(3)
Cl(3)	10,590(4)	9732(2)	1677(2)	151(2)
Cl(4)	10,209(3)	9269(1)	2567(1)	103(1)
Cl(5)	8787(2)	10,018(2)	2130(1)	103(1)

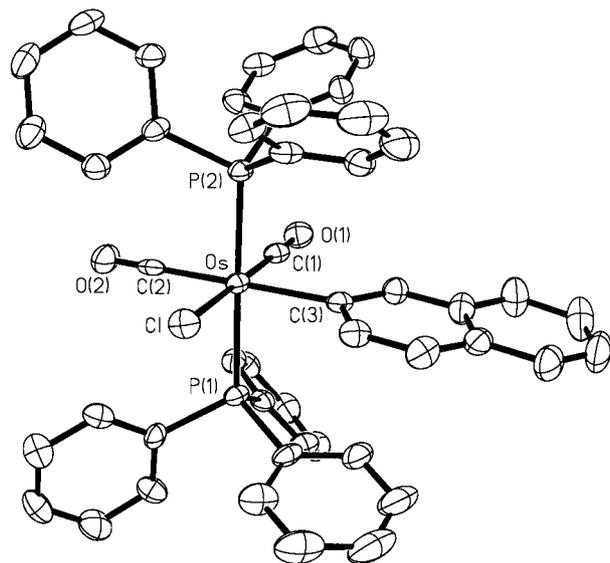


Fig. 3. The molecular structure of  $\text{Os}(2\text{-naphthyl})\text{Cl}(\text{CO})_2(\text{PPh}_3)_2$  (**20**).

formed. These reactions presumably proceed via the hydroxycarbene and acyl intermediates proposed in Scheme 4. Migration of the R group from the acyl ligand to the metal produces the  $\sigma$ -bound naphthyl ligand in the final step. This hydrolysis reaction could provide an alternative route to sterically encumbered  $\sigma$ -aryl complexes of osmium that are difficult to prepare by other routes.

Table 6  
Selected bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ) for **20**

Os–C(1)	1.855(7)
Os–C(2)	1.939(7)
Os–C(3)	2.162(5)
Os–P(2)	2.3846(14)
Os–P(1)	2.396(2)
Os–Cl	2.452(2)
O(1)–C(1)	1.131(8)
O(2)–C(2)	1.118(8)
C(1)–Os–C(2)	89.5(3)
C(1)–Os–C(3)	87.4(3)
C(2)–Os–C(3)	176.4(3)
C(1)–Os–P(2)	90.4(2)
C(2)–Os–P(2)	92.2(2)
C(3)–Os–P(2)	89.6(2)
C(1)–Os–P(1)	93.9(2)
C(2)–Os–P(1)	90.8(2)
C(3)–Os–P(1)	87.6(2)
P(2)–Os–P(1)	174.80(6)
C(1)–Os–Cl	177.5(2)
C(2)–Os–Cl	92.3(2)
C(3)–Os–Cl	90.9(2)
P(2)–Os–Cl	87.82(6)
P(1)–Os–Cl	87.81(6)
O(1)–C(1)–Os	179.0(6)
O(2)–C(2)–Os	175.2(6)

Table 7

Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for **20**.  $U(\text{eq})$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor

	x	y	z	$U(\text{eq})$
Os	2572(1)	5997(1)	6258(1)	21(1)
Cl	2128(1)	4525(1)	6191(1)	33(1)
P(1)	4504(1)	5616(1)	6333(1)	23(1)
P(2)	611(1)	6263(1)	6229(1)	22(1)
O(1)	3019(4)	7800(3)	6372(2)	35(1)
O(2)	2826(4)	6205(4)	4933(2)	43(1)
C(1)	2859(4)	7115(4)	6332(3)	24(1)
C(2)	2706(5)	6099(4)	5413(3)	24(1)
C(3)	2497(5)	5947(4)	7204(2)	24(1)
C(4)	2316(6)	5202(5)	7511(3)	31(2)
C(5)	2349(6)	5137(5)	8108(3)	36(2)
C(6)	2581(7)	5805(5)	8456(3)	35(2)
C(7)	2671(7)	5753(6)	9070(3)	46(2)
C(8)	2932(8)	6442(7)	9393(4)	57(3)
C(9)	3075(9)	7202(7)	9126(4)	59(3)
C(10)	2971(8)	7285(6)	8522(3)	48(2)
C(11)	2736(6)	6570(5)	8171(3)	35(2)
C(12)	2694(6)	6621(5)	7559(3)	28(2)
C(21)	5459(5)	6497(4)	6343(3)	25(1)
C(22)	6331(6)	6585(5)	6734(3)	36(2)
C(23)	7059(6)	7245(6)	6691(4)	42(2)
C(24)	6931(5)	7809(5)	6257(4)	40(2)
C(25)	6047(6)	7738(5)	5861(3)	32(2)
C(26)	5327(5)	7078(5)	5909(3)	28(2)
C(31)	5095(6)	5019(5)	5724(3)	26(2)
C(32)	4458(6)	4607(5)	5325(3)	33(2)
C(33)	4948(7)	4136(6)	4887(4)	44(2)
C(34)	6106(7)	4085(6)	4855(4)	42(2)
C(35)	6754(7)	4509(6)	5257(4)	44(2)
C(36)	6233(7)	4968(5)	5683(4)	35(2)
C(41)	4844(6)	5001(5)	6966(3)	31(2)
C(42)	4943(7)	5368(7)	7524(4)	46(2)
C(43)	5126(8)	4877(9)	7997(5)	62(3)
C(44)	5205(7)	4051(9)	7952(5)	73(4)
C(45)	5092(8)	3665(7)	7411(5)	63(3)
C(46)	4915(7)	4162(6)	6920(4)	44(2)
C(51)	–287(5)	5762(5)	6767(3)	30(2)
C(52)	–197(6)	5950(6)	7357(3)	35(2)
C(53)	–942(7)	5576(7)	7758(4)	51(3)
C(54)	–1707(8)	5016(7)	7573(5)	57(3)
C(55)	–1765(7)	4822(6)	7001(5)	49(2)
C(56)	–1076(6)	5178(5)	6588(4)	34(2)
C(61)	352(4)	7369(4)	6278(3)	23(1)
C(62)	–29(6)	7783(5)	6766(3)	32(2)
C(63)	–181(7)	8613(5)	6761(4)	39(2)
C(64)	31(6)	9067(5)	6263(4)	40(2)
C(65)	418(6)	8665(5)	5766(3)	34(2)
C(66)	590(6)	7842(5)	5772(3)	33(2)
C(71)	–94(5)	5993(5)	5545(3)	27(2)
C(72)	279(6)	5379(5)	5182(3)	30(2)
C(73)	–287(7)	5194(6)	4670(4)	39(2)
C(74)	–1217(7)	5617(6)	4517(3)	40(2)
C(75)	–1622(6)	6231(6)	4881(3)	39(2)
C(76)	–1070(5)	6432(5)	5385(3)	33(2)
O(3)	8718(9)	2882(8)	4569(4)	116(3)
O(4)	–630(11)	7472(8)	8469(5)	143(4)
O(5)	6671(9)	6670(8)	8487(5)	123(4)
O(6)	291(12)	8171(10)	9417(6)	181(6)

