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SYNTHESIS, STRUCTURE AND REACTIONS OF A *dihapto*-FORMALDEHYDE COMPLEX, $Os(\eta^2\text{-}CH_2O)(CO)_2(PPh_3)_2$

G.R. CLARK, C.E.L. HEADFORD, K. MARSDEN and W.R. ROPER *
Department of Chemistry, University of Auckland, Auckland (New Zealand)

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Summary

$Os(\eta^2\text{-}CH_2O)(CO)_2(PPh_3)_2$ results from direct reaction of formaldehyde with the zerovalent complex, $Os(CO)_2(PPh_3)_3$. The structure of $Os(\eta^2\text{-}CH_2O)(CO)_2(PPh_3)_2$ was determined by X-ray crystallography. The crystals are triclinic, space group $P\bar{1}$, a 18.739(2), b 11.157(1), c 9.986(1) Å, α 116.70(1), β 93.20(1), γ 107.93(1)°, V 1727.69 Å^3, $Z = 2$, D_m 1.55(2), D_c 1.57 g cm^{-3}. Refinement of atomic parameters was by full-matrix least-squares methods, employing anisotropic thermal parameters for all non-hydrogen atoms except for the carbon atoms of the phenyl rings. The formaldehyde hydrogen atoms were located from difference electron density maps, other hydrogens were included in calculated positions. Final residuals were $R = 0.047$ and $R_w = 0.061$ for 3508 unique observed reflections measured on an automatic diffractometer.

The complex itself is monomeric, although interstices in the crystal lattice are occupied by hydrogen-bonded water dimers which fulfil a purely space-filling role. The osmium is bonded to two mutually *trans* triphenylphosphines, two carbonyls, and the η^2-formaldehyde, in an arrangement which is best described as distorted octahedral. The geometry of the coordinated formaldehyde is characterised by Os—O 2.039(7), Os—C 2.186(8) and C—O 1.584(11) Å. The Os—P bonds are equivalent at 2.372(2) and 2.378(2) Å but the Os—CO bond *trans* to the formaldehyde carbon 1.931(7) Å is longer than that *trans* to the formaldehyde oxygen 1.907(7) Å.

$Os(\eta^2\text{-}CH_2O)(CO)_2(PPh_3)_3$ has proved to be a useful synthetic precursor for stable formyl, hydroxymethyl, methoxymethyl, and halomethyl (CH_2X, X = Cl, Br, I) complexes. The compounds $Os(CHO)H(CO)_2(PPh_3)_2$, $Os(CH_2OH)H(CO)_2(PPh_3)_2$, $Os(CH_2OMe)Cl(CO)_2(PPh_3)_2$ and $Os(CH_2Cl)Cl(CO)_2(PPh_3)_2$ are illustrative of the many compounds which have been characterised. A general synthetic route to neutral formyl osmium complexes, $Os(CHO)X(CO)_2(PPh_3)_2$ (X = halide or alkyl) has been developed from reaction of the cations $[OsX(CO)_3(PPh_3)_2]^+$ with BH_4^-.

Acetaldehyde also reacts with $Os(CO)_2(PPh_3)_3$ forming $Os(\eta^1\text{-}C[O]CH_3)$-

$H(CO)_2(PPh_3)_2$. No reaction was observed with benzaldehyde, and trichloroacetaldehyde affords the cation, $[OsCl(CO)_2(PPh_3)_3]^+$.

Introduction

Over a period of years we have been interested in identifying migratory insertion reactions involving transition metal—hydride bonds and various carbon donor ligands. The production of an iminoformyl ligand from hydride and isocyanide [1] and thioformyl and thioformaldehyde ligands from hydride and thiocarbonyl [2] has already been achieved. The work reported in this paper was begun with a view to extending this interest to the reduction of the carbonyl ligand. A principal aim of this project was the generation of carbon donor ligand types proposed to be intermediates in the metal-catalysed reduction of CO by H_2 and the study of the reactions of these species. The preparation of the versatile synthetic intermediate, $Os(\eta^2\text{-}CH_2O)(CO)_2(PPh_3)_2$, realized this objective and the synthesis, structure determination and further reactions of this compound are detailed in this paper. Preliminary reports of this work have appeared [3,4].

Results and discussion

Previous literature reports of formaldehyde complexes are confined to a compound of reported composition $RuH_2(CH_2O)(PPh_3)_3$, [5], which could not be isolated in an analytically pure form and therefore was not well characterised, and bridging formaldehyde ligands in $(Cp_2ZrCl)_2CH_2O$ [6], and $Cp_2(CO)NbCH_2OZrH(C_5Me_5)_2$ [7].

Preparation of $Os(\eta^2\text{-}CH_2O)(CO)_2(PPh_3)_2$

The mononuclear, zerovalent osmium entity $Os(CO)_2(PPh_3)_2$ has not been isolated as such, but solutions of $Os(CO)_2(PPh_3)_3$ [8,9] must be in equilibrium with small amounts of $Os(CO)_2(PPh_3)_2$ (eq. 1), just as $RhCl(PPh_3)_3$ is in equilibrium with small amounts of $RhCl(PPh_3)_2$ [10] and $Pt(PPh_3)_3$ with $Pt(PPh_3)_2$ [11]. $Os(CO)_2(PPh_3)_2$ forms complexes with many unsaturated molecules including C_2H_4 [12], O_2 [8], S_2 [13], Se_2 [14] and CH_2S [15,2], and there appeared to be no reason, therefore, why CH_2O could not be added to this list.

$$Os(CO)_2(PPh_3)_3 \rightleftharpoons Os(CO)_2(PPh_3)_2 + PPh_3 \qquad (1)$$

When a 40% aqueous formaldehyde solution (approximately 1.5 equivalents) was added to a bright yellow degassed benzene or toluene solution of $Os(CO)_2(PPh_3)_3$ at room temperature decolourization took place over 48 h. The reaction time could be reduced to only a few hours by conducting the reaction under a tungsten-halogen sun-lamp. The reaction temperature was then maintained at ~25°C by cooling the reaction flask since elevated temperatures lead to decomposition products. From the colourless solution could be isolated crystals of composition $Os(\eta^2\text{-}CH_2O)(CO)_2(PPh_3)_2$.

In the IR spectrum of $Os(\eta^2\text{-}CH_2O)(CO)_2(PPh_3)_2$ the two $\nu(CO)$ bands at 1977 and 1902 cm^{-1} are found at positions similar to those found for other

TABLE 1

IR AND ^{1}H NMR DATA FOR RELATED ADDUCTS OF $Os(CO)_2(PPh_3)_2$

Compound	$\nu(CO)$ (cm^{-1})	^{1}H NMR data ($CDCl_3$) (τ)	Ref.
$Os(\eta^2-C_2H_4)(CO)_2(PPh_3)_2$	1955, 1895	9.55, t, 4 H, $^3J(H-P)$ 7 Hz	12
$Os(\eta^2-CH_2O)(CO)_2(PPh_3)_2$	1977, 1902	7.44, t, 2 H, $^3J(H-P)$ 4.0 Hz	
$Os(\eta^2-CH_2S)(CO)_2(PPh_3)_2$	1985, 1915	9.1, t, 2 H, $^3J(H-P)$ 4.6 Hz	2
$Os(\eta^2-O_2)(CO)_2(PPh_3)_2$	1995, 1925		8
$Os(\eta^2-S_2)(CO)_2(PPh_3)_2$	1998, 1944		13

η^2-adducts of $Os(CO)_2(PPh_3)_2$ (see Table 1). The interesting observation can be made from Table 1, that the $\nu(CO)$ bands of the adducts of $Os(CO)_2(PPh_3)_2$ shown, increase with the unsaturated addend according to the series $H_2C{=}CH_2 < O{=}CH_2 < S{=}CH_2 < O_2 < S_2$. This suggests that $O{=}CH_2$ may be a stronger π-acceptor ligand than C_2H_4. As numerous η^2-ethylene adducts of low-valent metal centres are known many η^2-formaldehyde adducts ought to be stable. Indeed, $Pt(\eta^2-CH_2O)(PPh_3)_2$ has been reported recently [16a], the corresponding ethylene adduct, $Pt(\eta^2-C_2H_4)(PPh_3)_2$ has been known for many years. Also the compound $Fe(\eta^2-CH_2O)(CO)_2[P(OMe)_3]_2$ has been described [16b].

Formaldehyde $\nu(CH)$ in $Os(\eta^2-CH_2O)(CO)_2(PPh_3)_2$ occurs at 2910w and 2820m cm^{-1} and a band of medium intensity at 1017 cm^{-1} is assigned to formaldehyde $\nu(CO)$; in the free ligand $\nu(CO)$ is at 1746 cm^{-1} [17]. This unusually large decrease upon coordination is in accord with the structural data which are presented below.

That the formation of the formaldehyde complex is reversible was shown by the regeneration of the zerovalent complex $Os(CO)_2(PPh_3)_3$ through extended heating of a suspension of the adduct in methanol with excess PPh_3.

