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SYNTHESIS AND SOME REACTIONS OF A TERMINAL CARBYNE COMPLEX OF OSMIUM. CRYSTAL STRUCTURES OF $Os(\equiv CR)Cl(CO)(PPh_3)_2$ AND $\overline{Os(=C[Ag}Cl]R)Cl(CO)(PPh_3)_2$

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Summary

The reaction of two equivalents of LiR (R = *p*-tolyl) with the dichlorocarbene complex $OsCl_2(=CCl_2)(CO)(PPh_3)_2$ gives the carbyne complex $Os(\equiv CR)Cl(CO)(PPh_3)_2$ (I) in good yield. X-ray crystal structure determination shows that I is mononuclear with an $Os\equiv C$ distance of 1.78(2) Å. The $Os\equiv C$ bond reacts with electrophiles rather than nucleophiles. Thus, HCl adds to give the alkylidene complex $OsCl_2(=CHR)(CO)(PPh_3)_2$, Cl_2 forms $OsCl_2(=CClR)(CO)(PPh_3)_2$ and sulphur, selenium and tellurium react to yield to corresponding *dihapto*-chalcoacyls $Os(\eta^2\text{-}\overline{C[X]}R)Cl(CO)(PPh_3)_2$ (X = S, Se, Te). Group Ib metal halides also add to the $Os\equiv C$ bond to form the adducts $\overline{Os(=C[M}X]R)Cl(CO)(PPh_3)_2$ (MX = CuI, AgCl, AuCl). The X-ray crystal structure determination of $\overline{Os(=C[Ag}Cl]R)Cl(CO)(PPh_3)_2$ (II) suggests that this complex can be considered as a dimetallacyclopropene derivative.

Crystals of I are monoclinic, space group $P2_1/n$, a 17.030(2), b 12.774(1), c 18.315(3) Å, β 107.96 (1)°, V 3793.2 Å^3, $Z = 4$, D_m 1.53(1), D_c 1.54. Crystals of II are monoclinic, space group $P2_1/n$, a 13.021(2), b 23.714(2), c 12.999(2) Å, β 90.556(2)°, V 4013.7 Å^3, $Z = 4$, D_m 1.705(5), D_c 1.695. The structures were solved by conventional heavy-atom methods, and refined by full-matrix least-squares employing anisotropic thermal parameters for all non-hydrogen atoms except for the carbon atoms of the phenyl rings. Phenyl hydrogen atoms were included in calculated positions. Final residuals R were 0.040 and 0.037, respectively.

Introduction

The first terminal carbyne complex was reported in 1973 [1]. From that time interest in this class of compounds has remained high, not only because these species are intrinsically interesting, but also because of applications to acetylene metathesis [2] and metal cluster synthesis [3]. However, the range of complexes

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containing this ligand has remained very limited and fully characterized examples before our initial report [4] were confined to Groups Va, VIa and VIIa. The lack of suitable synthetic approaches is undoubtedly responsible for this restricted development.

In a previous communication we reported the synthesis, preliminary X-ray crystal structure, and some reactions of the first fully characterized Group VIII metal carbyne complex, $Os(\equiv CR)Cl(CO)(PPh_3)_2$ (R = *p*-tolyl throughout this paper unless otherwise specified), which was prepared by the action of LiR on the dichlorocarbene complex $OsCl_2(=CCl_2)(CO)(PPh_3)_2$ [4]. A preliminary X-ray crystal structure determination of the AgCl adduct, $Os(=C[AgCl]R)Cl(CO)(PPh_3)_2$, has also been communicated [5]. We now report the details of this work in full.

Results and discussion

Previous routes to carbyne complexes have generally involved modification of alkoxycarbene complexes through reactions with boron trihalides [6] (which may involve halocarbene intermediates) or α-H abstraction reactions from suitable ligands such as neopentyl or benzyl [7]. One example of a vinylmolybdenum compound rearranging to give a carbyne complex has been reported [8] and the novel halocarbyne complexes $Mo(CX)(CO)_2HB(3,5\text{-}Me_2C_3HN_2)_3$ have been prepared in a reaction involving halomethane radicals [9].

Attempts to generate di-*p*-tolylcarbene complexes by reaction of organolithium reagents with the dichlorocarbene complex $OsCl_2(=CCl_2)(CO)(PPh_3)_2$ led unexpectedly to the isolation of a carbyne complex, $Os(\equiv CR)Cl(CO)(PPh_3)_2$. The reaction proceeds in high yield when two equivalents of LiR are used and the reaction is carried out at low temperature. It appears that the reaction does not proceed via prior formation of the chloro-*p*-tolyl-carbene complex $OsCl_2(=CClR)(CO)(PPh_3)_2$ since, when independently synthesized, this compound does not react further with LiR or rearrange to give the carbyne complex [10]. The intermediacy of the chlorocarbyne complex "$Os(\equiv CCl)Cl(CO)(PPh_3)_2$", resulting from lithium–halogen exchange appears an attractive postulate (Scheme 1) although no direct evidence for this intermediate has thus far been obtained. Attempts to isolate such an intermediate through reaction of one equivalent of LiR with $OsCl_2(=CCl_2)(CO)(PPh_3)_2$ were unsuccessful. Only reduced yields of $Os(\equiv CR)Cl(CO)(PPh_3)_2$ could be isolated from such reactions. This suggests that if $Os(\equiv CCl)Cl(CO)(PPh_3)_2$ is an intermediate in this reaction it reacts with LiR faster than does $OsCl_2(=CCl_2)(CO)(PPh_3)_2$. The one chlorocarbyne complex that has recently been isolated is reported to react with LiPh to yield the corresponding phenylcarbyne complex [11].

Spectral data for the complex $Os(\equiv CR)Cl(CO)(PPh_3)_2$ (and all other new compounds reported in this paper) are collected in Tables 1 and 2. Of particular interest in the very low value for $\nu(CO)$ (1864 cm^{-1}), indicating a very electron rich metal centre, and a medium to strong intensity band at 1359 cm^{-1}. This latter band is tentatively assigned to $\nu(Os\equiv C)$ by analogy with the 1315 cm^{-1} band assigned to $\nu(W\equiv C)$ in $W(\equiv CCD_3)Br(CO)_4$ [12].

A single crystal X-ray structure determination (vide infra) shows the molecule to have a distorted trigonal bipyramidal geometry with the two PPh_3 ligands occupying the axial positons. The extremely short Os–C (carbyne) bond distance of 1.78(2)

(*Continued on p. 215*)

TABLE 1

IR DATA (cm^{-1}) FOR OSMIUM COMPLEXES [a]

Compound	ν(CO) [b]	ν(OsCl) [c]	Other bands
$Os(\equiv CR)Cl(CO)(PPh_3)_2$	1864	266	1598m,1172m,813w;1359s(Os≡C)
$OsCl_2(=CHR)(CO)(PPh_3)_2$	1967,1950 [d]	281,256	1596s,1280s,1173s,893w,790w
$[OsCl(OH_2)(=CHR)(CO)(PPh_3)_2]ClO_4 \cdot H_2O$	1940		1597s,1291m,1180m,890w,809w,788w; 1095vs [e] 622m (ClO_4)
$OsCl_2(=CClR)(CO)(PPh_3)_2$	1957	280,257	1598m,1275w,1180m,895w, 800m (C[carbene]-Cl)
$OsCl_2(=C[R]NHR)(CO)(PPh_3)_2$	1960	280,255	3160w (NH); 1596m,1509s,1311w, 1280w,810w,791w
$Os(\eta^2\text{-}C[S]R)Cl(CO)(PPh_3)_2$	1902	273	1600m,1315s,1300s,1293m,1178m, 975w,830m,818m,789w,635w
$Os(\eta^2\text{-}C[Se]R)Cl(CO)(PPh_3)_2$	1927(sh),1911, 1899(sh)	270	1601s,1305s,1293s,1173s,940w,818w
$Os(\eta^2\text{-}C[Te]R)Cl(CO)(PPh_3)_2$	1932(sh),1914, 1902(sh)	270	1599s,1285s,1176m,927w,815w
$Os(=C[CuI]R)Cl(CO)(PPh_3)_2$	1912	255	1595s,1317vs,1174s,810w
$Os(=C[AgCl]R)Cl(CO)(PPh_3)_2$	1911	266	1597s,1320s,1173m,816w
$Os(=C[AuCl]R)Cl(CO)(PPh_3)_2$	1915	268	1597s,1313vs,1173s,810w
$[Os(=C[AgOClO_3]R)(NCMe)(CO)(PPh_3)_2]ClO_4 \cdot 2H_2O$	1939		1595s,1334s;1090s [e],621m (ClO_4)