The single crystal X-ray structure of Os(2-naphthyl)Cl(CO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (**20**) was determined. The coordination geometry about osmium is best described in terms of an octahedron with two mutually *trans* triphenylphosphine, and two mutually *cis* carbonyl ligands. The Os-(2-naphthyl) bond length of 2.162(5) Å is consistent with a single bond formulation. The naphthyl ring is coplanar with the equatorial plane defined by the atoms C(1), C(2), C(3), and Cl. The molecular structure of Os(2-naphthyl)Cl(CO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> is depicted in Fig. 3 while selected bond lengths and bond angles are listed in Table 6, and atomic coordinates are listed in Table 7.

Preliminary attempts to extend this chemistry to the larger aryl system, anthracenyl, appear to have been successful. Although the anthracenylcarbyne complex Os(≡C-9-anthracenyl)Cl(CO)(PPh<sub>3</sub>)<sub>2</sub> has not been obtained in a pure form, the product obtained after treatment of Os(=CCl<sub>2</sub>)Cl<sub>2</sub>(CO)(PPh<sub>3</sub>)<sub>2</sub> with anthracenyl-lithium showed a distinctively low ν(CO) at 1863 cm<sup>-1</sup> which supports the carbyne formulation. Furthermore, treatment of the crude material with HCl gave the carbene-containing complex Os(=CH-9-anthracenyl)Cl<sub>2</sub>(CO)(PPh<sub>3</sub>)<sub>2</sub> which has been fully characterised by infrared, <sup>1</sup>H NMR, FAB<sup>+</sup> mass spectroscopy and elemental analysis [8].

The chemistry involving the L<sub>n</sub>M≡CR bond that is described here shows that in many ways this bond behaves similarly to the all carbon analogue RC≡CR. In the neutral complexes, M(≡CR)Cl(CO)(PPh<sub>3</sub>)<sub>2</sub>, the M≡C bond is susceptible to electrophilic attack by protons, chlorine, and silver salts just as the C≡C bond is in alkynes. The chemical reactivity of the naphthyl complexes described here is similar to that previously reported for the corresponding *p*-tolyl complexes, however, in a subsequent paper examples will be presented in which the chemistry of the naphthyl carbyne complexes differs significantly from that of their six membered homologues.

### 3. Experimental details

Standard Schlenk techniques were used for all manipulations involving oxygen- or moisture-sensitive compounds. Solvents used were freshly distilled from appropriate drying agents prior to use. When procedures involved materials that were not air-sensitive, solvent removal under reduced pressure was achieved using a rotary evaporator. Routine recrystallisations were achieved by the following method; the sample was dissolved in a low boiling point solvent and a higher boiling point solvent, in which the compound was insoluble was added. Evaporation at reduced pressure effected gradual crystallisation.

Infrared spectra (4000–400 cm<sup>-1</sup>) were recorded on a Bio Rad FTS-7 FTIR spectrophotometer. All spectra were recorded as Nujol mulls or as dichloromethane

solutions between KBr plates. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on Bruker DRX-400 or AC-200 instruments using CDCl<sub>3</sub> as solvent. NMR chemical shifts are recorded in ppm, and coupling constants are recorded in Hertz. All <sup>13</sup>C NMR spectra were recorded in the presence of chromium acetylacetonate which acted as a spin relaxant. As a result the pulse delay (*d*<sub>1</sub>) was decreased to 0.2 s, allowing for a shorter acquisition time. FAB<sup>+</sup> mass spectra were recorded on a VG 7070 spectrometer operating at 70 eV using argon as a source; *m*-nitrobenzyl alcohol was used as the matrix. Analytical data were obtained from the Microanalytical Laboratory, University of Otago. Melting points were determined on a Reichert microscope hot stage and are uncorrected. OsHCl(CO)(PPh<sub>3</sub>)<sub>3</sub> [9], RuHCl(CO)(PPh<sub>3</sub>)<sub>3</sub> [10], Hg(CCl<sub>3</sub>)<sub>2</sub> [11], Os(=CCl<sub>2</sub>)Cl<sub>2</sub>(CO)(PPh<sub>3</sub>)<sub>2</sub> [12], and Ru(=CCl<sub>2</sub>)Cl<sub>2</sub>(CO)(PPh<sub>3</sub>)<sub>2</sub> [13] were prepared by literature methods.