To confirm the mononuclear formulation rather than the possible alternative with bridging CH_2O groups, an X-ray crystal structure determination was undertaken.

Description and discussion of the crystal structure

The crystals contain discrete molecules of complex together with water dimers of crystallisation. The latter occupy interstices in the lattice and fulfil a purely space-filling role. The overall geometry of the complex is shown in Fig. 1. Bond lengths and bond angles are listed in Tables 2 and 3, respectively. It should be noted that in a previous communication [3] the Os—carbonyl bond lengths were inadvertently interchanged and these are now corrected.

The osmium atom is bonded to two mutually *trans* triphenylphosphines, two carbonyls, and the formaldehyde. The coordination geometry could be described as being either 6-coordinate distorted octahedral or 5-coordinate distorted trigonal bipyramidal, depending on whether one considers the formaldehyde to be monodentate or bidentate. In view of the angles observed in the equatorial plane (in particular, the angle C(2)—Os—C(3) which is 98.3° compared to 120° expected for a trigonal bipyramidal arrangement) and the nature of the formaldehyde bonding (to be described shortly) we prefer to regard the overall coordination geometry as being distorted octahedral.

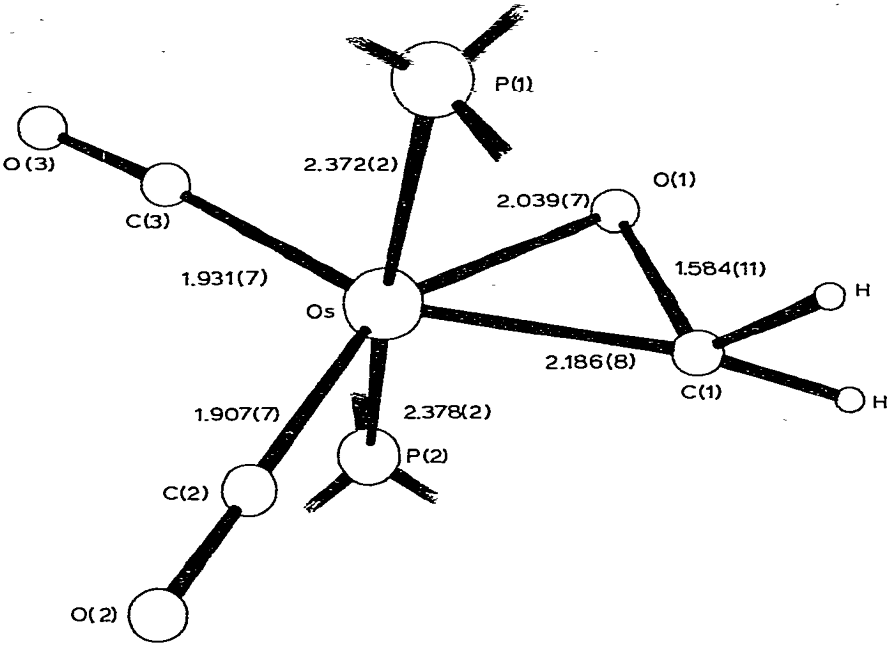


Fig. 1. The molecular geometry, atomic numbering scheme and bond distances in the inner coordination sphere for $Os(\eta^2\text{-}CH_2O)(CO)_2(PPh_3)_2 \cdot H_2O$.

TABLE 2

BOND LENGTHS (Å) FOR $Os(\eta^2\text{-}CH_2O)(CO)_2(PPh_3)_2 \cdot H_2O$

Os—P(1)	2.372(2)	Os—C(1)	2.186(8)
Os—P(2)	2.378(2)	Os—O(1)	2.039(7)
Os—C(2)	1.907(7)	Os—C(3)	1.931(7)
C(1)—O(1)	1.584(11)	C(2)—O(2)	1.111(10)
C(3)—O(3)	1.101(10)		
P(1)—C(11)	1.822(7)	P(2)—C(41)	1.819(8)
P(1)—C(21)	1.824(7)	P(2)—C(51)	1.827(7)
P(1)—C(31)	1.819(7)	P(2)—C(61)	1.853(8)
C(11)—C(12)	1.394(10)	C(41)—C(42)	1.40(1)
C(12)—C(13)	1.38(1)	C(42)—C(43)	1.41(2)
C(13)—C(14)	1.33(1)	C(43)—C(44)	1.37(2)
C(14)—C(15)	1.340(11)	C(44)—C(45)	1.36(1)
C(15)—C(16)	1.390(11)	C(45)—C(46)	1.377(11)
C(16)—C(11)	1.357(10)	C(46)—C(41)	1.374(10)
C(21)—C(22)	1.332(10)	C(51)—C(52)	1.335(10)
C(22)—C(23)	1.41(2)	C(52)—C(53)	1.41(1)
C(23)—C(24)	1.37(2)	C(53)—C(54)	1.35(2)
C(24)—C(25)	1.33(1)	C(54)—C(55)	1.30(2)
C(25)—C(26)	1.390(11)	C(55)—C(56)	1.40(1)
C(26)—C(21)	1.368(10)	C(56)—C(51)	1.373(10)
C(31)—C(32)	1.383(10)	C(61)—C(62)	1.378(10)
C(32)—C(33)	1.420(11)	C(62)—C(63)	1.43(1)
C(33)—C(34)	1.352(11)	C(63)—C(64)	1.33(2)
C(34)—C(35)	1.338(11)	C(64)—C(65)	1.37(2)
C(35)—C(36)	1.423(11)	C(65)—C(66)	1.44(2)
C(36)—C(31)	1.388(10)	C(66)—C(61)	1.36(1)
O(S)—O(S)′	2.56(1)		

TABLE 3

BOND ANGLES (degrees) FOR $Os(\eta^2\text{-}CH_2O)(CO)_2(PPh_3)_2 \cdot H_2O$

P(1)—Os—P(2)	173.98(6)		
P(1)—Os—C(1)	85.3(2)	P(2)—Os—C(1)	91.3(2)
P(1)—Os—O(1)	89.1(2)	P(2)—Os—O(1)	85.0(2)
P(1)—Os—C(2)	92.2(2)	P(2)—Os—C(2)	93.5(2)
P(1)—Os—C(3)	90.8(2)	P(2)—Os—C(3)	90.3(2)
C(1)—Os—O(1)	43.9(3)	O(1)—Os—C(2)	149.2(3)
C(1)—Os—C(2)	105.5(3)	O(1)—Os—C(3)	112.5(3)
C(1)—Os—C(3)	155.9(3)	C(2)—Os—C(3)	98.3(3)
Os—C(1)—O(1)	63.1(4)	Os—C(2)—O(2)	179.6(7)
Os—O(1)—C(1)	73.0(4)	Os—C(3)—O(3)	176.1(7)
Os—P(1)—C(11)	112.2(2)	Os—P(2)—C(41)	116.5(2)
Os—P(1)—C(21)	114.2(2)	Os—P(2)—C(51)	114.4(2)
Os—P(1)—C(31)	118.0(2)	Os—P(2)—C(61)	113.7(2)
C(11)—P(1)—C(21)	104.8(3)	C(41)—P(2)—C(51)	103.3(3)
C(11)—P(1)—C(31)	105.8(3)	C(41)—P(2)—C(61)	102.8(3)
C(21)—P(1)—C(31)	100.3(3)	C(51)—P(2)—C(61)	104.7(3)
P(1)—C(11)—C(12)	121.9(5)	P(2)—C(41)—C(42)	120.7(7)
P(1)—C(11)—C(16)	118.8(5)	P(2)—C(41)—C(46)	121.0(6)
C(12)—C(11)—C(16)	119.3(7)	C(42)—C(41)—C(46)	118.3(8)
C(11)—C(12)—C(13)	119.1(8)	C(41)—C(42)—C(43)	119.2(10)
C(12)—C(13)—C(14)	121.0(9)	C(42)—C(43)—C(44)	120.0(11)
C(13)—C(14)—C(15)	120.1(8)	C(43)—C(44)—C(45)	120.6(11)
C(14)—C(15)—C(16)	121.4(7)	C(44)—C(45)—C(46)	119.9(8)
C(15)—C(16)—C(11)	119.0(7)	C(45)—C(46)—C(41)	122.0(7)
P(1)—C(21)—C(22)	124.7(6)	P(2)—C(51)—C(52)	120.9(6)
P(1)—C(21)—C(26)	117.8(5)	P(2)—C(51)—C(56)	122.0(6)
C(22)—C(21)—C(26)	117.5(7)	C(52)—C(51)—C(56)	117.1(7)
C(21)—C(22)—C(23)	121.6(8)	C(51)—C(52)—C(53)	121.9(8)
C(22)—C(23)—C(24)	119.1(11)	C(52)—C(53)—C(54)	119.4(10)
C(23)—C(24)—C(25)	119.8(11)	C(53)—C(54)—C(55)	119.5(11)
C(24)—C(25)—C(26)	119.9(8)	C(54)—C(55)—C(56)	121.9(10)
C(25)—C(26)—C(21)	122.0(7)	C(55)—C(56)—C(51)	120.2(8)
P(1)—C(31)—C(32)	121.1(5)	P(2)—C(61)—C(62)	118.5(6)
P(1)—C(31)—C(36)	120.1(5)	P(2)—C(61)—C(66)	121.2(7)
C(32)—C(31)—C(36)	118.8(6)	C(62)—C(61)—C(66)	120.2(8)
C(31)—C(32)—C(33)	119.8(7)	C(61)—C(62)—C(63)	120.0(7)
C(32)—C(33)—C(34)	120.2(7)	C(62)—C(63)—C(64)	119.7(10)
C(33)—C(34)—C(35)	121.0(8)	C(63)—C(64)—C(65)	121.4(11)
C(34)—C(35)—C(36)	120.5(7)	C(64)—C(65)—C(66)	119.7(11)
C(35)—C(36)—C(31)	119.6(7)	C(65)—C(66)—C(61)	119.1(10)