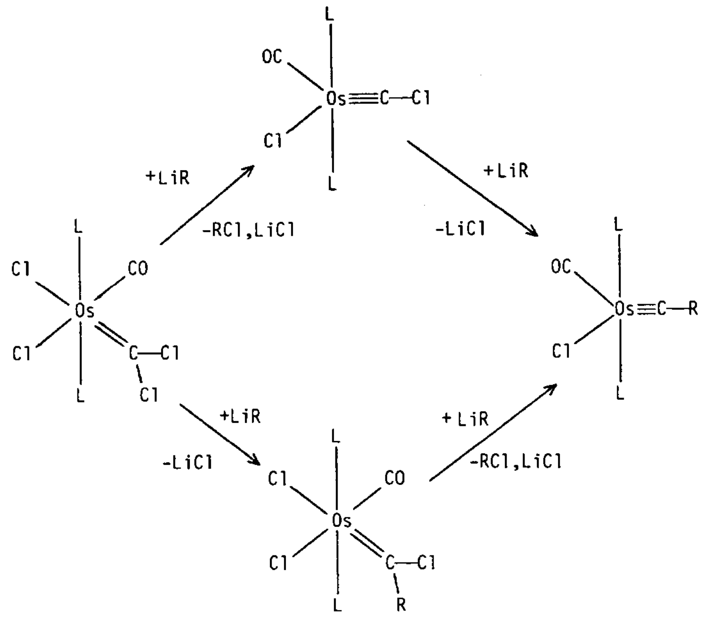
[a] Measured as Nujol mulls. [b] All bands very strong. [c] All bands weak. [d] Solid state splitting. Only one band observed in CH_2Cl_2 solution (1954 cm^{-1}). [e] Broad structured band.

TABLE 2

^{1}H NMR DATA [a] FOR OSMIUM COMPLEXES

Compound	Chemical shifts (δ) and coupling constants (Hz)
$Os(\equiv CR)Cl(CO)(PPh_3)_2$	1.81,s,3H,$C_6H_4CH_3$; 7.00–7.90, m,34H,C_6H_5 and $C_6H_4CH_3$
$OsCl_2(=CHR)(CO)(PPh_3)_2$	1.99,s,3H,$C_6H_4CH_3$; 6.65-8.10,m,34H,$C_6H_4CH_3$ and C_6H_5; 18.05,t,1H,=CHR,^3J(HP) 2.5
$[OsCl(H_2O)(=CHR)(CO)(PPh_3)_2]ClO_4 \cdot H_2O$	1.62,s,4H,H_2O; 2.05,s,3H,$C_6H_4CH_3$; 6.57–7.60,m,34H,$C_6H_4CH_3$ and C_6H_5; 17.04 [b],s,1H,=CHR
$OsCl_2(=CClR)(CO)(PPh_3)_2$	2.21,s,3H,$C_6H_4CH_3$; 6.54–8.00,m,34H,$C_6H_4CH_3$ and C_6H_5
$OsCl_2(=C[R]NHR)(CO)(PPh_3)_2$	2.13,s,3H,$C_6H_4CH_3$; 2.25,s,3H,$C_6H_4CH_3$; 5.40–8.00,m,38H, $C_6H_4CH_3$ and C_6H_5; 11.94,s,1H,NHR
$Os(\eta^2\text{-}C[S]R)Cl(CO)(PPh_3)_2$ [c]	2.10,s,3H,$C_6H_4CH_3$; 6.83,m,4H,$C_6H_4CH_3$; 7.40,m,30H,C_6H_5
$Os(\eta^2\text{-}C[Se]R)Cl(CO)(PPh_3)_2$	8.01,s,3H,$C_6H_4CH_3$; 6.40–7.90,m,34H,$C_6H_4CH_3$ and C_6H_5
$Os(\eta^2\text{-}C[Te]R)Cl(CO)(PPh_3)_2$	1.92,s,3H,$C_6H_4CH_3$; 6.36–7.90,m,34H,$C_6H_4CH_3$ and C_6H_5
$Os(=C[CuI]R)Cl(CO)(PPh_3)_2$	[d]
$Os(=C[AgCl]R)Cl(CO)(PPh_3)_2$	2.13,s,3H,$C_6H_4CH_3$; 6.60–7.84,m,34H,$C_6H_4CH_3$ and C_6H_5
$Os(=C[AuCl]R)Cl(CO)(PPh_3)_2$	[d]
$[Os(=C[AgOClO_3]R)(NCMe)(CO)(PPh_3)_2]ClO_4 \cdot 2H_2O$	1.95,t,3H,$NCCH_3$,^5J(HP) 1.2; 2.23,s,3H,$C_6H_5CH_3$; 2.84,s,4H,H_2O, 6.80–7.60,m,34H,$C_6H_4CH_3$ and C_6H_5

[a] Measured in $CDCl_3$. [b] Broad resonance, coupling to P not resolved. [c] Ref. 18. [d] Too insoluble to obtain a satisfactory spectrum.



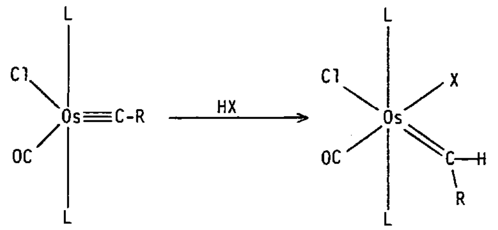
SCHEME 1. Possible mechanisms for the formation of $Os(\equiv CR)Cl(CO)(PPh_3)_2$ (R = *p*-tolyl, L = PPh_3).

Å is consistent with the triple bond formulation. This distance is 0.13 Å shorter than the Os–C (carbonyl) bond length in the same molecule.

Chemically, the Os≡C moiety in $Os(\equiv CR)Cl(CO)(PPh_3)_2$ is found to react with electrophiles rather than nucleophiles. Thus acids, chlorine, sulphur, selenium, tellurium and the Group Ib halides all react at ambient conditions whereas nucleophiles such as amines, carbon monoxide and triphenylphosphine do not. The reactions of each of these classes of compounds will now be considered separately.

(i) Reaction of $Os(\equiv CR)Cl(CO)(PPh_3)_2$ with acids

Addition of aqueous hydrochloric acid in ethanol to a green dichloromethane solution of $Os(\equiv CR)Cl(CO)(PPh_3)_2$ causes the colour to change instantly to bright red. Red crystals of the alkylidene complex, $OsCl_2(=CHR)(CO)(PPh_3)_2$ are obtained in almost quantitative yield on removal of the dichloromethane under reduced pressure (Scheme 2).



SCHEME 2. Reaction of $Os(\equiv CR)Cl(CO)(PPh_3)_2$ with acids (R = *p*-tolyl, L = PPh_3, X = Cl, ClO_4).

The resonance due to the alkylidene proton is observed in the ^1H NMR spectrum as a triplet ($^3J(HP)$ 2.5 Hz) centred at δ 18.05 ppm downfield from TMS. Alkylidene proton resonances are typically observed at low field values [13]. The far IR shows two bands assigned to ν(Os–Cl). The most likely structure is that shown in Scheme 2 and for R = Ph this has been confirmed by crystal structure determination [14]. Surprising features of this compound include lack of reactivity with excess acid, triphenylphosphine or amines. The compound is also air stable.

A similar complex, $OsCl(OClO_3)(=CHR)(CO)(PPh_3)_2 \cdot 2H_2O$, is isolated after reaction with perchloric acid. It seems likely that this compound contains one coordinated water molecule with the ClO_4^- ion and the other water molecule hydrogen bonded to this in the solid state [15]. The compound may thus be more accurately formulated as $[OsCl(OH_2)(=CHR)(CO)(PPh_3)_2]ClO_4 \cdot H_2O$. Complete structural identification will have to await an X-ray crystallographic study. The compound can be converted to $OsCl_2(=CHR)(CO)(PPh_3)_2$ in high yield by reaction with LiCl. It is more reactive than $OsCl_2(=CHR)(CO)(PPh_3)_2$, however, and further chemistry of this compound is currently being explored.

The products derived from the protonation of $Os(\equiv CR)Cl(CO)(PPh_3)_2$ can be contrasted with those obtained from $W(\equiv CH)Cl(PMe_3)_4$ and $Mo(\equiv CCH_2CMe_3)(\eta^5\text{-}C_5H_5)(P[OMe]_3)_2$. The former compex yields a compound best described as a face-protonated methylidyne complex [16], whereas the molybdenum compound yields an hydrido, carbyne complex, $[Mo(\equiv CCH_2CMe_3)H(\eta^5\text{-}C_5H_5)(P[OMe]_3)_2]BF_4$ [8].