#### 3.1. Os(≡C-1-naphthyl)Cl(CO)(PPh<sub>3</sub>)<sub>2</sub> (**1**)

1-Bromonaphthalene (0.414 ml, 2.96 mmol) was stirred in diethyl ether (3 ml) in a 100 ml round bottom flask and a solution of <sup>n</sup>BuLi in hexanes (1.25 M, 2.37 ml, 1 equivalent) was added at room temperature. Within seconds the pale yellow solution turned dark yellow, and then a white powder crystallised. At this point the round bottom flask was immediately cooled to -40°C. In a Schlenk tube, and at room temperature, Os(=CCl<sub>2</sub>)Cl<sub>2</sub>(CO)(PPh<sub>3</sub>)<sub>2</sub> (1.00 g, 1.11 mmol) was dissolved in thf (30 ml). The resulting orange solution was rapidly transferred by syringe to the 1-naphthyl-lithium suspension. The orange solution immediately turned green or greenish-brown. It was left at -40°C for 5 min and then removed from the cold bath. The solution was allowed to warm up to ca. 0°C over a period of 10 min. A green solid usually precipitated at this point and diethyl ether (50 ml) was then added to ensure complete crystallisation. The green solid was collected by rapid filtration and was washed with water (20 ml), a 1:1 mixture of water-ethanol (20 ml), and finally hexane (20 ml). The product was dried in vacuo, to give pure **1** as a light green microcrystalline solid (900 mg, 88%). m.p. 157°C. *M* = 917.42 g mol<sup>-1</sup>, *m/z* 919.1693 (C<sub>48</sub>H<sub>37</sub>ClOOSp<sub>2</sub> (MH)<sup>+</sup> requires 919.1701). This compound could not be purified sufficiently to obtain satisfactory elemental analysis but all derivatives obtained and described below gave satisfactory elemental analyses. <sup>1</sup>H NMR: 7.0–8.5, unresolved multiplet signals, PPh<sub>3</sub> and 1-naphthyl. <sup>13</sup>C NMR: 321.6, *t*, <sup>2</sup>*J*(CP) = 14.1, *C*(carbyne) 198.8, *t*, <sup>2</sup>*J*(CP) = 10.3, CO.

#### 3.2. Os(≡C-2-naphthyl)Cl(CO)(PPh<sub>3</sub>)<sub>2</sub> (**2**)

2-Bromonaphthalene (1.24 g, 5.98 mmol) and tmeda (7.23 ml, 8 mole equivalents relative to 2-

bromonaphthalene) were added to diethyl ether (20 ml) in a Schlenk tube. In a second Schlenk tube  $\text{Os}(\text{=CCl}_2)\text{Cl}_2(\text{CO})(\text{PPh}_3)_2$  (1.00 g, 1.11 mmol) was dissolved in thf (30 ml). A solution of  $^n\text{BuLi}$  in hexanes (1.25 M, 4.79 ml, 1 mole equivalent relative to 2-bromonaphthalene) was added at room temperature with rapid stirring to the Schlenk tube containing the 2-bromonaphthalene. After 15 s this mixture was cooled to  $-78^\circ\text{C}$ . The 2-naphthyllithium thus formed was titrated rapidly against diphenyl ketone tosylhydrazide (100 mg in thf (3 ml)) [14]. The Schlenk tube was cooled to  $-40^\circ\text{C}$  and 2-naphthyllithium (1.10 mole equivalents relative to  $\text{Os}(\text{=CCl}_2)\text{Cl}_2(\text{CO})(\text{PPh}_3)_2$ ), was added. The initial orange solution turned greenish-brown. After 2 min at  $-40^\circ\text{C}$  the cooling bath was removed and the solution was allowed to warm up to  $0^\circ\text{C}$  over a period of 10 min. The volume of thf was reduced to 10 ml under vacuum, and diethyl ether (50 ml) was added to afford crystallisation of a bright green microcrystalline solid. This was collected by filtration and washed with water (20 ml), a 1:1 mixture of water–ethanol (20 ml), and hexanes (20 ml). The product was dried in vacuo to give pure **2** as a bright green microcrystalline solid (920 mg, 91%). m.p.  $150^\circ\text{C}$ .  $M = 917.42 \text{ g mol}^{-1}$ . This compound could not be purified sufficiently to obtain satisfactory elemental analysis but all derivatives obtained and described below gave satisfactory elemental analyses.  $^1\text{H}$  NMR: 7.0–8.5, unresolved multiplet signals,  $\text{PPh}_3$  and 1-naphthyl.  $^{13}\text{C}$  NMR: 325.6, t,  $^2J(\text{CP}) = 14.1$ , C(carbyne) 198.9, t,  $^2J(\text{CP}) = 10.1$ , CO.

### 3.3. $\text{Ru}(\equiv\text{CPh})\text{Cl}(\text{CO})(\text{PPh}_3)_2$ (**3**)

In a Schlenk tube and at room temperature,  $\text{Ru}(\text{=CCl}_2)\text{Cl}_2(\text{CO})(\text{PPh}_3)_2$  (1.00 g, 1.24 mmol) was dissolved in thf (30 ml). A solution of PhLi (2.00 ml, 1.25 M) was added via a syringe to the orange solution. The orange solution immediately turned greenish-brown. The Schlenk tube was left at  $-78^\circ\text{C}$  for 5 min and then removed from the cold bath. The solution was allowed to warm to ca.  $0^\circ\text{C}$  over a period of 10 min. The volume of thf was then reduced to 10 ml under reduced pressure and diethyl ether (50 ml) was added. A light brown solid was collected by rapid filtration and washed with water (20 ml), a 1:1 mixture of water–ethanol (20 ml), ethanol (20 ml) and finally hexane (20 ml). The product was dried in vacuo to give **3** as a dark green coloured microcrystalline solid, (830 mg, 86%). m.p.  $134^\circ\text{C}$ .  $M = 778.23 \text{ g mol}^{-1}$ . This compound could not be purified sufficiently to obtain satisfactory elemental analysis but all derivatives obtained and described below gave satisfactory elemental analyses.