The triphenylphosphine ligands

The geometry of the coordinated triphenylphosphine ligands is similar to that observed in other osmium complexes containing mutually *trans* triphenylphosphine groups. The Os—P distances (2.372, 2.378(2) Å), and P—Os—P angle (173.98(6)°) lie within the commonly observed ranges of 2.33—2.46 Å and 164—180° respectively [18]. The average P—C distance (1.81 Å), Os—P—C (114.8°) and C—P—C angles (103.6°) are normal. The small deviation from linearity of P—Os—P bonds is usually attributed to intermolecular steric interactions associated with the packing of bulky triphenylphosphines, however, in the present complex the presence of water dimers introduces an additional element to be considered when assessing the total effect of intermolecular forces. This aspect of the structure will be described later.

The formaldehyde ligand

The η^2-bonding of the formaldehyde to osmium is asymmetric, with the Os—O(1) distance of 2.039(7) Å being shorter than the Os—C(1) distance of 2.186(8) Å by 0.147 Å (19 σ). This asymmetry can not be ascribed to differing *trans* influences of opposite ligands (since both *trans* ligands are CO) and is deduced to be an inherent property of the coordinated formaldehyde ligand. The C—O bond of the formaldehyde is 1.584(11) Å, very considerably lengthened from the C—O double bond length of 1.21 Å, determined for formaldehyde itself [19]. Lengthening of a double (or triple) bond of an unsaturated molecule upon π-coordination to a metal is associated with back donation of electron density from hybrid orbitals on the metal into empty π^* orbitals on the unsaturated molecule. This is well-established. However, the extent to which the unsaturated bond lengthens has never been observed to be as great as is found in this formaldehyde complex. As the back donation is obviously very substantial, the osmium—formaldehyde interaction is best described as forming a cyclopropane-like structure with an accompanying partial oxidation of the osmium. This explains our preference for labelling the coordination geometry as being distorted octahedral.

The lack of other structural data on coordinated formaldehyde complexes precludes direct comparisons, but we can note that the C—O bond length in methanol, as measured by X-ray diffraction, is 1.42 Å [20]. The lengthening in the formaldehyde complex is so great that one is tempted to suggest an incipient carbon—oxygen bond rupture leading to a metal carbene—oxide species, along the lines of that proposed in the Fischer—Tropsch synthesis reaction [21]. Such a carbon—oxygen bond breaking occurs in the reaction of the complex $[(\eta^5\text{-}C_5Me_4Et)Cl_2(H)Ta\overline{C(H)OTa}Cl_2(\eta^5\text{-}C_5Me_4Et)]$ with PMe_3 to yield $[(\eta^5\text{-}C_5Me_4Et)TaCl_2H](\mu\text{-}CHPMe_3)(\mu\text{-}O)[(\eta^5\text{-}C_5Me_4Et)TaCl_2]$, [22].

A limited number of π-bonded ketones and aldehydes have been structurally characterised. Those offering the best comparison with the present formaldehyde complex are listed in Table 4. It can be seen that their C—O bond lengths are only 0.1 Å longer than in the free aldehyde or ketone. The different bond-

TABLE 4

COMPARATIVE STRUCTURAL DATA OF η^2-CARBONYL COMPLEXES

Compound	C—O (Å)		M—C (Å)	M—O (Å)	Ref.
	Ligand	Free			
$Os(\eta^2\text{-}CH_2O)(CO)_2(PPh_3)_2$	1.584(11)	1.21 [a]	2.186(8)	2.039(7)	This work
$Cp(Mo(\eta^2\text{-}PhCHO)(\eta^2\text{-}C[2\text{-}py][Ph]NHMe)(CO)$	1.333(12)	1.22 [b]	2.258(14)	2.071(8)	23
$Ni(\eta^2\text{-}[Ph]_2CO)(PEt_3)_2$	1.335(4)	1.23 [c]	1.974(3)	1.849(2)	24
$Ni(\eta^2\text{-}[CF_3]_2CO)(PPh_3)_2$	1.32(2)	1.23 [b]	1.89(2)	1.87(1)	25

[a] Ref. 19. [b] The C—O bond lengths in free benzaldehyde and hexafluoroacetone are not known, but would not be expected to differ greatly from 1.22 and 1.23 Å which are values generally observed for aldehydes and unfluorinated ketones [19]. [c] Ref. 26.

ing strengths presumably arise because osmium, being considerably more basic than either molybdenum or nickel, should enhance the extent of π-back donation. It is difficult to compare the metal—aldehyde/ketone distances when the metals are dissimilar, however we note that in each case the M—C bond is longer than M—O. The difference is very significant for the molybdenum and first nickel complexes which are the more reliably determined.

The angle between the planes defined by C(2),Os,C(3) and O(1),Os,C(1) is 6.2°. Atom C(1) is 0.115 Å above the plane defined by Os,C(2),C(3) while O(1) is 0.056 Å below this plane.

The carbonyl ligands

The distances from osmium to the two carbonyl carbon atoms are significantly different, the Os—C(2) bond of 1.907(7) Å *trans* to the formaldehyde oxygen being 0.024 Å shorter than the Os—C(3) bond of 1.931(7) Å *trans* to the formaldehyde carbon. This difference presumably reflects the differing *trans* influencing capabilities of the carbon and oxygen atoms of the formaldehyde ligand. A similar difference has been observed in $Ni[\eta^2\text{-}(Ph)_2CO][P(C_2H_5)_3]_2$ where the Ni—P bond *trans* to the oxygen atom was 0.054 Å shorter than that *trans* to the carbon atom [24]. In other π-complexes in which the two ends of the unsaturated coordinated ligands are at different distances from the metal the *cis* and *trans* ligand distances are also not equal. For example, in $Ni[PO\text{-}o\text{-}tol_3]_2[H_2C{=}CH(CN)]$ the cyano-substituted end of the olefin is significantly closer to the metal, and the *trans* phosphite is closer to the metal than is the *cis* phosphite [27]. In $(t\text{-}BuNC)_2Ni[t\text{-}BuN{=}C{=}C(CN)_2]$ the more electronegative nitrogen is closer to the metal, as is the ligand *trans* to the nitrogen [28].

A *trans* influence of the above nature in π-complexes of electron-rich metal centres derives from an important π-backbonding contribution. The presence of an electron-withdrawing substituent, which lowers the energy of the antibonding π^* orbital of the unsaturated ligand, favours the formation of the π-complex. An effect similar to the introduction of an electron-withdrawing substituent is the replacement of a trigonal carbon with a more electronegative atom such as oxygen [29]. With either type of unsaturated ligand, the more electron-deficient terminus will have a stronger π-accepting capability, thus diminishing the electron density on the metal centre. In the case of σ-donor *trans* ligands, this reduction of electron density will result in an enhanced σ-donation and hence the formation of shorter bonds.

The water dimer

The water dimer (O···O distance 2.56(1) Å) is unusual in that it is not hydrogen-bonded to any part of the complex molecule. Figure 2 gives a stereoscopic view of the environment of the water dimers, to a sphere radius of 6 Å from the centre of symmetry. It is clearly seen that the pairs of water molecules are sited in interstices in the crystal lattice and are encapsulated by hydrophobic phenyl groups of the triphenylphosphine ligands. There is no evidence in the diagram to either support or refute a claim that the inclusion of the water dimer into the crystal lattice is responsible for the previously noted small deviation from linearity of the P—Os—P bonds. The closest neighbouring atom

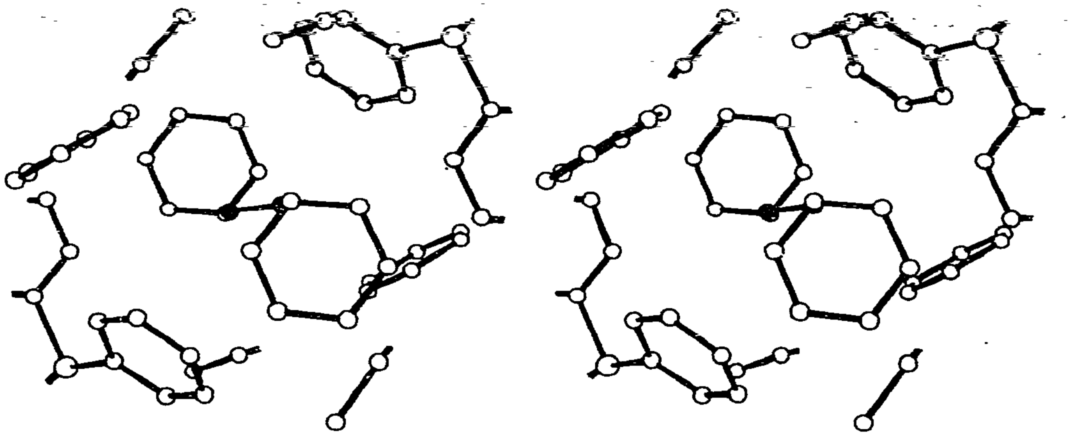


Fig. 2. Stereo-pair diagrams showing the hydrophobic environment about the water dimers.

of the water oxygen is the carbon of a phenyl ring at a distance of 3.55 Å. We also note that the five intermolecular contacts shorter than 3.5 Å (Table 5) each involve a phenyl carbon atom.