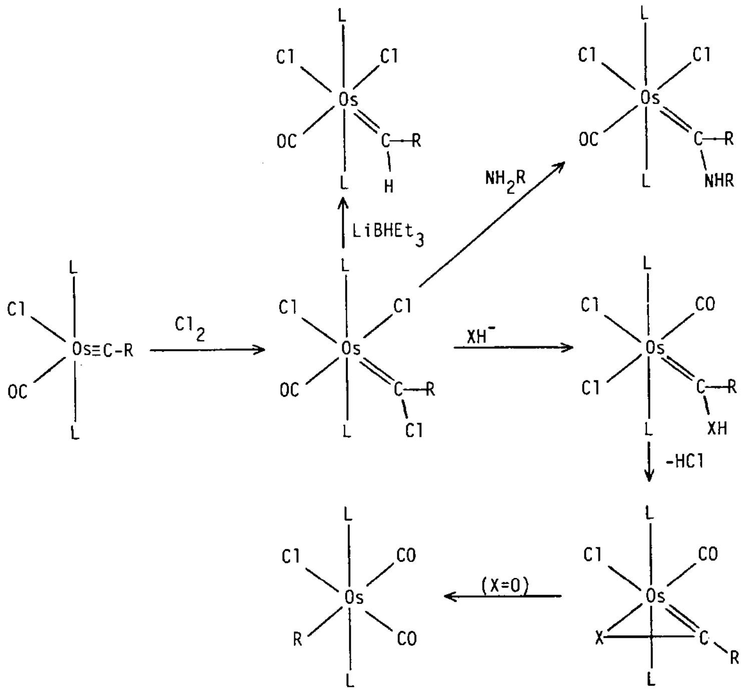
It is currently not known whether protonation of $Os(\equiv CR)Cl(CO)(PPh_3)_2$ occurs at C(carbyne) directly or whether rapid migration onto C(carbyne) follows initial addition to the metal.

(ii) Reaction of $Os(\equiv CR)Cl(CO)(PPh_3)_2$ with chlorine

Addition of one equivalent of chlorine dissolved in carbon tetrachloride to a solution of $Os(\equiv CR)Cl(CO)(PPh_3)_2$ in benzene causes the colour to change instantly from green to orange. Slow addition of dry hexane causes the crystallization of dark orange crystals of the chloro-*p*-tolylcarbene complex $OsCl_2(=CClR)(CO)(PPh_3)_2$. ν(CO) is observed in a position similar to that for the alkylidene complex $OsCl_2(=CHR)(CO)(PPh_3)_2$ and ν(CCl) is assigned to the band at 800 cm^{-1}. As might be expected, the good leaving group Cl^- is easily displaced from the carbene ligand by suitable nucleophiles. A number of new carbene complexes and derived products has thus been synthesised (Scheme 3).

Reaction of $OsCl_2(=CClR)(CO)(PPh_3)_2$ with the hydride transfer reagent $LiBHEt_3$ yields the previously described alkylidene complex $OsCl_2(=CHR)(CO)(PPh_3)_2$. Similarly, on heating with *p*-methylaniline in benzene for a few minutes, the aminocarbene complex $OsCl_2(=C[R]NHR)(CO)(PPh_3)_2$ is formed.

The nucleophiles XH^- (X = S, Se, Te) [17] attack the carbene carbon atom in a similar manner displacing the chloride substituent. The intermediate carbene compexes $OsCl_2(=C[XH]R)(CO)(PPh_3)_2$ readily eliminate HCl and the corresponding *dihapto*-chalcoacyl complexes $Os(\eta^2\text{-}C[X]R)Cl(CO)(PPh_3)_2$ are formed. $Os(\eta^2\text{-}C[S]R)Cl(CO)(PPh_3)_2$ has already been prepared from $OsClR(CO)(CS)(PPh_3)_2$ via a migratory insertion reaction [18]. In constrast, when the nucleophile used is OH^- the *dihapto*-acyl form is not detected, instead further reaction ensues yielding the corresponding rearranged σ-arylcarbonyl complex, $OsClR(CO)_2(PPh_3)_2$. The last



SCHEME 3. Formation and reactions of a chloro-*p*-tolylcarbene complex (L = PPh_3, R = *p*-tolyl, X = O, S, Se, Te).

complex has also been reported previously and the failure of attempts to induce migratory insertion reactions of the CO and *p*-tolyl groups noted [19].

These are the first examples of *dihapto*-selenoacyl and telluroacyl complexes to be reported. The *dihapto* bonding mode is remarkably stable and is retained even in the presence of strongly coordinating neutral ligands such as CO or PPh_3. These same compounds may be prepared by a different route involving the interaction of the carbyne complex, $Os(\equiv CR)Cl(CO)(PPh_3)_2$ with the elemental chalcogens (see below).

(iii) Reaction of $Os(\equiv CR)Cl(CO)(PPh_3)_2$ with the chalcogens, S, Se and Te.

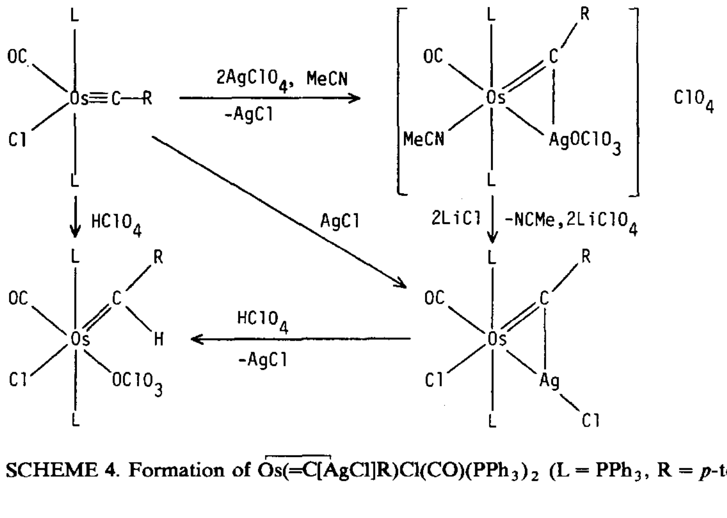
On stirring a benzene solution of $Os(\equiv CR)Cl(CO)(PPh_3)_2$ with elemental sulphur at room temperature the solution slowly turns from green to bright red over a period of a few minutes. Crystals of the red *dihapto*-thioacyl complex, $Os(\eta^2\text{-}C[S]R)Cl\text{-}(CO)(PPh_3)_2$, can be isolated in almost quantitative yield from solution. Reaction with elemental selenium and tellurium proceeds in a similar manner yielding the red-purple $Os(\eta^2\text{-}C[Se]R)Cl(CO)(PPh_3)_2$ and the blue-green $Os(\eta^2\text{-}C[Te]\text{-}R)Cl(CO)(PPh_3)_2$ after 1 and 22 h, respectively. These longer reaction times probably reflect the much lower solubility of selenium and tellurium in benzene.

No reports of the reactions of other carbyne complexes with these chalcogens have, as yet, appeared and so it is not known whether this will be a general reaction. Precedent for this reaction, however, is found in acetylene chemistry. Sulphur atoms are well known to add to carbon–carbon triple bonds producing unsaturated episulphides. If the osmium–carbon triple bond is thought of as having "acetylene-like" character then the thioacyl derivative can be thought of as an unsaturated episulphide derived from the carbyne complex. The acetylene analogy, though simplistic, proves to be a very useful model for understanding many of the reactions of the Os≡C bond in $Os(\equiv CR)Cl(CO)(PPh_3)_2$. Among these is the interaction with the Group Ib metal halides.

(iv) Reaction of $Os(\equiv CR)Cl(CO)(PPh_3)_2$ with Group Ib metal halides.

When a benzene solution of $Os(\equiv CR)Cl(CO)(PPh_3)_2$ reacts with the electrophiles AgCl, CuI or $AuClPPh_3$ at room temperature for a number of hours the corresponding metal halide adducts of the $Os-C_{carbyne}$ triple bond, $Os(=C[AgCl]R)Cl(CO)(PPh_3)_2$, $Os(=C[CuI]R)Cl(CO)(PPh_3)_2$, and $Os(=C[AuCl]R)Cl(CO)(PPh_3)_2$ are formed in high yield. All three compounds have very similar IR spectra (Table 1). The compounds are relatively insoluble and this has precluded ^1H NMR spectral analysis for the last two compounds. However, a single crystal X-ray structure determination has been completed for $Os(=C[AgCl]R)Cl(CO)(PPh_3)_2$ (vide infra) and this confirms the dimetallacyclopropene formulation. The silver atom interacts with the Os≡C bond relatively weakly and is readily cleaved by acids. Thus on reacting this complex with $HClO_4$ the previously described yellow/orange $[OsCl(H_2O)(=CHR)(CO)(PPh_3)_2]ClO_4 \cdot H_2O$ is formed and white AgCl is precipitated.