### 3.4. $\text{Ru}(\equiv\text{C-1-naphthyl})\text{Cl}(\text{CO})(\text{PPh}_3)_2$ (**4**)

1-Bromonaphthalene (0.414 ml, 2.96 mmol) was stirred in diethyl ether (3 ml) in a 100 ml round bottom

flask. A solution of  $^n\text{BuLi}$  in hexanes (1.25 M, 2.37 ml, 1.00 mole equivalent) was added at room temperature. Within seconds the pale yellow solution turned dark yellow, and then a white solid crystallized. At this point the round bottom flask was immediately cooled to  $-78^\circ\text{C}$ .  $\text{Ru}(\text{=CCl}_2)\text{Cl}_2(\text{CO})(\text{PPh}_3)_2$  (1.00 g, 1.24 mmol) was dissolved in thf (30 ml) in a Schlenk tube at room temperature. The orange solution was rapidly transferred by syringe in a single portion to the round bottom flask. The orange solution immediately turned greenish-brown. It was left at  $-78^\circ\text{C}$  for 5 min and then removed from the cold bath. The solution was allowed to warm to ca.  $0^\circ\text{C}$  over a period of 10 min. The volume of thf was then reduced to 10 ml under reduced pressure and diethyl ether (50 ml) was added. A light brown solid was collected by rapid filtration and washed with water (20 ml), a 1:1 mixture of water–ethanol (20 ml), ethanol (20 ml) and finally hexane (20 ml). The product was dried in vacuo to give pure **4** as a bright maize coloured microcrystalline solid, (145 mg, 14%). m.p.  $134^\circ\text{C}$ .  $M = 828.29 \text{ g mol}^{-1}$ . This compound could not be purified sufficiently to obtain satisfactory elemental analysis but all derivatives obtained and described below gave satisfactory elemental analyses.

### 3.5. $[\text{Os}(\text{C-1-naphthyl})(\text{CO})_2(\text{PPh}_3)_2]\text{ClO}_4$ (**5**)

A solution of  $\text{AgClO}_4$  (45.2 mg, 0.220 mmol) in dichloromethane (20 ml) and ethanol (20 ml) was pressurised with CO (4 atm) for 1 min in a carbonylation tube (CAUTION: extreme care should be exercised in the handling of solutions of perchlorates in the presence of oxidisable materials as explosive mixtures could result. Perchlorate salts of oxidisable cations such as **5–8** are also potentially explosive). The pressure was released and  $\text{Os}(\equiv\text{C-1-naphthyl})\text{Cl}(\text{CO})(\text{PPh}_3)_2$  (200 mg, 0.220 mmol) was added rapidly and the vessel re-pressurised with CO (4 atm). The greenish solid dissolved to give a red solution. CO pressure was maintained for 15 min. After filtration through a Celite pad to remove the precipitated AgCl, the solvent volume was cautiously reduced to ca. 20 ml on a rotary evaporator without applying heat, in order to induce crystallisation. After recrystallisation from dichloromethane-ethanol the red crystals were collected by filtration and washed with hexane to give pure **5**, (150 mg, 68%). m.p.  $190^\circ\text{C}$ .  $M = 1009.43 \text{ g mol}^{-1}$ . Anal. Found: C, 55.82; H, 3.32%  $\text{C}_{49}\text{H}_{37}\text{ClO}_6\text{OsP}_2 \cdot 2/3\text{CH}_2\text{Cl}_2$  ( $\text{CH}_2\text{Cl}_2$  evident in the  $^1\text{H}$  NMR spectrum) requires C, 55.96; H, 3.62%.  $^1\text{H}$  NMR: 7.0–8.5, unresolved multiplet signals,  $\text{PPh}_3$  and 1-naphthyl.  $^{13}\text{C}$  NMR: 327.8, t,  $^2J(\text{CP}) = 11.2$ , C(carbyne) 198.9, t,  $^2J(\text{CP}) = 9.5$ , CO. A single crystal suitable for X-ray study (see Section 3.21) was grown from  $\text{CHCl}_3$  and had the formula  $\text{C}_{49}\text{H}_{37}\text{ClO}_6\text{OsP}_2 \cdot 2\text{CHCl}_3$ .

### 3.6. $[Os(\equiv C-2\text{-naphthyl})(CO)_2(PPh_3)_2]ClO_4$ (**6**)

$Os(\equiv C-2\text{-naphthyl})Cl(CO)(PPh_3)_2$  was treated as in 3.05 above to yield pure **6** as red crystals, (140 mg, 64%). m.p. 180°C.  $M = 1009.43 \text{ g mol}^{-1}$   $m/z$  911.1870 ( $C_{49}H_{37}O_2OsP_2$  requires 911.1884). Anal. Found: C, 54.79; H, 3.47%  $C_{49}H_{37}ClO_6OsP_2 \cdot CH_2Cl_2$  ( $CH_2Cl_2$  evident in the  $^1H$  NMR spectrum) requires C, 54.88; H, 3.59%.  $^1H$  NMR: 7.0–8.5, unresolved multiplet signals,  $PPh_3$  and 2-naphthyl.  $^{13}C$  NMR: 331.8, t,  $^2J(CP) = 11.0$ , C(carbyne) 183.0, t,  $^2J(CP) = 9.8$ , CO.

### 3.7. $[Ru(\equiv CPh)(CO)_2(PPh_3)_2]ClO_4$ (**7**)

$Ru(\equiv CPh)Cl(CO)(PPh_3)_2$  was treated as in 3.05 above to yield pure **7** as deep red crystals, (155 mg, 70%). m.p. 144–145°C. Anal. Found: C, 60.92; H, 3.95%  $C_{45}H_{35}ClO_6P_2Ru \cdot 1/3CH_2Cl_2$  ( $CH_2Cl_2$  evident in the  $^1H$  NMR spectrum) requires C, 60.60; H, 4.00%.