A number of reviews of hydrogen bonding have appeared in recent years [30—34], and one of the questions posed concerns the existence of water molecules which occupy a space-filling role without forming any specific directional bonds [30]. The $(H_2O)_2$ unit in the present crystal structure assumes such a space-filling function, and is probably only the second known example of this type of hydrate. The other example is $RuI_2[CHN(CH_3)(p\text{-}CH_3C_6H_4)](CO)(CN\text{-}p\text{-}CH_3C_6H_4)[P(C_6H_5)_3]\cdot H_2O$ [35]. In both instances the water molecules are related by centres of symmetry. The O···O distance in the ruthenium complex is 2.60(2) Å which is similar to that found in the present osmium complex (2.56(1) Å). These are very short hydrogen-bonding O···O separations, and are of a magnitude generally associated with intramolecular interactions involving acid salts of carboxylic acids, and not ordinary water molecules [34]. By comparison, the O···O distance in ice lies in the range 2.76 to 2.95 Å [32,36]. Since the $(H_2O)_2$ unit is surrounded by hydrophobic groups it resembles the much sought after classical water dimer. The latter has been studied by spectroscopic methods in both a frozen inert gas matrix [37] and carbon tetrachloride [38, 39]. Under these conditions it has been proposed that moderately weak hydro-

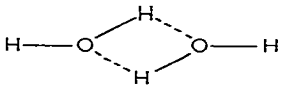
TABLE 5

INTERMOLECULAR APPROACHES SHORTER THAN 3.5 Å

Atom(1)—Atom(2)	Distance (Å)	Position of Atom(2)		
O(1)—C(44)	3.43(1)	x	y	$1+z$
O(1)—C(45)	3.38(1)	x	y	$1+z$
O(2)—C(63)	3.46(1)	x	$y-1$	$z-1$
O(2)—C(64)	3.39(1)	x	$y-1$	$z-1$
O(3)—C(23)	3.48(2)	$-x$	$-y$	$1-z$

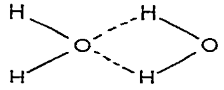
gen bonding occurs, and that the O—O separation sould be approximately 2.71 Å. A number of theoretical calculations postulate a range of O···O separations between 2.53 and 3.00 Å, with the majority predicting a distance greater than that of ice [40]. Thus the relative shortness of the O···O distance in both the osmium and ruthenium examples is somewhat surprising. Indeed it has been suggested that stronger hydrogen bonds form only with polymers, where the formation of one hydrogen bond increases the energy of formation of a second bond to the same centre [41].

Three structures are possible for water dimers. These are shown below. I represents a cyclic structure, whereas II and III represent linear and bifurcated models, respectively.



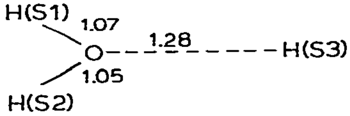
(I)

(II)



(III)

In the present case (and with the ruthenium example also) the water dimer is situated about a crystallographic centre of symmetry. Only the cyclic structure is capable of possessing a centre of symmetry. If the structure were linear or bifurcated, the hydrogen atoms would of necessity be disordered. A difference Fourier synthesis in the region of the water dimer reveals a single peak of electron density at the centre of symmetry and two other peaks at equal distances from the oxygen atom and positioned away from the centre of symmetry. Such an arrangement of electron density is consistent only with a linear structure. (A cyclic or bifurcated description of the dimer structure would imply two regions of electron density between the oxygen atoms, each displaced from the centre). Consequently a linear structure is deduced for the dimer in the present case, with the disorder of the hydrogen atoms assumed to be of the type shown in II. The geometry about the oxygen atom, based on this assumption, is shown below.



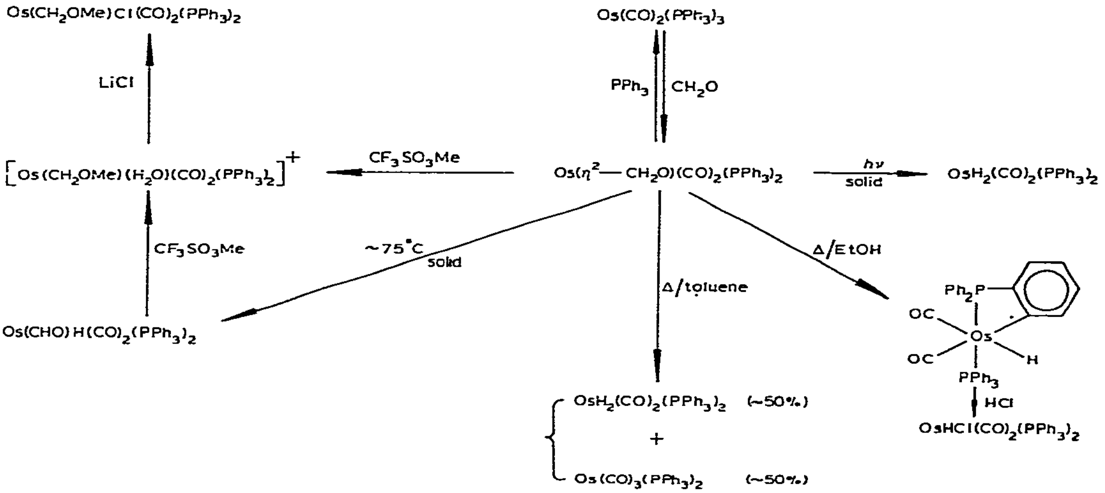
Reactions of $Os(\eta^2\text{-}CH_2O)(CO)_2(PPh_3)_2$ and derived products

A study of the ligand reactions of $Os(\eta^2\text{-}CH_2O)(CO)_2(PPh_3)_2$ was undertaken with the intention of defining the kind of chemistry to be expected from such transition metal complexes and derivatives thereof since these compounds might model some of the unusual intermediates and reactions which are proposed to occur in CO reduction.

(i) Rearrangement-elimination reactions

Several "decomposition" routes have been observed for the formaldehyde complex. Selectivity exists in the thermal rearrangement-elimination reactions in the solid state and in solution (see Scheme 1).

SCHEME 1
Synthesis and some reactions of $Os(\eta^2\text{-}CH_2O)(CO)_2(PPh_3)_2$.



Heating the crystalline η^2-formaldehyde complex at ~75°C for several hours resulted in a novel rearrangement with the formation of the formylhydrido complex $Os(CHO)H(CO)_2(PPh_3)_2$. The formyl proton in the ^{1}H NMR spectrum (CH_2Cl_2) appears as a multiplet at the low field position of τ −4.41 (similar ^{1}H NMR behaviour is exhibited by other reported formyl complexes [42—44,2] and the osmium hydride resonance occurs at τ 15.35 (^2J(H—P) 21.5 Hz). Formyl ν(CH) is at 2760w and 2540m cm^{-1} and formyl ν(CO) at 1601 cm^{-1}.

The rate of the rearrangement reaction was found to be dependent upon the solvent in which the formaldehyde adduct had been prepared and upon temperature. The solvent dependence is presumably due to the presence of solvate molecules (benzene) in the crystals of the formaldehyde complex, which in some way facilitate the rearrangement reaction. Samples prepared in benzene underwent complete rearrangement to the formylhydrido complex within 8 h at ~75°C; in contrast a sample prepared in toluene was only about 35% converted (by comparison of IR bands with a pure sample) under identical heating conditions. Continued heating of this sample for 20 h in total effected approximately 50% conversion; appreciable decomposition accompanied this reaction and the sample still contained significant amounts of the formaldehyde adduct. Recrystallization of the toluene-prepared sample from dichloromethane/benzene/ethanol prior to heating effected a facile rearrangement comparable to that of the initially benzene-prepared sample. A detectable, although trivial, increase in the percentage of $Os(CHO)H(CO)_2(PPh_3)_2$ in samples of the formaldehyde complex was noted after storage at room temperature in the absence of light for several weeks indicating that the rearrangement does occur at room temperature but is extremely slow. Heating benzene-prepared samples at temperatures lower than ~75°C did not cause the rearrangement reaction to occur to any great extent. For example, continuous heating at ~65°C for 15 h effected only ~5—10% conversion. The use of temperatures in excess of 80°C saw considerable decomposition accompanying the rearrangement reaction.