Silver perchlorate will also react with the Os≡C bond of $Os(\equiv CR)Cl(CO)(PPh_3)_2$. Addition of two equivalents of $AgClO_4$ to a solution of this complex in dichloromethane/acetonitrile results in the precipitation of AgCl and the pink compound isolated from solution is $[Os(=C[AgOClO_3]R)(CO)(NCMe)(PPh_3)_2]ClO_4 \cdot 2H_2O$. Treatment of this compound with LiCl in dichloromethane/ethanol causes the colour to change rapidly to violet and $Os(=C[AgCl]R)Cl(CO)(PPh_3)_2$ is formed in good yield (Scheme 4). This provides a more convenient preparative route for this compound.



SCHEME 4. Formation of $Os(=C[AgCl]R)Cl(CO)(PPh_3)_2$ ($L = PPh_3$, $R = p$-tolyl).

Description of the crystal structures

Single crystal X-ray structure determinations have been carried out for the carbyne complex $Os(\equiv CR)Cl(CO)(PPh_3)_2$ and its silver chloride adduct, $\overline{Os(=C[Ag}Cl]R)Cl(CO)(PPh_3)_2$.

Both complexes are monomeric, with geometries as depicted in Figs. 1 and 2. The carbyne complex adopts a trigonal bipyramidal coordination with *trans*-axial phosphine ligands. In the AgCl adduct the silver atom adds across the Os≡C bond with the covalent Ag–Cl bond projecting away from the metal coordination centre. Addition of AgCl causes only minor changes to the geometry of the remainder of the molecule compared with that of the parent carbyne.

The Os–P(triphenylphosphine) bond lengths are 2.381(4) and 2.392(5) Å in the carbyne and 2.410(1) and 2.410(1) Å in the adduct. These compare well with similar distances for other mutually *trans* triphenylphosphine osmium complexes [18]. The P–Os–P bonds in such *trans*-phosphine complexes frequently bend from linearity to give angles in the range 174–180° or they may be even lower. Crystal packing forces are frequently cited as the reason for such deviations. In the present compounds, the P–Os–P angle in the carbyne is 174.1°, but that in the adduct is 170.0°. Examination of mathematical models reveals that if this latter angle were made equal to 180° the number of intermolecular non-bonded contacts shorter than 3.8 Å would increase from 10 to 25. The most significant reductions in intermolecular contacts

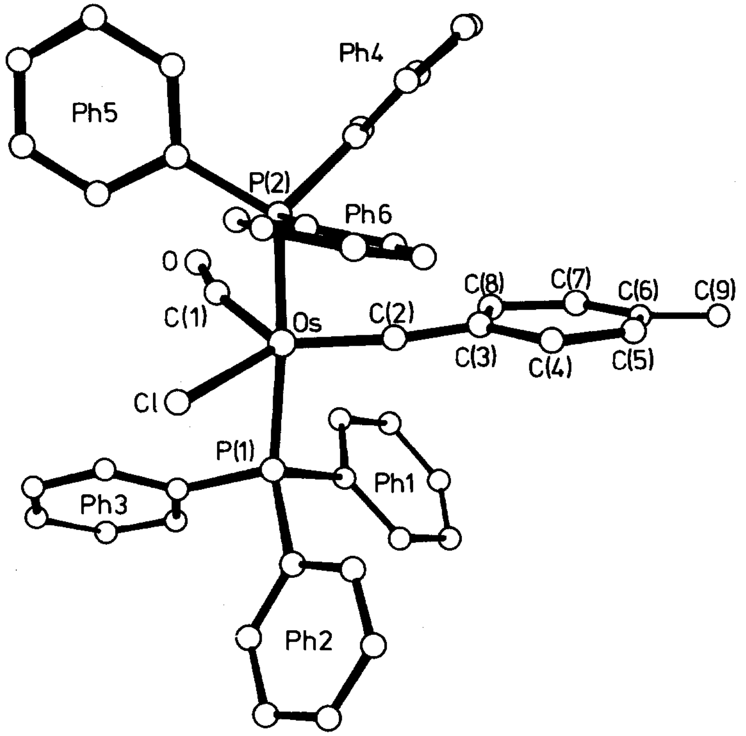


Fig. 1. The molecular geometry and atomic numbering for $Os(\equiv CR)Cl(CO)(PPh_3)_2$ (R = *p*-tolyl).

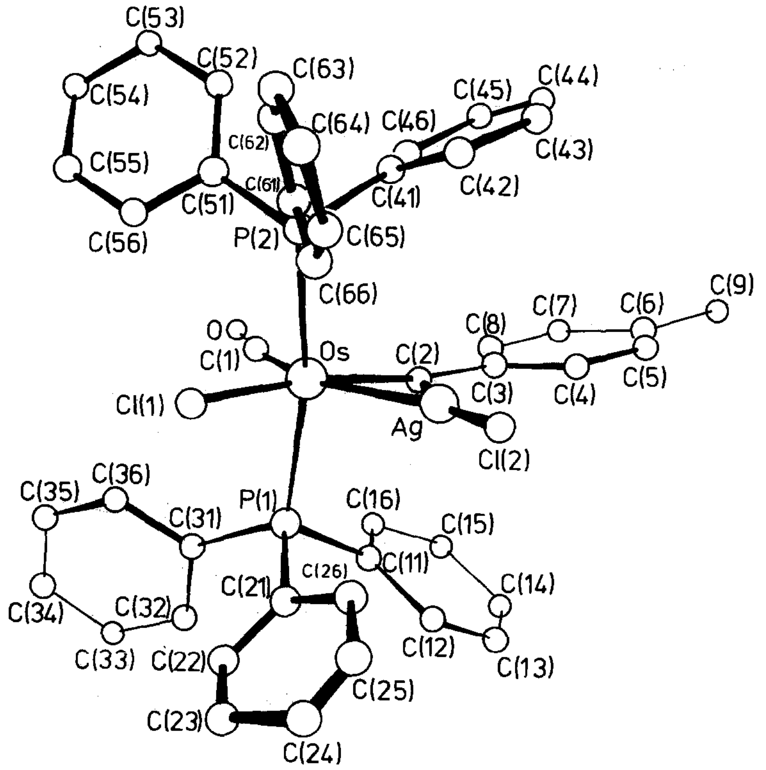


Fig. 2. The molecular geometry and atomic numbering for $\overline{Os(=C[AgCl]}R)Cl(CO)(PPh_3)_2$ (R = *p*-tolyl).

are: C(9) to C(24′), reducing from 3.60 to 3.44 Å; C(24) to C(24′), reducing from 3.68 to 3.56 Å; C(24) to C(25′), reducing from 3.52 to 3.37 Å. Although none of these contact distances is extremely short, it is likely that the observed P–Os–P bending occurs to reduce the effect of such interactions. It can be seen in the stereopair diagram of the AgCl adduct (Fig. 3) that the triphenylphosphine groups are aligned such that phenyl rings 1 and 4 project to the same side of the central coordination plane as the *p*-tolyl constituent of the carbyne, and that ring 4, in particular, is oriented so that it approximately overlaps the *p*-tolyl group. The bending of the P–Os–P bonds are in a direction to reduce this contact.

Although the Os–C–O angle of 170.1(5)° in the AgCl adduct is a considerable deviation from the ideal value of 180°, it is similar to that found in the parent carbyne 166(3)° and lies well within the range of 153 to 179° found in other osmium carbonyl complexes. Os–C–O bends in the plane containing the C(2) and Ag atoms, away from the Cl(1) ligand, towards C(2), making close approaches with C(7) of 3.332(8) Å, C(8) of 3.361(7) Å and C(15) of 3.504(7) Å. This deviation may be due to the effect of the triphenylphosphine ligands leaning towards Cl(1).

The Os–Cl and Os–CO bonds show small but significant differences between the two compounds, with Os–Cl bond lengths of 2.507(4) and 2.488(1) Å, and Os–CO bond lengths of 1.91(2) and 1.844(6) Å in the carbyne and AgCl adduct, respectively. Both sets of bonds are shorter in the adduct. On the other hand the Os–P distances are both slightly longer in the adduct than those in the parent carbyne.