### 3.8. $[Ru(\equiv C-1\text{-naphthyl})(CO)_2(PPh_3)_2]ClO_4$ (**8**)

$Ru(\equiv C-1\text{-naphthyl})Cl(CO)(PPh_3)_2$  was treated as in 3.05 above to yield pure **8** as deep red crystals, (180 mg, 81%). m.p. 161°C.  $M = 920.30 \text{ g mol}^{-1}$   $m/z$  821.1309 ( $C_{49}H_{37}O_2P_2Ru$  requires 821.1312). Anal. Found: C, 61.50; H, 3.88%  $C_{49}H_{37}ClO_6RuP_2 \cdot 1/2CH_2Cl_2$  ( $CH_2Cl_2$  evident in the  $^1H$  NMR spectrum) requires C, 61.75; H, 3.98%.

### 3.9. $[Ru(CPh\{AgOCIO_3\})(NCMe)(CO)(PPh_3)_2]ClO_4$ (**9**)

$Ru(\equiv CPh)Cl(CO)(PPh_3)_2$  (200 mg, 0.260 mmol) was added to a solution of  $AgClO_4$  (54 mg, 0.260 mmol) in dichloromethane (10 ml) and acetonitrile (20 ml) (see CAUTION in Section 3.5). The green starting material yielded a purple emulsion. After stirring the mixture for 30 min the precipitated  $AgCl$  was removed by filtration through a Celite pad. Ethanol (20 ml) was added to the filtrate and the solvent volume was cautiously reduced on a rotary evaporator in order to effect crystallisation. The purple crystals were collected by filtration, recrystallised from dichloromethane-ethanol, and dried in a desiccator to give pure **9**, (210 mg, 75%). m.p. 131–132°C.  $M = 1090.60 \text{ g mol}^{-1}$ . Anal. Found: C, 49.22; H, 3.53; N, 1.85%  $C_{46}H_{38}AgCl_2NO_9P_2Ru \cdot 0.5MeCN \cdot 2H_2O$  requires C, 49.21; H, 3.82; N, 1.83%.

### 3.10. $Ru(CPh\{AgCl\}Cl(CO)(PPh_3)_2)$ (**10**)

$[Ru(CPh\{AgOCIO_3\})(MeCN)(CO)(PPh_3)_2]ClO_4$  (100 mg, 0.110 mmol) was dissolved in a mixture of dichloromethane (20 ml) and ethanol (10 ml) containing

$LiCl$  (47 mg, 1.10 mmol, 10 mole equivalents). The resulting olive-green product was removed by filtration and recrystallised twice from dichloromethane-ethanol to give pure **10** as an olive-green microcrystalline solid, (54 mg, 65%). m.p. 150°C.  $M = 921.55 \text{ g mol}^{-1}$ . Anal. Found: C, 55.20; H, 3.53%  $C_{44}H_{35}AgCl_2P_2ORu \cdot 1/2CH_2Cl_2$  ( $CH_2Cl_2$  evident in the  $^1H$  NMR spectrum) requires C, 55.44; H, 3.76%.

### 3.11. $Os(\equiv CH-1\text{-naphthyl})Cl_2(CO)(PPh_3)_2$ (**11**)

$Os(\equiv C-1\text{-naphthyl})Cl(CO)(PPh_3)_2$  (200 mg, 0.220 mmol) was added to a solution of concentrated  $HCl$  (1 ml) in ethanol (15 ml) and dichloromethane (15 ml). The solution was stirred for 1 min and then the solvent volume reduced to ca. 16 ml on a rotary evaporator to induce crystallisation. Recrystallisation was performed from dichloromethane:ethanol to yield reddish black crystals of pure **11** (160 mg, 77%). m.p. 237–239°C.  $M = 953.88 \text{ g mol}^{-1}$   $m/z$  919 ( $M-Cl$ ). Anal. Found: C, 58.09; H, 3.52%  $C_{48}H_{38}Cl_2OOSp_2 \cdot 1/2CH_2Cl_2$  ( $CH_2Cl_2$  evident in the  $^1H$  NMR spectrum) requires C, 58.47; H, 3.95%.  $^1H$  NMR: 19.6, t, 1H,  $^3J(PH) = 2.2$  ( $=CH$ ); 7.0–8.5, unresolved multiplet signals,  $PPh_3$  and 1-naphthyl.  $^{13}C$  NMR: 283.2, t,  $^2J(CP) = 9.0$  C(carbene); 178.3, t,  $^2J(CP) = 8.4$ , CO.

### 3.12. $Os(\equiv CH-2\text{-naphthyl})Cl_2(CO)(PPh_3)_2$ (**12**)

$Os(\equiv C-2\text{-naphthyl})Cl(CO)(PPh_3)_2$  (200 mg, 0.220 mmol) was treated as above to yield reddish crystals of pure **12** (140 mg, 67%). m.p. 157–158°C.  $M = 953.88 \text{ g mol}^{-1}$   $m/z$  919 ( $M^+-Cl$ ). Anal. Found: C, 60.43; H, 4.44%  $C_{48}H_{38}Cl_2OOSp_2$  requires C, 60.44; H, 4.02%.  $^1H$  NMR: 18.4, t, 1H,  $^3J(PH) = 2.8$  ( $=CH$ ); 7.0–8.5, unresolved multiplet signals,  $PPh_3$  and 2-naphthyl.  $^{13}C$  NMR: 291.3, t,  $^2J(CP) = 8.1$ , C(carbene) 178.0, t,  $^2J(CP) = 8.4$ , CO. A single crystal suitable for X-ray study (see Section 3.21) was grown from  $CHCl_3$  and had the formula  $C_{48}H_{38}Cl_2OOSp_2 \cdot CHCl_3$ .