The formylhydrido complex possesses reasonable stability; for example, no decomposition was observed upon heating under reflux in dichloromethane for 30 min. However, solutions of the complex are unstable at temperatures above 40°C decomposing to form both $OsH_2(CO)_2(PPh_3)_2$ and $Os(CO)_3(PPh_3)_2$ in approximately equimolar quantities (as estimated by a comparison of IR bands). This result suggests that two competing decomposition routes exist for the formylhydrido complex; (i) loss of CO to form $OsH_2(CO)_2(PPh_3)_2$ and, (ii) loss of H_2 to form $Os(CO)_3(PPh_3)_2$. The corresponding formylhalo complexes $Os(CHO)X(CO)_2(PPh_3)_2$ (X = Cl, Br) lose CO exclusively (eq. 2) [45,2]. Loss of

$$Os(CHO)X(CO)_2(PPh_3)_2 \rightarrow OsHX(CO)_2(PPh_3)_2 + CO\uparrow \qquad (2)$$

CO is, in fact, a recognised mode of decomposition for a number of formyl complexes. The formylosmium complex $Os(CHO)H(CO)_2(PPh_3)_2$, however, is distinct in that it also contains a hydrido ligand. Decomposition by elimination of H_2 is then a credible alternative mode to loss of CO.

In refluxing toluene solution the formaldehyde complex also afforded an approximately equimolar mixture of $OsH_2(CO)_2(PPh_3)_2$ and $Os(CO)_3(PPh_3)_2$ intimating that in solution (as in the solid state) the formaldehyde complex undergoes an initial rearrangement to form the formylhydrido species $Os(CHO)H(CO)_2(PPh_3)_2$; the final reaction products ensue from the solution instability of the formyl complex at moderately high temperatures.

Heating a suspension of $Os(\eta^2\text{-}CH_2O)(CO)_2(PPh_3)_2$ under reflux in ethanol resulted in an unusual elimination-rearrangement with formation of the *ortho*-metallated species $\overline{OsH(C_6H_4P}Ph_2)(CO)_2(PPh_3)$. The hydrido ligand in the ^1H NMR spectrum ($CDCl_3$) appears as a triplet at τ 14.73 (^2J(H—P) 20.0 Hz). In the IR spectrum a strong band is observed at 730 cm^{-1}, which is in the range characteristic of the C—H out-of-plane deformation for *ortho*-disubstituted aromatics [46]. The mechanism for this reaction presumably involves initial loss of CH_2O from the complex thus generating the coordinatively unsaturated zerovalent moiety $Os(CO)_2(PPh_3)_2$, which undergoes rapid intramolecular hydride transfer from ligand to metal to yield the coordinatively saturated *ortho*-metallated species observed. Intramolecular hydride transfers of this type are well known [47]. The osmium *ortho*-metallated derivative could also be produced by elimination of ethylene from $Os(\eta^2\text{-}C_2H_4)(CO)_2(PPh_3)_2$. Reaction of $\overline{OsH(C_6H_4P}Ph_2)(CO)_2(PPh_3)$ with PPh_3 returned the zerovalent complex $Os(CO)_2(PPh_3)_3$, while hydrochloric acid afforded $OsHCl(CO)_2(PPh_3)_2$.

Photochemically induced decomposition of the formaldehyde complex in the solid state was also observed. A sample of the complex inadvertently subjected to pyrex-filtered sunlight for several weeks was totally converted to the dihydrido complex $OsH_2(CO)_2(PPh_3)_2$. In contrast, solid samples appeared to be relatively stable in the absence of light suggesting that pyrex-filtered light had promoted the decomposition of the formaldehyde ligand through loss of CO.

(ii) Hydroxymethyl complexes and derived products

Electrophilic attack at the oxygen atom of the formaldehyde ligand with accompanying ring opening has been observed and the details of these reactions follow.

(a) Synthesis. Reaction of $Os(\eta^2\text{-}CH_2O)(CO)_2(PPh_3)_2$ with excess acid HX ($X = Cl, Br, I$) yielded the halomethyl complexes $Os(CH_2X)X(CO)_2(PPh_3)_2$. In the ^1H NMR spectra ($CDCl_3$) of these complexes the methylene groups appear as triplets at τ 6.37 (^3J(H—P) 9.0 Hz), 6.73 (^3J(H—P) 9.4 Hz), and 7.59 (^3J(H—P) 9.8 Hz) for the chloro-, bromo- and iodo-substituted species, respectively. Chloromethyl ν(CCl) occurs at 650wm cm^{-1} while bromomethyl ν(CBr) occurs at 578m cm^{-1} in the IR spectra; an unambiguous assignment for iodomethyl ν(CI) was not possible. The reactivity of the halomethyl complexes and, in particular, the unusual reactivity of the iodomethyl complex $Os(CH_2I)I(CO)_2(PPh_3)_2$ will be the subject of a separate paper [48].

The intermediate hydroxymethyl complexes $Os(CH_2OH)X(CO)_2(PPh_3)_2$ ($X = Cl, Br$), formed by initial protonation at the oxygen atom of the formaldehyde ligand, could be isolated if only one equivalent of acid was treated with $Os(\eta^2\text{-}CH_2O)(CO)_2(PPh_3)_2$. Reaction of the formaldehyde complex with CF_3CO_2H yielded the hydroxymethyl derivative $Os(CH_2OH)(\eta^1\text{-}OC[O]CF_3)(CO)_2(PPh_3)_2$. The hydroxy protons of the chloro- and bromo-hydroxymethyl complexes appear as broad peaks at τ 8.27 and 8.42 respectively in the ^1H NMR spectra ($CDCl_3$) and a very diffuse signal centred at τ 7.02 for the trifluoroacetato derivative is ascribed to the hydroxy proton of this complex. These signals disappear upon exchange with D_2O. Triplets at τ 5.70 (^3J(H—P) 7.8 Hz), 5.57 (^3J(H—P) 8.2 Hz) and 5.55 (^3J(H—P) 7.9 Hz) are assigned to the methylene groups of the chloro-, bromo and trifluoroacetato-substituted complexes respectively. The IR spectra (Nujol) show ν(OH) at 3585m (sharp) cm^{-1} for both of the halo-containing complexes and at 3515m (sharp) cm^{-1} for the trifluoroacetato derivative. In the D_2O-exchanged samples these bands are shifted to 2650m (sharp) cm^{-1} for the chlorohydroxymethyl complex and to 2600m (sharp) cm^{-1} for the trifluoroacetato species. Bands of medium intensity at 947, 946 and 954 cm^{-1} in the IR spectra of the chloro-, bromo- and trifluoroacetato-substituted complexes respectively are probably associated with hydroxymethyl ν(CO).

Only one other authenticated hydroxymethyl complex has been reported in the literature and that is the rhenium complex $CpRe(CH_2OH)(CO)(NO)$ which was independently synthesized by Casey [49,50] and Graham [51].

(b) Reactions. The reduction of the hydroxymethyl ligand to a methyl group using sodium borohydride has been demonstrated by Graham [51] for the rhenium complex $CpRe(CH_2OH)(CO)(NO)$. Reaction of $Os(CH_2OH)Cl(CO)_2(PPh_3)_2$ with sodium borohydride in dichloromethane/ethanol, however, yielded the novel hydroxymethylhydrido complex $Os(CH_2OH)H(CO)_2(PPh_3)_2$, which exhibits a structured hydrido ^1H NMR triplet resonance at τ 16.48 showing coupling to the ^{31}P nuclei and weak coupling to the CH_2 protons (^2J(H—P) 21.2 Hz). A complex triplet at τ 6.07 (^3J(H—P) 9.0 Hz) is assigned to the methylene group and a broad resonance at τ 8.43, which exchanges with D_2O, is ascribed to the hydroxy proton. The IR spectrum shows ν(OH) as a sharp band of medium intensity at 3560 cm^{-1}, which is shifted to 2630m (sharp) cm^{-1}