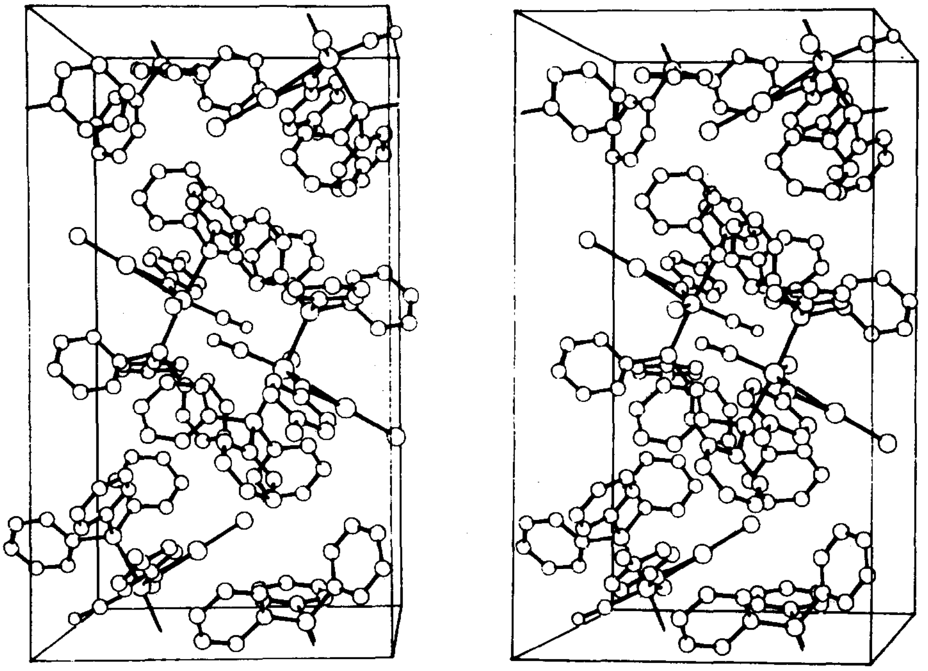


Fig. 3. Stereoview of the molecular packing in $Os(=C[AgCl]R)Cl(CO)(PPh_3)_2$ (R = *p*-tolyl).

The most notable feature of the carbyne complex is the very short Os–C(carbyne) bond length. At 1.78(2) Å, this is fully consistent with an Os–C(carbyne) triple bond formulation.

In the silver chloride adduct this bond increases by 0.06 to 1.839(5) Å. This distance is practically identical to the Os–CO bond length of 1.844(6) Å in the same molecule. The Os–Ag distance of 2.7994(4) Å is longer than the value of 2.67 Å which is expected for a single Os–Ag bond from the sum of the covalent radii of these metals [20]. The Ag–C(carbyne) distance of 2.170(5) Å is longer than the Ag–C(*sp*) σ-bond in $Ag(C{\equiv}CPh)(PMe_3)$ (2.04 Å) [21], but shorter than the Ag–C bond lengths of 2.3–2.4 Å typically found in alkene and alkyne complexes of silver [22]. We therefore believe that the AgCl adduct of the carbyne complex can be viewed as a dimetallacyclopropene complex.

The interaction between Ag^I and Os≡C in this compound can be compared to that between Pt^0 and W≡C in $W(=C[Pt\{PMe_2Ph\}_2]R)(\eta^5\text{-}C_5H_5)(CO)_2$ (R = *p*-tolyl) [23]. Here the Pt–W bond length (2.753(1) Å) is considerably shorter than the distance predicted for a single bond on the basis of the sum of the covalent radii (2.85 Å). The W–C (carbyne) bond increases in length by 0.14 Å (from 1.82 to 1.96(2) Å) upon coordination of Pt^0 and the Pt–C bond length of 2.05 Å is at the short end of the range (1.99(3)–2.15(2) Å) typically found for Pt–C single bonds [24].

Although the two dimetallacycles are both formed by the interaction of a d^{10} metal fragment with a TM≡C triple bond, these results indicate that Pt^0 interacts more strongly with W≡C in $W(=C[Pt\{PMe_2Ph\}_2]R)(\eta^5\text{-}C_5H_5)(CO)_2$ (R = *p*-tolyl) than does the isoelectronic Ag^I with Os≡C in $Os(=C[AgCl]R)Cl(CO)(PPh_3)_2$.

Experimental

Solvents were degassed either by the freeze-thaw method using nitrogen (<6 ppm oxygen) or by passing a stream of nitrogen through the boiling solvent for 10 minutes prior to use. Reactions involving heating under reflux were performed in a nitrogen atmosphere. Characterisation of new compounds was achieved by means of elemental analysis, IR and ^{1}H NMR spectroscopy. Analytical data were obtained from the Microanalytical Laboratory, University of Otago and the services of Professor A.D. Campbell are gratefully acknowledged. IR spectra (4000–200 cm^{-1}) were measured on a Perkin–Elmer 597 spectrometer as nujol mulls or dichloromethane solutions between KBr plates. ^{1}H NMR spectra were recorded on a Varian Associates T60 spectrometer using tetramethylsilane (δ, 0 ppm) as internal calibrant. Melting points (uncorrected) were measured on a Reichert hot-stage microscope. Osmium tetroxide was obtained commercially from Johnson–Matthey Chemicals Limited. $(NH_4)_2[OsCl_6]$ [25], $OsClH(CO)(PPh_3)_3$ [26] and $OsCl_2(=CCl_2)(CO)(PPh_3)_2$ [27] were prepared by literature methods.

$Os(\equiv CR)Cl(CO)(PPh_3)_2$

$OsCl_2(=CCl_2)(CO)(PPh_3)_2$ (1.00 g) was dissolved in a minimum of freshly distilled, dry THF and cooled to -40 °C. A solution of *p*-tolyllithium (2 equiv.) [28] was added dropwise and the resulting solution stirred for 5 min during which time the colour changed from deep orange to dark green/brown and green material crystallized from solution. Freshly distilled diethyl ether (50 ml) was then added dropwise to ensure complete crystallization of the product. This was then rapidly filtered, washed with water, ethanol and finally n-hexane to yield dark green crystals of $Os(\equiv CR)Cl(CO)(PPh_3)_2$ (0.835 g, 85%).The product obtained by this method was of high purity and recrystallization was not normally necessary. The analytical sample was obtained by recrystallization from dry dichloromethane/hexane solution containing diethylamine (ca. 0.02 cm^3 per 0.10 g of product). M.p. 190–191 °C. Anal. Found: C, 61.49; H, 4.55. $C_{45}H_{37}ClOOsP_2$ calcd.: C, 61.32; H, 4.23%.

$OsCl_2(=CHR)(CO)(PPh_3)_2$

$Os(\equiv CR)Cl(CO)(PPh_3)_2$ (0.30 g) was added to a solution of concentrated hydrochloric acid (0.08 cm^3) in ethanol (25 cm^3) and dichloromethane (10 cm^3). The solution was stirred for 1 min and then the dichloromethane removed under reduced pressure. The resulting red product was collected, washed well with ethanol and recrystallized from dichloromethane/ethanol to give red, rectangular platelets (0.30 g, 93%). M.p. 254–255 °C. Anal. Found: C, 57.27; H, 4.35. $C_{45}H_{37}Cl_2OOsP_2$ calcd.: C, 56.76; H, 3.92%.

$[OsCl(OH_2)(=CHR)(CO)(PPh_3)_2]ClO_4 \cdot H_2O$

$Os(\equiv CR)Cl(CO)(PPh_3)_2$ (0.30 g) was treated with perchloric acid (0.08 cm^3) as above. The yellow product was recrystallized from dichloromethane/ethanol to give yellow-orange rectangular crystals (0.29 g, 84%). M.p. 145–146 °C. Anal. Found: C, 52.86; H, 4.52. $C_{45}H_{38}Cl_2O_5OsP_2 \cdot 2H_2O$ calcd.: C, 53.10; H, 4.16%.

$OsCl_2(=CClR)(CO)(PPh_3)_2$

$Os(\equiv CR)Cl(CO)(PPh_3)_2$ (0.20 g) was dissolved in freshly distilled benzene (20 cm^3) and one equivalent of a CCl_4 solution of chlorine was added dropwise. Freshly distilled n-hexane was then added slowly to crystallize the dark orange/red product, (0.192 g, 89%). M.p. 127–128°C. Anal. Found: C, 56.49; H, 4.42. $C_{45}H_{37}Cl_3OOsP_2$ calcd.: C, 56.76; H, 3.92%.

$OsCl_2(=C[R]NHR)(CO)(PPh_3)_2$

$OsCl_2(=CClR)(CO)(PPh_3)_2$ (0.30 g) and p-$NH_2C_6H_4Me$ (0.15 g) were heated under reflux in benzene (40 cm^3) for 7 min. The solution was allowed to cool, ethanol (40 cm^3) was added and the solvent volume lowered under reduced pressure to effect crystallization. The product was collected and recrystallized twice from dichloromethane/ethanol to give white needles (0.15 g, 47%). M.p. 235–237°C. Anal. Found: C, 60.52; H, 4.71; N, 0.80. $C_{52}H_{45}Cl_2NOOsP_2$ calcd.: C, 61.05; H, 4.43; N, 1.37%.