### 3.13. $Ru(\equiv CHPh)Cl_2(CO)(PPh_3)_2$ (**13**)

$Ru(\equiv CPh)Cl(CO)(PPh_3)_2$  (200 mg, 0.220 mmol) was treated as above to yield reddish crystals of pure **13** (160 mg, 68%). m.p. 168–169°C. Anal. Found: C, 62.63; H, 4.22%  $C_{44}H_{36}Cl_2ORuP_2 \cdot 1/2CH_2Cl_2$  ( $CH_2Cl_2$  evident in the  $^1H$  NMR spectrum) requires C, 62.36; H, 4.35%.

### 3.14. $Ru(\equiv CH-1\text{-naphthyl})Cl_2(CO)(PPh_3)_2$ (**14**)

$Ru(\equiv C-1\text{-naphthyl})Cl(CO)(PPh_3)_2$  (200 mg, 0.220 mmol) was treated as above to yield reddish crystals of pure **14** (180 mg, 86%). m.p. 165–166°C.  $M = 864.75$

g mol<sup>-1</sup> Anal Found: C, 64.63; H, 4.46% C<sub>48</sub>H<sub>38</sub>Cl<sub>2</sub>ORuP<sub>2</sub> · 1/2CH<sub>2</sub>Cl<sub>2</sub> (CH<sub>2</sub>Cl<sub>2</sub> evident in the <sup>1</sup>H NMR spectrum) requires C, 64.21; H, 4.33%. <sup>1</sup>H NMR: 18.1, t, 1H, <sup>3</sup>J(PH) = 2.8 (=CH); 7.0–8.5, unresolved multiplet signals, PPh<sub>3</sub> and 1-naphthyl.

### 3.15. Os(=CH-1-naphthyl)Cl(OClO<sub>3</sub>)(CO)(PPh<sub>3</sub>)<sub>2</sub> (**15**)

Os(≡C-1-naphthyl)Cl(CO)(PPh<sub>3</sub>)<sub>2</sub> (200 mg, 0.220 mmol) was treated as above but with perchloric acid to yield bright orange-yellow crystals of **15** (190 mg, 85%). m.p. 135–136°C. *M* = 1017.88 g mol<sup>-1</sup> *m/z* 919 (M<sup>+</sup>-OClO<sub>3</sub>). Anal Found: C, 54.15; H, 3.69% C<sub>48</sub>H<sub>38</sub>Cl<sub>2</sub>O<sub>5</sub>OsP<sub>2</sub> · 2/3CH<sub>2</sub>Cl<sub>2</sub> (CH<sub>2</sub>Cl<sub>2</sub> evident in the <sup>1</sup>H NMR spectrum) requires C, 54.40; H 3.69%. <sup>1</sup>H NMR: 18.5, s, 1H; 7.0–8.5, unresolved multiplet signals, PPh<sub>3</sub> and 1-naphthyl. <sup>13</sup>C NMR: 277.8, t, <sup>2</sup>J(CP) = 9.0, C(carbene); 180.9, t, <sup>2</sup>J(CP) = 9.1, CO.

### 3.16. Os(=CH-1-naphthyl)ClF(CO)(PPh<sub>3</sub>)<sub>2</sub> (**16**)

Os(≡C-1-naphthyl)Cl(CO)(PPh<sub>3</sub>)<sub>2</sub> (200 mg, 0.220 mmol) was treated as above but with HF to yield light red crystals of **16** (150 mg, 70%). m.p. 158–159°C. *M* = 937.43 g mol<sup>-1</sup> *m/z* 919.1711; (M<sup>+</sup>-F) requires 919.1701. Anal Found: C, 58.50, H 4.21% C<sub>48</sub>H<sub>38</sub>ClFOOsP<sub>2</sub> · 2/3CH<sub>2</sub>Cl<sub>2</sub> (CH<sub>2</sub>Cl<sub>2</sub> evident in the <sup>1</sup>H NMR spectrum) requires C, 58.80, H, 3.99%. <sup>1</sup>H NMR: 17.3, s, 1H; 7.0–8.5, unresolved multiplet signals, PPh<sub>3</sub> and 1-naphthyl. <sup>13</sup>C NMR (CDCl<sub>3</sub>, ppm): 283.6, t, <sup>2</sup>J(CP) = 9.0 C(carbene); 182.3, t, <sup>2</sup>J(CP) = 8.4, CO.

### 3.17. Os(=CCl-1-naphthyl)Cl<sub>2</sub>(CO)(PPh<sub>3</sub>)<sub>2</sub> (**17**)

Os(≡C-1-naphthyl)Cl(CO)(PPh<sub>3</sub>)<sub>2</sub> (200 mg, 0.220 mmol) was dissolved in a mixture of dry dichloromethane (20 ml) and benzene (20 ml) to give a green solution. PhICl<sub>2</sub> (60 mg, 1 mole equivalent) was added in small portions over a period of 5 min. The resulting orange solution was decreased in volume to ca. 2 ml under reduced pressure and the product was precipitated by the slow addition of hexanes (30 ml). The light orange crystals were collected by filtration and washed with hexane to give pure **17**, (110 mg, 51%). m.p. 145°C. *M* = 988.33 g mol<sup>-1</sup>. Anal. Found: C, 57.31; H, 4.00% C<sub>48</sub>H<sub>37</sub>Cl<sub>3</sub>OOsP<sub>2</sub> · 1/4CH<sub>2</sub>Cl<sub>2</sub> (CH<sub>2</sub>Cl<sub>2</sub> evident in the <sup>1</sup>H NMR spectrum) requires: C, 57.40; H, 3.73%.

### 3.18. Os[=CCl-2-naphthyl]Cl<sub>2</sub>(CO)(PPh<sub>3</sub>)<sub>2</sub> (**18**)

Os(≡C-2-naphthyl)Cl(CO)(PPh<sub>3</sub>)<sub>2</sub> (200 mg, 0.220 mmol) was treated as above to yield rust red crystals which were collected by filtration and washed with hexane to give pure **18**, (140 mg, 65%). m.p. 150°C.