TABLE 6

IR DATA [a] FOR OSMIUM COMPLEXES

Compound	ν(CO)	Other bands
$Os(\eta^2\text{-}CH_2O)(CO)_2(PPh_3)_2$	1977, 1902	2910w, 2820m (ν(CH)) [b]; 1017m (ν(C—O))
$Os(CHO)H(CO)_2(PPh_3)_2$	2023, 1972	2760w, 2680w, 2540m (ν(CH)); 1905 (ν(OsH)); 1601 (ν(C=O)); 890w, 875w (δ(OsH))
$Os(CHO)(CH_3)(CO)_2(PPh_3)_2$	1998, 1930	2820m, 2715w, 2540m (ν(CH)); 1604 (ν(C=O))
$Os(CHO)(CH_2OMe)(CO)_2(PPh_3)_2$	2005, 1940	2795m, 2530m (ν(CH)); 1608 (ν(C=O)); 1068m, 906m (ν(C—O))
$Os(CHO)Cl(CO)_2(PPh_3)_2$ [d]	2020, 1960	2660w, 2540w (ν(CH)); 1610 (ν(C=O))
$Os(CHO)Br(CO)_2(PPh_3)_2$ [d]	2040, 1970	2695w, 2555w (ν(CH)); 1609ms (ν(C=O))
$\overline{OsH(C_6H_4P}Ph_2)(CO)_2(PPh_3)$	2010, 1958	1888ms (ν(OsH)); 1565w, 730ms ($C_6H_4PPh_2$)
$Os(CH_2OH)Cl(CO)_2(PPh_3)_2$	2005, 1935	3585m (ν(OH)); 1625w (δ(OH)); 947m (ν(C—O)); 285w (ν(OsCl))
$Os(CH_2OH)Br(CO)_2(PPh_3)_2$	2005, 1935	3585m (ν(OH)); 1625w (δ(OH)); 946m (ν(C—O))
$Os(CH_2OH)(\eta^1\text{-}OC[O]CF_3)(CO)_2(PPh_3)_2$	2025, 1957	3515m (ν(OH)); 1695 (ν(C=O)); 1196, 1154, 785m, 731ms (η^1-$OC[O]CF_3$); 954m (ν(C—O))
$Os(CH_2OH)H(CO)_2(PPh_3)_2$	2020, 1965	3560m (ν(OH)); 2820m (ν(CH)); 1910 (ν(OsH)); 928 (ν(C—O)); 815w (δ(OsH))
$Os(CH_2Cl)Cl(CO)_2(PPh_3)_2$	2042, 2032, 2020, 1972, 1959, 1943 [c]	2960w, 2930w (ν(CH)) [b]; 650m (ν(CCl)); 285w (ν(OsCl))
$Os(CH_2Br)Br(CO)_2(PPh_3)_2$	2030, 2015, 1965, 1953, 1942 [c]	578m (ν(CBr))
$Os(CH_2I)I(CO)_2(PPh_3)_2$	2025, 1960	
$Os(CH_2Br)Cl(CO)_2(PPh_3)_2$	2030, 2015, 1974, 1960, 1943 [c]	587m (ν(CBr)); 286w (ν(OsCl))
$Os(CH_2I)Cl(CO)_2(PPh_3)_2$	2030, 2020, 1974, 1960, 1942 [c]	288w (ν(OsCl))
$[Os(CH_2OMe)(H_2O)(CO)_2(PPh_3)_2]CF_3SO_3$	2045, 1967	3310w, 3150w (ν(OH)); 2810w (ν(CH)); 1615w (δ(OH)); 1298ms, 1242, 1168ms, 1030, 637ms (CF_3SO_3); 1067ms, 912w (ν(C—O))
$Os(CH_2OMe)Cl(CO)_2(PPh_3)_2$	2028, 2018, 1952 [c]	2815w, 2795w (ν(CH)); 1070ms, 905w (ν(C—O)); 283w (ν(OsCl))
$Os(\eta^1\text{-}C[O]CH_3)H(CO)_2(PPh_3)_2$	2025, 1975	1907 (ν(OsH)); 1585 (ν(C=O)); 830w (δ(OsH))
trans-$[OsCl(CO)_2(PPh_3)_3]ClO_4$	2090wm, 2000	1090, 622m (ClO_4); 280w (ν(OsCl))

[a] cm^{-1}, measured as Nujol mulls; all bands strong unless indicated otherwise. [b] Measured as Kel-F mull. [c] Solid-state splitting. [d] Ref. 2.

in the D_2O-exchanged sample, and an absorption at 928m cm^{-1} is probably associated with hydroxymethyl ν(CO). Heating $Os(CH_2OH)H(CO)_2(PPh_3)_2$ in degassed toluene in the presence of excess PPh_3 for 2 h failed to promote a clean reductive elimination of methanol and led to an intractable mixture of products.

The hydroxymethylhalo complexes, $Os(CH_2OH)X(CO)_2(PPh_3)_2$ (X = Cl, Br) reacted smoothly with hydrogen halides, HX^1 (X = Cl, X^1 = Cl, Br, I; X = X^1 =

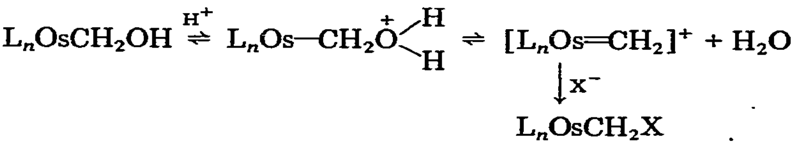
TABLE 7

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

Compound	Chemical shift (τ) and coupling constants (Hz)
$Os(\eta^2\text{-}CH_2O)(CO)_2(PPh_3)_2$	7.44, t, 2 H, CH_2O, ^3J(H—P) 4.0; 2.62, m, 32 H, Ph [b,d]
$Os(CHO)H(CO)_2(PPh_3)_2$ [c]	15.35, t, 1 H, Os—H, ^2J(H—P) 21.5; 2.53, m, 35 H, Ph; —4.41, m, 1 H, CHO
$Os(CHO)(CH_3)(CO)_2(PPh_3)_2$ [c]	10.02, t, 3 H, CH_3, ^3J(H—P) 7.0; 2.50, m, 33 H, Ph; —3.63, m, 1 H, CHO
$Os(CHO)(CH_2OMe)(CO)_2(PPh_3)_2$ [c]	7.28, s, 3 H, OMe; 6.05, t, 2 H, CH_2—OMe, ^3J(H—P) 8.0; 2.57, m, 35 H, Ph; —3.78, m, 1 H, CHO
$\overline{OsH(C_6H_4PPh_2)}(CO)_2(PPh_3)$	14.73, t, 1 H, Os—H, ^2J(H—P) 20.0; 2.63, m, 32 H, Ph
$Os(CH_2OH)Cl(CO)_2(PPh_3)_2$	8.27, s, 1 H, OH [e]; 5.70, t, 2 H, CH_2—OH, ^3J(H—P) 7.8; 2.63, 2.30, 2m, 30 H,
$Os(CH_2OH)Br(CO)_2(PPh_3)_2$	8.42, s, 1 H, OH; 5.57, t, 2 H, CH_2—OH [e], ^3J(H—P) 8.2; 2.60, 2.27, 2m 32 H, Ph
$Os(CH_2OH)(\eta^1\text{-}OC[O]CF_3)(CO)_2(PPh_3)_2$	7.02, s(br), 1 H, OH [e], 5.55, t, 2 H, CH_2—OH, ^3J(H—P) 7.9, 2.60, m, 30 H, Ph
$Os(CH_2OH)H(CO)_2(PPh_3)_2$	16.48, t, 1 H, Os—H, ^2J(H—P) 21.2; 8.43, s, 1 H, OH [e]; 6.07, t, 2 H, CH_2—OH, ^3J(H—P) 9.0; 2.58, m, 32 H, Ph
$Os(CH_2Cl)Cl(CO)_2(PPh_3)_2$	6.37, t, 2 H, CH_2—Cl, ^3J(H—P) 9.0; 2.55, 2.20, 2m, 31 H, Ph
$Os(CH_2Br)Br(CO)_2(PPh_3)_2$	6.73, t, 2 H, CH_2—Br, ^3J(H—P) 9.4; 2.57, 2.23, 2m, 30 H, Ph
$Os(CH_2I)I(CO)_2(PPh_3)_2$	7.59, t, 2 H, CH_2—I, ^3J(H—P) 9.8; 2.57, 2.23, 2m, 30 H, Ph
$Os(CH_2Br)Cl(CO)_2(PPh_3)_2$	6.70, t, 2 H, CH_2—Br, ^3J(H—P) 9.0; 2.61, 2.30, 2m, 32 H, Ph
$Os(CH_2I)Cl(CO)_2(PPh_3)_2$	7.45, t, 2 H, CH_2—I, ^3J(H—P) 9.6; 2.57, 2.27, 2m, 30 H, Ph
$[Os(CH_2OMe)(H_2O)(CO)_2(PPh_3)_2]CF_3SO_3$	7.37, s, 3 H, OMe; 6.20, t, 2 H, CH_2—OMe, ^3J(H—P) 7.6; 4.42, s, 2 H, H_2O [f]; 2.53, m, 32 H, Ph
$Os(CH_2OMe)Cl(CO)_2(PPh_3)_2$	7.47, s, 3 H, OMe; 4.04, t, 2 H, CH_2—OMe, ^3J(H—P) 7.5; 2.60, 2.27, 2m, 32 H, Ph
$Os(\eta^1\text{-}C[O]CH_3)H(CO)_2(PPh_3)_2$	15.08, t, 1 H, Os—H, ^2J(H—P) 20.5; 8.87, s, 3 H, C[O]—CH_3; 2.57, m, 33 H, Ph

[a] $CDCl_3$ used as solvent for all spectra unless otherwise specified. [b] All phenyl resonances quoted as mid-point of multiplet in all ^{1}H NMR tables. [c] In CD_2Cl_2. [d] Phenyl resonances include $CHCl_3$ impurities in $CDCl_3$. [e] OH signal disappears on addition of D_2O. [f] H_2O signal disappears on addition of D_2O.