$Os(\eta^2$-$C[S]R)Cl(CO)(PPh_3)_2$

Method (a). $Os(\equiv CR)Cl(CO)(PPh_3)_2$ (0.30 g) and elemental sulphur (0.012 g) were stirred in deoxygenated benzene (40 cm^3) for 15 min. The solution was then filtered through a celite pad, ethanol (30 cm^3) added and the solvent volume lowered under reduced pressure to effect crystallization. The product was collected and recrystallized from dichloromethane/ethanol to yield red crystals (0.30 g, 96%). The product was characterized by comparison of the IR spectrum with that of an authentic sample [18].

Method (b). $OsCl(=CClR)(CO)(PPh_3)_2$ (0.30 g) was dissolved in dichloromethane (10 cm^3) and NaSH solution [17] (1.50 cm^3) added. After stirring for 1 min hexane (30 cm^3) was added and the solvent volume lowered under reduced pressure. The resulting product was collected and purified by column chromatography on silica gel (Riedel de Haen Kieselgel S) using dichloromethane as eluant. The central portion of the red band was collected and after additon of ethanol (15 cm^3) the dichloromethane was removed under reduced pressure to effect crystallization (0.10 g, 32%). The product was characterized by comparison of the IR spectrum with that of an authentic sample [18].

$Os(\eta^2$-$C[Se]R)Cl(CO)(PPh_3)_2$

Method (a). $Os(\equiv CR)Cl(CO)(PPh_3)_2$ (0.30 g) and elemental selenium powder (0.25 g) were stirred in deoxygenated benzene (40 cm^3) for 2.5 h. The solution was then filtered through a celite pad, ethanol (30 cm^3) added and the solvent volume lowered under reduced pressure to effect crystallization. The product was collected and recrystallized from dichloromethane/ethanol to give purple-red needles (0.30 g, 92%). M.p. 248–250°C. Anal. Found: C, 55.80; H, 3.84. $C_{45}H_{37}ClOOsP_2Se$ calcd.: C, 56.28; H, 3.88%.

Method (b). $OsCl_2(=CClR)(CO)(PPh_3)_2$ (0.30 g) was dissolved in dichloromethane (10 cm^3) and NaSeH solution [17] (1.05 cm^3) added. After stirring for 1 min hexane (30 cm^3) was added and the solvent volume lowered under reduced pressure. The resulting product was collected and purified by column chromatography as before to yield purple-red crystals (0.10 g, 33%). The product was identified by comparison of the IR spectrum with that of an authentic sample.

$Os(\eta^2$-$C[Te]R)Cl(CO)(PPh_3)_2$

Method (a). $Os(\equiv CR)Cl(CO)(PPh_3)_2$ (0.30 g) and elemental tellurium powder (0.40 g) were stirred in deoxygenated benzene (40 cm^3) for 21 h. The solution was then filtered through a celite pad, ethanol added, and the solvent volume lowered to effect crystallization. The product was collected and recrystallized from dichloromethane/ethanol to yield deep blue-green flaky crystals (0.27 g, 79%). M.p. 239–240°C. Anal. Found: C, 53.67; H, 3.95. $C_{45}H_{37}ClOOsP_2Te$ calcd.: C, 53.57; H, 3.70%.

Method (b). $OsCl_2(=CClR)(CO)(PPh_3)_2$ (0.30 g) was dissolved in dichloromethane (10 cm^3) and unbuffered NaTeH solution [17] (1.05 cm^3) added. After stirring for 1 min hexane (30 cm^3) was added and the solvent volume lowered under reduced pressure. The resulting product was collected and purified by column chromatography as before to yield blue-green crystals (0.11 g, 35%). The product was characterized by comparison of the IR spectrum with that of an authentic sample.

$[\overline{Os(=C[Ag}OClO_3]R)(NCMe)(CO)(PPh_3)_2]ClO_4 \cdot 2H_2O$

$Os(\equiv CR)Cl(CO)(PPh_3)_2$ (0.50 g) was added to a solution of $AgClO_4$ (0.25 g) in acetonitrile (40 cm^3). After stirring for 30 min the AgCl was removed by filtration through a celite pad, ethanol (40 cm^3) was added to the filtrate and the solvent volume carefully lowered under reduced pressure to effect crystallization. The product was collected and recrystallized from dichloromethane/ethanol to give pink flaky crystals of the aquo solvate $[\overline{Os(=C[Ag}OClO_3]R)(NCMe)(CO)(PPh_3)_2]ClO_4 \cdot 2H_2O$ (0.56 g, 80%). M.p. 139–140°C. Anal. Found: C, 45.96; H, 3.79; N, 1.00. $C_{47}H_{40}AgCl_2NO_9OsP_2 \cdot 2H_2O$ calcd.: C, 45.90; H, 3.61; N, 1.14%.

$Os(=C[AgCl]R)Cl(CO)(PPh_3)_2$

Method (a). $[\overline{Os(=C[Ag}OClO_3]R)(NCMe)(CO)(PPh_3)_2]ClO_4 \cdot 2H_2O$ (0.50 g) was dissolved in dichloromethane (35 cm^3) and a solution of LiCl (0.20 g) in ethanol (25 cm^3) added. The solution was stirred for a few minutes and the dichloromethane then removed under reduced pressure. The resulting pale purple product was collected and recrystallized from dichloromethane/ethanol to give pale purple platelets of the dichloromethane solvate $\overline{Os(=C[Ag}Cl]R)Cl(CO)(PPh_3)_2 \cdot 0.3CH_2Cl_2$ (0.35 g, 82%). ^1H NMR ($CDCl_3$) showed δ 5.27 ppm (s, 0.7H, CH_2Cl_2). M.p. 225–226°C. Anal. Found: C, 51.87; H, 3.80. $C_{45}H_{37}AgCl_2OOsP_2 \cdot 0.3CH_2Cl_2$ calcd.: C, 51.71; H, 3.61%.

Method (b). $Os(\equiv CR)Cl(CO)(PPh_3)_2$ (0.50 g) and freshly precipitated, dry AgCl (0.20 g) were stirred in benzene (60 cm^3) for 24 h. Dichloromethane (80 cm^3) was added and the solution filtered through a celite pad. Ethanol (30 cm^3) was added to the filtrate and the solvent volume lowered under reduced pressure to effect crystallization. The product was collected and recrystallized from dichloromethane/ethanol to give pale purple platelets (0.42 g, 80%). The product was characterized by comparison of the IR spectrum with that of an authentic sample.

$[\overline{Os(=C[Cu}I]R)Cl(CO)(PPh_3)_2$

$Os(\equiv CR)Cl(CO)(PPh_3)_2$ (0.50 g) and CuI (0.20 g) were treated as in method (b) above. Recrystallization from dichloromethane/ethanol gave khaki platelets (0.48 g, 79%). M.p. 235–236°C. Anal. Found: C, 50.73; H, 3.84. $C_{45}H_{37}ClCuIOOsP_2$ calcd.: C, 50.43; H, 3.48%.

[Os(=C[AuCl]R)Cl(CO)(PPh$_3$)$_2$

$Os(\equiv CR)Cl(CO)(PPh_3)_2$ (0.50 g) and $AuCl(PPh_3)$ (0.33 g) were stirred in benzene (50 cm^3) for 2.5 h. The solvent volume was lowered to ca. 25 cm^3 under reduced pressure and the product collected by filtration. Recrystallization from dichloromethane/ethanol afforded pink platelets (0.52 g, 82%). M.p. 264–266°C. Anal. Found: C, 47.93; H, 3.47; P, 5.48. $C_{45}H_{37}AuCl_2OOsP_2$ calcd.: C, 48.53; H, 3.35; P, 5.56%.

X-ray experimental

Preliminary X-ray photography showed that crystals of both compounds belonged to the monoclinic system with systematic absences ($0\ k\ 0$, $k = 2n + 1$; $h\ 0\ l$, $h + l = 2n + 1$) characteristic of space group $P2_1/n$. This space group was retained, in preference to the more conventional $P2_1/c$, in order to keep the beta angles closer to 90°. Lattice constants were derived from least-squares fits to the setting angles of twenty-five reflections on a Nonius CAD-4 diffractometer using graphite-monochromated Mo-K_α radiation.

Intensity data collections employed the $2\theta/\omega$ scan technique with a total background/peak count time ratio of 1/2. The ω scan angle for each reflection was $(0.70 + 0.35\ \tan\theta)$. No attenuators were required and there were no non-statistical variations in the intensities of standard reflections monitored throughout the data collection. Absorption corrections were deemed unnecessary as crystal sizes and linear absorption coefficients were small for both compounds. Details of unit cell parameters and intensity data collection procedures are summarized in Table 3.