*M* = 988.33 g mol<sup>-1</sup>. Anal. Found C, 62.24 H, 4.01% C<sub>48</sub>H<sub>37</sub>Cl<sub>3</sub>OOsP<sub>2</sub> · 1.5C<sub>6</sub>H<sub>6</sub> requires: C, 61.93; H, 4.19%.

### 3.19. Os(1-naphthyl)Cl(CO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (**19**)

Os(=CCl-1-naphthyl)Cl<sub>2</sub>(CO)(PPh<sub>3</sub>)<sub>2</sub> (200 mg, 0.202 mmol) was dissolved in a mixture of dichloromethane (15 ml) and ethanol (5 ml). Water (2 drops) was added and the mixture heated under reflux on a hot water bath for 5 min. The dichloromethane was removed under reduced pressure on a rotary evaporator to give a colourless solid. This was collected by filtration and after recrystallisation from dichloromethane-ethanol the colourless crystals were collected by filtration, washed with ethanol and dried in vacuo to give pure **19** (90 mg, 48%). m.p. 205–206°C. *M* = 933.42 g mol<sup>-1</sup> *m/z* 906 (M<sup>+</sup>-CO). Anal. Found: C, 56.81; H, 3.71% C<sub>48</sub>H<sub>37</sub>ClO<sub>2</sub>OsP<sub>2</sub> · 1.2CH<sub>2</sub>Cl<sub>2</sub> (CH<sub>2</sub>Cl<sub>2</sub> evident in the <sup>1</sup>H NMR spectrum) requires C, 57.08; H, 3.84%. <sup>1</sup>H NMR: 7.0–8.5, unresolved multiplet signals, PPh<sub>3</sub> and 1-naphthyl.

### 3.20. Os(2-naphthyl)Cl(CO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (**20**)

Os(=CCl-2-naphthyl)Cl<sub>2</sub>(CO)(PPh<sub>3</sub>)<sub>2</sub> (200 mg, 0.202 mmol) was treated as above and the light pink crystals were collected by filtration, washed with ethanol and dried in vacuo to give pure **20**, (150 mg, 80%). m.p. 214–215°C. *M* = 933.42 g mol<sup>-1</sup> *m/z* 934 (M<sup>+</sup>). Anal. Found: C, 58.67, H 4.15% C<sub>48</sub>H<sub>37</sub>ClO<sub>2</sub>OsP<sub>2</sub> · 3/4CH<sub>2</sub>Cl<sub>2</sub> (CH<sub>2</sub>Cl<sub>2</sub> evident in the <sup>1</sup>H NMR spectrum) requires C, 58.72, H 3.89%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm): 7.0–8.5, unresolved multiplet signals, PPh<sub>3</sub> and 2-naphthyl. <sup>13</sup>C NMR: 181.5, t, <sup>2</sup>J(CP) = 5.9, CO; 178.1, t, <sup>2</sup>J(CP) = 7.0, CO. A single crystal suitable for X-ray study (see Section 3.21) was grown from CHCl<sub>3</sub>/EtOH/H<sub>2</sub>O and had the formula C<sub>48</sub>H<sub>37</sub>ClO<sub>2</sub>OsP<sub>2</sub> · 4H<sub>2</sub>O.

### 3.21. X-ray crystal structure determinations

Data were collected on a Nonius CAD-4 diffractometer for **5** and on a Siemens diffractometer for **12** and **20**. Unit cell parameters were obtained by least squares fit to 25 reflections for the CAD-4 data and all reflections with *I* > 10σ(*I*) for the SMART data. The data were corrected for Lorentz and polarisation effects and absorption corrections applied using psi [15] scans for the CAD-4 data and the method of Blessing [16] for the SMART data. Details of the crystal data, intensity data collection parameters and refinement parameters are given in Table 8.

The structures were solved by Patterson and electron density syntheses. Refinement on *F*<sup>2</sup> employed SHELXL-93 [17], minimising the function Σ $w||F_o| -$