Br) to afford the halomethyl complexes $Os(CH_2X^1)X(CO)_2(PPh_3)_2$, which have all been characterised by elemental analysis, ^{1}H NMR and IR spectroscopy (see Tables 6 and 7). The reactivity order observed for the hydrogen halides was HI > HBr > HCl, a likely mechanism is shown in eq. 3.



$$L_nOsCH_2OH \overset{H^+}{\rightleftharpoons} L_nOs{-}CH_2\overset{+}{O}H_2 \rightleftharpoons [L_nOs{=}CH_2]^+ + H_2O \xrightarrow{X^-} L_nOsCH_2X \qquad (3)$$

Attempts to obtain the postulated intermediate methylene complex $[OsCl(CH_2)(CO)_2(PPh_3)_2]^+$ by the interaction of acids with "non-coordinating" anions, e.g. $HClO_4$ were not successful.

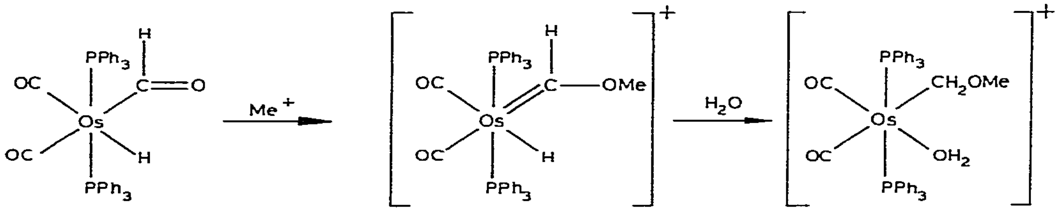
(iii) Methoxymethyl complexes

Treatment of $Os(\eta^2\text{-}CH_2O)(CO)_2(PPh_3)_2$ with methyl triflate in benzene resulted in alkylation at the oxygen atom to yield the methoxymethyl cation $[Os(CH_2OMe)(H_2O)(CO)_2(PPh_3)_2]^+$, which reacted rapidly with lithium chloride in ethanol to afford the neutral complex $Os(CH_2OMe)Cl(CO)_2(PPh_3)_2$.

(iv) $Os(CHO)H(CO)_2(PPh_3)_2$

The formyl ligand in $Os(CHO)H(CO)_2(PPh_3)_2$ may be viewed as having a weakly electrophilic carbon atom and a moderately nucleophilic oxygen atom; this is evidenced by the low formyl $\nu(CO)$ of 1601 cm^{-1}, which occurs at significantly lower frequency than $\nu(CO)$ of organic amides. The oxygen atom of the formyl ligand is thus susceptible to attack by electrophiles.

Reaction of methyl triflate with $Os(CHO)H(CO)_2(PPh_3)_2$ is rapid to yield the methoxymethyl complex $[Os(CH_2OMe)(H_2O)(CO)_2(PPh_3)_2]^+$. The mechanism of this reaction is thought to involve initial alkylation at the formyl O-atom to form the methoxymethylidene derivative $[Os(CHOMe)H(CO)_2(PPh_3)_2]^+$, which undergoes a rapid hydride transfer (migration) from the metal centre to the carbene ligand to afford the observed product (see eq. 4).

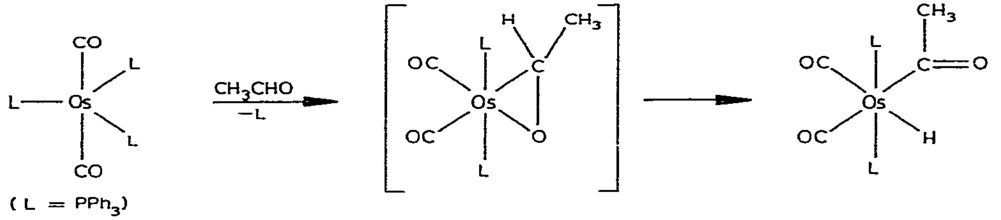


The formylchloro complex $Os(CHO)Cl(CO)(CNR)(PPh_3)_2$ ($R = p$-tolyl) yields the stable methoxymethylidene containing complex $[OsCl(CHOMe)(Cl)(CNR)(PPh_3)_2]^+$ by alkylation with methyl triflate [2] and Gladysz has prepared the stable methoxymethylidenerhenium complex $[CpRe(CHOMe)(PPh_3)(NO)]^+$ through reaction of the formyl complex $CpRe(CHO)(PPh_3)(NO)$ with the methylating agent CH_3SO_3F [52].

Reactions of $Os(CO)_2(PPh_3)_3$ with other aldehydes

The interaction of some simple aldehydes (namely, acetaldehyde, benzaldehyde and trichloroacetaldehyde) with $Os(CO)_2(PPh_3)_3$ was investigated in an endeavour to prepare analogues of $Os(\eta^2\text{-}CH_2O)(CO)_2(PPh_3)_2$. Treatment of a degassed benzene solution of $Os(CO)_2(PPh_3)_3$ (exposed to the light from a tungsten-halogen sun-lamp) with excess acetaldehyde afforded the stable *monohapto*-acetylhydrido complex $Os(\eta^1\text{-}C[O]CH_3)H(CO)_2(PPh_3)_2$. The reaction time was found to be considerably longer than for the reaction of $Os(CO)_2(PPh_3)_3$ with formaldehyde; for example, complete reaction of $Os(CO)_2(PPh_3)_3$ (0.50 g) with formaldehyde requires 1 h, but with acetaldehyde a reaction time of 9 h is necessary. In the ^1H NMR spectrum ($CDCl_3$) the acetyl-methyl group appears as a singlet at τ 8.87 and the osmium hydride as a triplet at τ 15.08 (^2J(H—P) 20.5 Hz). Acetyl ν(CO) occurs at 1585s cm^{-1} in the IR spectrum.

While no direct evidence was obtained for an η^2-acetaldehyde complex, the formation of a species such as $Os(\eta^1\text{-}C[O]CH_3)H(CO)_2(PPh_3)_2$ is reminiscent of the rearrangement reaction of $Os(\eta^2\text{-}CH_2O)(CO)_2(PPh_3)_2$ to $Os(CHO)H(CO)_2(PPh_3)_2$. Reaction between $Os(CO)_2(PPh_3)_3$ and acetaldehyde is thus proposed to initially involve the formation of the η^2-acetaldehyde complex $Os(\eta^2\text{-}CH_3CHO)(CO)_2(PPh_3)_2$ which under the reaction conditions rearranges (eq. 5).



(5)

Heating $Os(\eta^1\text{-}C[O]Me)(CO)_2(PPh_3)_2$ in refluxing toluene for 1.5 h led to the formation of an intractable mixture, which, nonetheless, contained significant amounts of $Os(CO)_3(PPh_3)_2$ (by IR spectrum) suggesting that some reductive elimination of methane had occurred. The acetylhydridoosmium complex therefore represents a stable intermediate formed during aldehyde decarbonylation by a transition metal complex.

No interaction was observed between $Os(CO)_2(PPh_3)_3$ and benzaldehyde in degassed benzene upon exposure to light from a tungsten-halogen sun-lamp for 4 h. Any reaction must be exceptionally slow.

In marked contrast to the other aldehydes examined trichloroacetaldehyde (CCl_3CHO) reacted instantaneously with $Os(CO)_2(PPh_3)_3$ in benzene to afford the triphosphine cation *trans*-$[OsCl(CO)_2(PPh_3)_3]^+$ which was characterised as the perchlorate salt following anion exchange (eq. 6). The two ν(CO) bands for this cation at 2090wm and 2000s cm^{-1} are found at positions identical to those found for the bromo analogue [53].

(6)

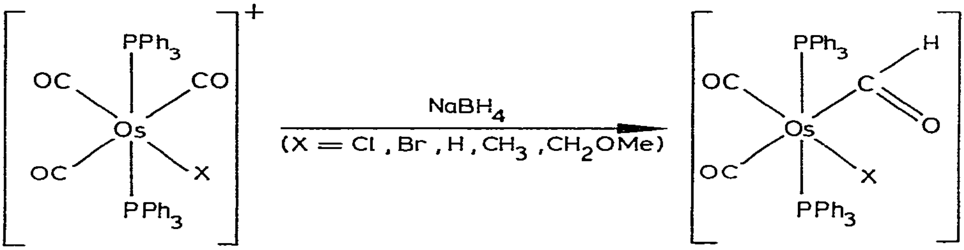
A general synthetic route to neutral formylosmium complexes

Since the first formyl complex $[Fe(CHO)(CO)_4]^-$ was prepared by Collman and Winter in 1973 by the reaction of $Na_2Fe(CO)_4$ with acetic formic anhydride [42], a number of formyl-transition metal complexes have been prepared, isolated, and studied because of the increased interest in CO hydrogenation reactions [43,44,51,2,3]. None, however, has been prepared directly from hydrogen and a molecular carbonyl-transition metal complex or from an hydrido-carbonyl complex. Of the synthetic procedures known, the most general and effective procedure comprises the reaction of a carbonyl-transition metal complex with a hydride ion transfer reagent such as BR_3H^- (R = alkyl or alkoxy group) [54].