Structure determinations and refinements

Both structures were solved using conventional heavy-atom Patterson and elec-

TABLE 3

SUMMARY OF CRYSTAL DATA AND INTENSITY DATA COLLECTIONS FOR $Os(\equiv CR)Cl(CO)(PPh_3)_2$ AND $Os(=C[AgCl]R)Cl(CO)(PPh_3)_2$

Formula	$C_{45}H_{37}ClOOsP_2$	$C_{45}H_{37}Cl_2AgOOsP_2$
Molecular weight	881.3	1023.9
Crystal habit and colour	equant, green	plates, purple
a	17.030(2) Å	13.021(2)
b	12.774(1)	23.714(2)
c	18.315(3)	12.999(2)
β	107.96(1)°	90.556(2)
V	3793.2 Å^3	4013.7
Z	4	4
ρ_c	1.54	1.695
ρ_0	1.53 (aqueous KI)	1.705 (aqueous $ZnBr_2$)
Space group	$P2_1/n$	$P2_1/n$
Crystal size	0.11×0.04×0.05 mm	0.22×0.12×0.04
μ(Mo-K_α)	37.65 cm^{-1}	40.88
Temperature	293 K	292
θ (maximum)	25°	25°
Scan type	$2\theta/\omega$	$2\theta/\omega$
Number of observed data ($I > 3\sigma(I)$)	2131	3898

TABLE 4

ATOMIC POSITIONS FOR $Os(\equiv CR)Cl(CO)(PPh_3)_2$

Atom	x	y	z
Os	0.04151(4)	0.07437(5)	0.29231(4)
Cl	−0.1055(2)	0.1217(3)	0.2238(3)
P(1)	0.0689(2)	0.2560(3)	0.3199(2)
P(2)	0.0004(2)	−0.1011(3)	0.2570(2)
O	0.1449(7)	0.073(1)	0.1911(6)
C(1)	0.101(1)	0.079(1)	0.2196(10)
C(2)	0.094(1)	0.033(1)	0.3878(11)
C(3)	0.155(1)	0.001(1)	0.4578(9)
C(4)	0.235(1)	0.009(2)	0.4674(12)
C(5)	0.292(1)	−0.015(2)	0.542(1)
C(6)	0.268(1)	−0.045(2)	0.5994(10)
C(7)	0.187(1)	−0.057(2)	0.5888(10)
C(8)	0.128(1)	−0.031(2)	0.5196(11)
C(9)	0.328(1)	−0.061(2)	0.6803(11)
C(11)	0.0694(9)	0.342(1)	0.2398(8)
C(12)	0.1246(9)	0.421(2)	0.2457(9)
C(13)	0.1235(11)	0.483(1)	0.1825(10)
C(14)	0.0647(11)	0.468(1)	0.1153(10)
C(15)	0.0094(10)	0.392(1)	0.1086(10)
C(16)	0.0102(10)	0.326(1)	0.1699(10)
C(21)	0.008(9)	0.324(1)	0.3634(8)
C(22)	−0.0252(9)	0.424(2)	0.3459(8)
C(23)	−0.0781(11)	0.473(2)	0.3819(10)
C(24)	−0.1045(11)	0.418(2)	0.4327(10)
C(25)	−0.0827(12)	0.317(2)	0.4496(11)
C(26)	−0.0314(10)	0.269(1)	0.4137(10)
C(31)	0.1731(8)	0.283(1)	0.3876(8)
C(32)	0.2374(10)	0.245(1)	0.3661(9)
C(33)	0.3187(12)	0.266(2)	0.4159(11)
C(34)	0.3275(11)	0.318(2)	0.4798(10)
C(35)	0.2669(11)	0.354(1)	0.5031(10)
C(36)	0.1846(10)	0.336(1)	0.4542(9)
C(41)	−0.0874(9)	−0.143(1)	0.2849(8)
C(42)	−0.0815(10)	−0.161(1)	0.3597(9)
C(43)	−0.1476(10)	−0.192(1)	0.3835(10)
C(44)	−0.2224(11)	−0.206(2)	0.3281(10)
C(45)	−0.2318(11)	−0.187(2)	0.2543(11)
C(46)	−0.1656(11)	−0.154(1)	0.2302(10)
C(51)	0.0813(9)	−0.197(1)	0.3016(8)
C(52)	0.1610(9)	−0.176(1)	0.3047(9)
C(53)	0.2226(10)	−0.248(1)	0.3383(10)
C(54)	0.2069(10)	−0.338(1)	0.3703(10)
C(55)	0.1296(10)	−0.359(1)	0.3647(9)
C(56)	0.0659(8)	−0.292(1)	0.3308(8)
C(61)	−0.0275(9)	−0.133(1)	0.1560(8)
C(62)	−0.0284(10)	−0.237(1)	0.1304(9)
C(63)	−0.0514(11)	−0.263(2)	0.0533(10)
C(64)	−0.0719(1)	−0.187(1)	0.0011(10)
C(65)	−0.0726(10)	−0.086(2)	0.0219(9)
C(66)	−0.0502(9)	−0.057(1)	0.0981(9)

tron density maps, and refined by full-matrix least-squares procedures [29]. Atomic scattering factors and dispersion corrections were from standard listings [30]. The function minimized was $\Sigma w(|F_0|-|F_c|)^2$, with weights w being $4F_0^2/\sigma^2(F_0^2)$. Residuals quoted are $R=\Sigma(|F_0|-|F_c|)/\Sigma|F_0|$ and $R_w=\{\Sigma w(|F_0|-|F_c|)^2/\Sigma w|F_0|^2\}^{1/2}$. Parameters refined in the final least-squares cycles were the positions and anisotropic thermal parameters of all non-hydrogen atoms except for the six phenyl rings of the triphenylphosphine ligands, which were constrained to isotropic values. All hydrogen atoms except those of the methyl groups were included in calculated positions for the structure factor calculations. Final residuals were $R = 0.040$ and $R_w = 0.054$ for Os(≡CR)Cl(CO)(PPh$_3$)$_2$ and $R = 0.037$ and $R_w = 0.037$ for Os(=C[AgCl]R)Cl(CO)(PPh$_3$)$_2$.

Final atomic positions are listed in Tables 4 and 6. The atomic numbering schemes are outlined in Figs. 1 and 2. Bond distances and angles are given in Table 5 and 7. Tables of calculated hydrogen positions, atomic thermal parameters, bond

TABLE 5

BOND LENGTHS (Å) AND ANGLES (degrees) FOR Os(≡CR)Cl(CO)(PPh$_3$)$_2$

Os–Cl	2.507(4)	P(2)–C(61)	1.81(2)
Os–P(1)	2.392(5)	O–C(1)	1.04(2)
Os–P(2)	2.381(4)	C(2)–C(3)	1.44(2)
Os–C(1)	1.91(2)	C(3)–C(4)	1.33(3)
Os–C(2)	1.78(2)	C(3)–C(8)	1.41(3)
P(1)–C(11)	1.84(2)	C(4)–C(5)	1.45(3)
P(1)–C(21)	1.82(2)	C(5)–C(6)	1.30(3)
P(1)–C(31)	1.86(2)	C(6)–C(7)	1.35(3)
P(2)–C(41)	1.81(2)	C(6)–C(9)	1.53(3)
P(2)–C(51)	1.84(2)	C(7)–C(8)	1.40(3)
Cl–Os–P(1)	88.3(2)	Os–C(2)–C(3)	165(2)
Cl–Os–P(2)	85.8(1)	C(2)–C(3)–C(4)	122(2)
Cl–Os–C(1)	108.0(6)	C(2)–C(3)–C(8)	118(2)
Cl–Os–C(2)	133.0(6)	C(4)–C(3)–C(8)	120(2)
P(1)–Os–P(2)	174.1(1)	C(3)–C(4)–C(5)	118(2)
P(1)–Os–C(1)	90.3(7)	C(4)–C(5)–C(6)	123(2)
P(1)–Os–C(2)	94.2(6)	C(5)–C(6)–C(7)	119(2)
P(2)–Os–C(1)	91.0(7)	C(5)–C(6)–C(9)	123(3)
P(2)–Os–C(2)	90.2(6)	C(7)–C(6)–C(9)	118(3)
C(1)–Os–C(2)	118.9(9)	C(6)–C(7)–C(8)	122(2)
Os–P(1)–C(11)	117.5(6)	C(7)–C(8)–C(9)	119(2)
Os–P(1)–C(21)	116.6(6)	P(1)–C(11)–C(12)	124(1)
Os–P(1)–C(31)	113.8(5)	P(1)–C(11)–C(16)	118(1)
Os–P(2)–C(41)	113.8(6)	P(1)–C(21)–C(22)	124(1)
Os–P(2)–C(51)	112.9(5)	P(1)–C(21)–C(26)	119(1)
Os–P(2)–C(61)	116.8(6)	P(1)–C(31)–C(32)	115(1)
C(11)–P(1)–C(21)	103.0(8)	P(1)–C(31)–C(36)	122(1)
C(11)–P(1)–C(31)	100.6(7)	P(2)–C(41)–C(42)	122(1)
C(21)–P(1)–C(31)	103.1(7)	P(2)–C(41)–C(46)	121(1)
C(41)–P(2)–C(51)	104.6(8)	P(2)–C(51)–C(52)	119(1)
C(41)–P(2)–C(61)	104.1(8)	P(2)–C(51)–C(56)	123(1)
C(51)–P(2)–C(61)	103.4(8)	P(2)–C(61)–C(62)	122(1)
Os–C(1)–O	166(3)	P(2)–C(61)–C(66)	123(1)