Table 8  
Data collection and processing parameters

	5	12	20
Formula	C <sub>49</sub> H <sub>37</sub> ClO <sub>6</sub> OsP <sub>2</sub> · 2CHCl <sub>3</sub>	C <sub>48</sub> H <sub>38</sub> Cl <sub>2</sub> OOSp <sub>2</sub> · CHCl <sub>3</sub>	C <sub>48</sub> H <sub>37</sub> ClO <sub>2</sub> OsP <sub>2</sub> · 4H <sub>2</sub> O
Molecular weight	1248.11	953.95	1005.37
Crystal system	Triclinic	Orthorhombic	Orthorhombic
Space group	P $\bar{1}$	Pbca	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>
<i>a</i> (Å)	11.872(4)	13.4351(3)	11.9515(1)
<i>b</i> (Å)	13.570(6)	22.7767(5)	16.2296(2)
<i>c</i> (Å)	17.413(5)	29.0765(7)	22.7996(1)
$\alpha$ (°)	73.73(3)		
$\beta$ (°)	74.56(3)		
$\gamma$ (°)	68.98(3)		
<i>V</i> (Å <sup>3</sup> )	2470(2)	8897.6(4)	4422.40(7)
<i>Z</i>	2	8	4
<i>d</i> <sub>calc</sub> (g cm <sup>-3</sup> )	1.678	1.602	1.402
<i>F</i> (000)	1236	4256	1888
$\mu$ mm <sup>-1</sup>	3.07	3.27	3.05
Radiation Mo <i>K</i> $\alpha$ (Monochromatic) $\lambda$ Å	0.71073	0.71073	0.71073
Temperature (K)	193	203	203
Diffractometer	Nonius CAD-4	Siemens SMART	Siemens SMART
Scan technique	$\omega/2\theta$	Area detector	Area detector
2 $\theta$ (min–max) (°)	2–52	3.0–56.5	2.5–56.5
<i>h, k, l</i> range	–14 ≤ <i>h</i> ≤ 14 –16 ≤ <i>k</i> ≤ 16 –21 ≤ <i>l</i> ≤ 0	–17 ≤ <i>h</i> ≤ 17 –28 ≤ <i>k</i> ≤ 28 36 ≤ <i>l</i> ≤ 36	–15 ≤ <i>h</i> ≤ 15 –21 ≤ <i>k</i> ≤ 21 –30 ≤ <i>l</i> ≤ 30
No. of reflections ( <i>R</i> <sub>int</sub> )	10,035(0.035)	11,049 (0.078)	10,712 (0.041)
No. of observed reflections <i>I</i> > 2 $\sigma$ ( <i>I</i> )	7408	7116	8741
Crystal size (mm)	0.50 × 0.35 × 0.33	0.38 × 0.22 × 0.05	0.40 × 0.16 × 0.12
<i>A</i> (min–max)	0.710–0.994	0.536–0.877	0.524–0.764
Least squares weights <i>a, b</i>	0.1841, 45.35	0.0385, 69.77	0.0499, 5.20
No. of variables in LS	575	523	503
Goodness of fit on <i>F</i> <sup>2</sup>	1.074	0.935	1.050
Function minimised	$\sum w(F_o^2 - F_c^2)^2$	$\sum w(F_o^2 - F_c^2)^2$	$\sum w(F_o^2 - F_c^2)^2$
<i>R</i> and <i>wR</i> <sup>2</sup> (obs. data)	0.0654, 0.1690	0.0518, 0.0969	0.0446, 0.1051
Flack parameter			
Peak height in final density map			0.003(8)
(min–max)e Å <sup>-3</sup>	3.19–3.15 <sup>a</sup>	+ 1.11–0.103	+ 1.51–1.36
$R = \sum   F_o  -  F_c   / \sum  F_o $	$wR^2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}$		
weight = 1.0/[ $\sigma^2(F_o^2) + a * P^2 + b * P$ ]	$P = (F_o^2 + 2F_c^2) / 3$		

<sup>a</sup>Spurious ripple adjacent to osmium position.

$|F_c|^2$ . Atomic scattering factors were for neutral atoms [18]. After initial isotropic refinement, anisotropic thermal parameters were refined for all non-hydrogen atoms. Hydrogen atoms were placed in calculated positions with an isotropic temperature factor set at 1.2 times that of the attached atom. In the structure determination of **5** one of the perchlorate oxygen atoms was split into two half-atoms, and the chloroform molecules were similarly disordered and each of these chlorines were modelled as two half-chlorines. Weights used in the least squares refinement were  $w = 1/[(\sigma^2(F_o^2) + (aP)^2 + bP)]$  where  $P = [(F_o^2) + 2(F_c^2)]/3$ , and the final values of *a* and *b* are given in Table 8. Final atomic coordinates and selected bond distances and angles for [Os(≡C-1-naphthyl)(CO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>]ClO<sub>4</sub> are given in Tables 3 and 2 while those for Os(=CH-2-

naphthyl)Cl<sub>2</sub>(CO)(PPh<sub>3</sub>)<sub>2</sub> are given in Tables 5 and 4 and those for Os(2-naphthyl)Cl(CO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> are given in Tables 7 and 6, respectively.

Supplementary data comprises hydrogen atom positions, anisotropic thermal parameters, and full listings of bonds and angles. Structure factor tables are available from the authors.

## Acknowledgements

We thank the University of Auckland Research Committee for partial support of this work through grants-in-aid.

## References

- [1] G.R. Clark, K. Marsden, W.R. Roper, L.J. Wright, *J. Am. Chem. Soc.* 102 (1980) 6570.
- [2] G.R. Clark, C.M. Cochrane, K. Marsden, W.R. Roper, L.J. Wright, *J. Organomet. Chem.* 315 (1986) 211.
- [3] W.R. Roper, *J. Organomet. Chem.* 300 (1986) 167.
- [4] G.R. Clark, N.R. Edmonds, R.A. Pauptit, W.R. Roper, J.M. Waters, A.H. Wright, *J. Organomet. Chem.* 244 (1983) C57.
- [5] B.J. Wakefield, *Organolithium Methods*, Academic Press (1988).
- [6] N.Q. Dao, E.O. Fischer, W.R. Wagner, *Angew. Chem. Int. Ed. Engl.* 17 (1978) 50.
- [7] G.R. Clark, C.M. Cochrane, W.R. Roper, L.J. Wright, *J. Organomet. Chem.* 199 (1980) C35.
- [8] S.D. Woodgate, M.Sc. Thesis, The University of Auckland (1994).
- [9] L. Vaska, *J. Amer. Chem. Soc.* 86 (1964) 1943.
- [10] J.W. DiLuzio, L. Vaska, *J. Am. Chem. Soc.* 83 (1961) 1262.
- [11] T.J. Logan, *J. Org. Chem.* 28 (1963) 1129.
- [12] G.R. Clark, K. Marsden, W.R. Roper, L.J. Wright, *J. Am. Chem. Soc.* 102 (1980) 1206.
- [13] A.H. Wright, W.R. Roper, *J. Organomet. Chem.* 233 (1982) C59.
- [14] M.F. Lipton, C.M. Sorensen, A.C. Sadler, *J. Organomet. Chemistry* 186 (1980) 155.
- [15] A.C. North, D.C. Phillips, F.S. Mathews, *Acta Crystallogr. Sect. A* 24 (1968) 351.
- [16] R.H. Blessing, *Acta Crystallogr. A* 51 (1995) 33–38.
- [17] G.M. Sheldrick, Institut für Anorganische Chemie, Universität Göttingen, Germany (1993).
- [18] *International Tables for Crystallography Vol. C, Tables 4.2.6.8 and 6.1.1.4* (1992).