TABLE 6

ATOMIC POSITIONS FOR $\overline{Os(=C[AgCl]}R)Cl(CO)(PPh_3)_2$

Atom	x	y	z
Os	0.18260(3)	0.05860(2)	0.25839(3)
Ag	0.36364(7)	0.12142(4)	0.27859(7)
Cl(1)	0.1873(2)	0.0462(1)	0.0684(2)
Cl(2)	0.5063(3)	0.1703(2)	0.2229(3)
P(1)	0.2592(2)	−0.0338(1)	0.2678(2)
P(2)	0.0907(2)	0.1447(1)	0.2226(2)
O	−0.0093(6)	0.0110(4)	0.3462(7)
C(1)	0.0614(9)	0.0277(4)	0.3040(9)
C(2)	0.2449(8)	0.0862(6)	0.3755(9)
C(3)	0.2498(8)	0.0991(5)	0.4812(8)
C(4)	0.3265(10)	0.1351(7)	0.5225(10)
C(5)	0.3273(10)	0.1485(7)	0.6281(11)
C(6)	0.2564(10)	0.1284(6)	0.6941(10)
C(7)	0.1818(12)	0.0928(6)	0.6534(10)
C(8)	0.1800(10)	0.0784(5)	0.5503(9)
C(9)	0.2555(14)	0.1457(8)	0.8042(10)
C(11)	0.2969(8)	−0.0512(5)	0.3999(8)
C(12)	0.3997(9)	−0.0562(6)	0.4306(9)
C(13)	0.4214(9)	−0.0663(6)	0.5348(9)
C(14)	0.3472(9)	−0.0713(5)	0.6052(10)
C(15)	0.2458(9)	−0.0664(5)	0.5766(9)
C(16)	0.2208(8)	−0.0566(5)	0.4733(8)
C(21)	0.3727(8)	−0.0449(4)	0.1898(8)
C(22)	0.3811(10)	−0.0896(6)	0.1234(10)
C(23)	0.4705(12)	−0.0964(7)	0.0644(12)
C(24)	0.5496(10)	−0.0602(7)	0.0747(10)
C(25)	0.5429(11)	−0.0159(6)	0.1399(11)
C(26)	0.4537(10)	−0.0076(6)	0.1964(10)
C(31)	0.1735(8)	−0.0909(4)	0.2338(8)
C(32)	0.1847(9)	−0.1455(5)	0.2751(9)
C(33)	0.1209(9)	−0.1879(5)	0.2473(9)
C(34)	0.0448(10)	−0.1798(5)	0.1749(10)
C(35)	0.0311(9)	−0.1270(5)	0.1321(9)
C(36)	0.0948(9)	−0.0826(5)	0.1586(9)
C(41)	0.0895(8)	0.1883(4)	0.3381(8)
C(42)	0.1582(10)	0.2316(6)	0.3515(10)
C(43)	0.1672(11)	0.2587(7)	0.4479(12)
C(44)	0.1041(12)	0.2424(7)	0.5233(12)
C(45)	0.0381(11)	0.1998(6)	0.5142(11)
C(46)	0.0292(9)	0.1709(5)	0.4212(9)
C(51)	−0.0444(8)	0.1353(4)	0.1906(8)
C(52)	−0.1200(8)	0.1738(5)	0.2217(8)
C(53)	−0.2214(10)	0.1661(5)	0.1956(10)
C(54)	−0.2502(9)	0.1200(5)	0.1377(9)
C(55)	−0.1789(10)	0.0821(5)	0.1056(10)
C(56)	−0.0741(8)	0.0881(5)	0.1299(9)
C(61)	0.1400(8)	0.1923(5)	0.1226(8)
C(62)	0.0781(11)	0.2367(6)	0.0889(11)
C(63)	0.1164(11)	0.2759(6)	0.0183(11)
C(64)	0.2146(10)	0.2708(6)	−0.0126(10)
C(65)	0.2781(11)	0.2284(6)	0.0189(11)
C(66)	0.2379(9)	0.1883(5)	0.0872(9)

TABLE 7

BOND LENGTHS (Å) AND ANGLES (degrees) FOR Os(=C[AgCl]R)Cl(CO)$(PPh_3)_2$

Os–Ag	2.7994(4)	P(2)–C(51)	1.819(5)
Os–Cl(1)	2.488(1)	P(2)–C(61)	1.842(5)
Os–P(1)	2.410(1)	O–C(1)	1.146(6)
Os–P(2)	2.410(1)	C(2)–C(3)	1.409(7)
Os–C(1)	1.844(6)	C(3)–C(4)	1.415(8)
Os–C(2)	1.839(5)	C(3)–C(8)	1.375(8)
Ag–Cl(2)	2.311(2)	C(4)–C(5)	1.410(8)
Ag–C(2)	2.170(5)	C(5)–C(6)	1.353(9)
P(1)–C(11)	1.829(5)	C(6)–C(7)	1.388(9)
P(1)–C(21)	1.820(5)	C(6)–C(9)	1.489(8)
P(1)–C(31)	1.806(5)	C(7)–C(8)	1.383(8)
P(2)–C(41)	1.823(5)		
Ag–Os–Cl(1)	97.29(3)	C(41)–P(2)–C(61)	103.9(2)
Ag–Os–P(1)	97.56(3)	C(51)–P(2)–C(61)	104.9(2)
Ag–Os–P(2)	89.02(3)	Os–C(1)–O	170.1(5)
Ag–Os–C(1)	154.8(2)	Os–C(2)–Ag	88.1(2)
Ag–Os–C(2)	50.8(2)	Os–C(2)–C(3)	154.2(4)
Cl(1)–Os–P(1)	85.92(4)	Ag–C(2)–C(3)	117.2(4)
Cl(1)–Os–P(2)	85.73(4)	C(2)–C(3)–C(4)	121.7(5)
Cl(1)–Os–C(1)	107.6(2)	C(2)–C(3)–C(8)	122.4(5)
Cl(1)–Os–C(2)	148.1(2)	C(3)–C(4)–C(5)	120.2(6)
P(1)–Os–P(2)	169.96(4)	C(4)–C(5)–C(6)	122.7(6)
P(1)–Os–C(1)	88.7(2)	C(5)–C(6)–C(7)	116.9(6)
P(1)–Os–C(2)	95.9(2)	C(5)–C(6)–C(9)	121.6(7)
P(2)–Os–C(1)	88.6(2)	C(7)–C(6)–C(9)	121.5(7)
P(2)–Os–C(2)	94.1(2)	C(6)–C(7)–C(8)	121.7(6)
C(1)–Os–C(2)	104.4(2)	C(3)–C(8)–C(7)	122.6(6)
Os–Ag–Cl(2)	156.36(6)	P(1)–C(11)–C(12)	122.3(4)
Os–Ag–C(2)	41.1(1)	P(1)–C(11)–C(16)	118.6(4)
Cl(2)–Ag–C(2)	162.5(2)	P(1)–C(21)–C(22)	122.2(4)
Os–P(1)–C(11)	111.1(2)	P(1)–C(21)–C(26)	119.9(4)
Os–P(1)–C(21)	116.2(2)	P(1)–C(31)–C(32)	122.4(4)
Os–P(1)–C(31)	114.5(2)	P(1)–C(31)–C(36)	122.2(4)
C(11)–P(1)–C(21)	106.2(2)	P(2)–C(41)–C(42)	121.2(4)
C(11)–P(1)–C(31)	102.8(2)	P(2)–C(41)–C(46)	118.5(4)
C(21)–P(1)–C(31)	105.0(2)	P(2)–C(51)–C(52)	122.2(4)
Os–P(2)–C(41)	109.2(2)	P(2)–C(51)–C(56)	118.8(4)
Os–P(2)–C(51)	114.7(2)	P(2)–C(61)–C(62)	118.7(4)
Os–P(2)–C(61)	118.7(2)	P(2)–C(61)–C(66)	121.9(4)
C(41)–P(2)–C(51)	104.0(2)		

distances and angles involving phenyl carbon atoms, and observed and calculated structure factors are available on request from the authors (G.R.C.).

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