For osmium, two synthetic routes of doubtful generality have led to the preparation of only four formyl complexes: $Os(CHO)X(CO)_2(PPh_3)_2$ (X = Cl, Br), $Os(CHO)Cl(CO)(CNR)(PPh_3)_2$ (R = *p*-tolyl) [2] and $Os(CHO)H(CO)_2(PPh_3)_2$ [3]. A preliminary investigation was, therefore, made into the reaction of sodium borohydride with several cationic carbonyl complexes of osmium, mindful of the increased susceptibility of the C-atom of the carbonyl ligand to nucleophilic attack in cationic complexes with a maximum number of π-acceptor ligands. Complexes of the type $[OsX(CO)_3(PPh_3)_2]^+$ (X = Cl, Br, H, CH_3 and CH_2OMe) were thus examined.

The chloro-containing cation $[OsCl(CO)_3(PPh_3)_2]^+$ has been previously reported [55], but was here prepared by a new synthetic route. Heating a dichloromethane solution of the trisphosphine-containing cation *trans*-$[OsCl(CO)_2(PPh_3)_3]ClO_4$ under carbon monoxide pressure effected substitution of the labile phosphine ligand by CO to yield $[OsCl(CO)_3(PPh_3)_2]^+$. The bromo- and hydrido-containing cations have been described in the literature [55,56]. A discussion of the preparation of the methyl and methoxymethyl cations will be published separately [48].

Treatment of $[OsX(CO)_3(PPh_3)_2]^+$ with excess sodium borohydride in ethanol yielded the corresponding formyl complexes $Os(CHO)X(CO)_2(PPh_3)_2$ as pale yellow crystalline solids (eq. 7).



(7)

The formyl complexes $Os(CHO)X(CO)_2(PPh_3)_2$ (X = Cl, Br) were contaminated by $OsHX(CO)_2(PPh_3)_2$, but the others were obtained in pure condition. Solid samples prepared by the above method were found to be unstable even in the absence of light. Decomposition through loss of CO was rather rapid (4—5 days for complete loss of formyl ν(CO)) and formation of $OsHX(CO)_2(PPh_3)_2$ was quantitative. No apparent decarbonylation of $[N(PPh_3)_2][Fe(CHO)(CO)_4]$ in the solid state was observed after 13 days at 0.2 mmHg (25°C) [42]. This new synthetic route to the formylhydrido complex $Os(CHO)H(CO)_2(PPh_3)_2$ offers significant time and yield improvements.

The novel formyl-methyl and -methoxymethyl complexes, $Os(CHO)(CH_3)(CO)_2(PPh_3)_2$ and $Os(CHO)(CH_2OMe)(CO)_2(PPh_3)_2$, were characterized by elemental analysis and IR and ^1H NMR spectroscopy. The IR spectra (Nujol) contain strong sharp formyl ν(CO) bands at 1604 and 1608 cm^{-1}, respectively, and weak to medium intensity bands between 2700 and 2500 cm^{-1} for formyl ν(CH). In the ^1H NMR spectra (CH_2Cl_2) the formyl protons of the respective complexes appear as multiplets at the low field positions of τ —3.63 and —3.78.

For the methyl-containing complex a triplet at τ 10.02 (^3J(H—P) 7.0 Hz) is assigned to the protons of the methyl group. The methoxymethyl complex exhibits a methylene group triplet resonance at τ 6.05 (^3J(H—P) 8.0 Hz) and a singlet for the methoxy group protons is observed at τ 7.28.

Crystalline samples of $Os(CHO)(CH_3)(CO)_2(PPh_3)_2$ appeared to be indefinitely stable in the absence of light; no perceptible decarbonylation was noted after storage for several weeks. In contrast, the methoxymethyl analogue was unstable to loss of CO and hydride formation in the solid state yielding $Os(CH_2OMe)H(CO)_2(PPh_3)_2$. The preparation of $Os(CH_2OMe)H(CO)_2(PPh_3)_2$ by a different synthetic route and the characterization of this complex will be discussed separately [48].

Experimental

General experimental conditions and instrumentation were as described previously [2].

Os(η²-CH₂O)(CO)₂(PPh₃)₂

$Os(CO)_2(PPh_3)_3$ [8,9] (5.0 g) was dissolved in degassed benzene (500 ml) and a 40% aqueous formaldehyde solution (0.6 ml, 1.5 equiv.) was added. The light from a 1000 watt tungsten-halogen sun-lamp (Thorn) was directed at the reaction flask which was cooled by a constant air flow across the surface. When the solution was quite colourless (3—4 h) the solvent volume was reduced to 25 ml and ethanol was added to effect complete crystallization. Recrystallization from dichloromethane/ethanol afforded pale yellow crystals of the solvate $Os(\eta^2\text{-}CH_2O)(CO)_2(PPh_3)_2 \cdot H_2O$ (3.85 g, 97.2%). ^{1}H NMR (τ, $CDCl_3$) 8.46 (s (broad), 2 H, H_2O). M.p. 191—194°C. This compound was further characterized by an X-ray crystal structure determination. Anal. Found: C, 57.06; H, 4.15; P, 7.25. $C_{39}H_{32}O_3OsP_2 \cdot H_2O$ calcd.: C, 57.21; H, 4.19; P, 7.57%.

Structure determination. Pale yellow acicular crystals were obtained by slow diffusion of ethanol into a solution of the complex in dichloromethane. The crystals exhibited $\bar{1}$ diffraction symmetry, and subsequent structure analysis confirmed the space group as $P\bar{1}$. The crystal selected for intensity data collection was developed on the forms {001}, {100} and {2$\bar{1}$0} and measured approximately 0.30 × 0.06 × 0.10 mm. Unit cell parameters were derived from a least-squares refinement of the setting angles of twelve high-θ reflections using a Hilger and Watts four-circle automatic diffractometer [57].

Crystal data. $C_{39}H_{32}O_3OsP_2 \cdot H_2O$, $M = 818.86$, Triclinic, a 18.739(2), b 11.157(1), c 9.986(1) Å, α 116.70(1), β 93.20(1), γ 107.93(1)°, V 1727.69 Å^3, space group $P\bar{1}$, $Z = 2$, $d_m = 1.55(2)$ by flotation in aqueous KI, $d_c = 1.57$, $F(000) = 824$, Cu-K_α radiation of $\lambda = 1.5418$ Å, Ni filter, μ(Cu-K_α) = 82.36 cm^{-1}, mosaic spread 0.11°.

Intensity data were collected to θ(max) of 53° using a $2\theta/\omega$ scan of 0.60° in θ, with each step of 0.02° being counted for 1.5 s. A stationary background count of 10 s was recorded at each end of the scan range. After scaling and averaging, the data were corrected for Lorentz and polarisation factors, and for absorption [58]. The maximum and minimum transmission coefficients were 0.652 and 0.243 respectively. After processing, the data set comprised 3508 unique observed reflections for which $I > 3\sigma(I)$ ($\sigma(I) = [T + t^2B + (pI)^2]^{1/2}$, T = integrated peak count, B = average background count, t = ratio of scan to background times, p was assigned an initial value of 0.04 which did not require changing during the refinement as the weighting remained approximately uniform throughout the range of data [59]).

Structure determination and refinement

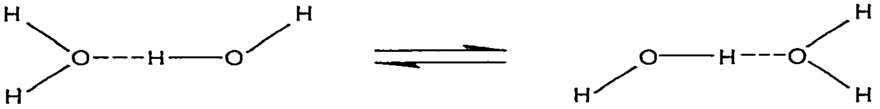
The atomic positions were deduced using conventional heavy-atom Patterson and Fourier techniques. No attempt was made at this stage to differentiate between the carbon and oxygen atoms of the coordinated formaldehyde, and they were both assigned atomic scattering factors appropriate to carbon atoms. A difference electron density synthesis revealed one large peak (of height similar to that of a phenyl carbon atom) which had not been assigned as an atomic site. This peak was further than 3.0 Å from any of the atom positions already included but was only 2.6 Å from its symmetry-related position at ($-x$, $-y$, $-z$). It was deduced that the peak was due to the oxygen atom of a water molecule, which hydrogen-bonded to a second water molecule through the centre of symmetry. The resulting water 'dimer' occupied an interstice in the crystal lattice. The origin of these water molecules is not clear, but it is possible that the dichloromethane/ethanol solvent used to recrystallise the sample was not completely dry. It is noted that the NMR spectrum shows corroborative evidence for the presence of water molecules.

Refinement of atomic parameters employed the full least-squares matrix and minimised the function $\Sigma w(|F_o| - |F_c|)^2$, with weights $w = 4|F_o|^2/\sigma^2(F_o)^2$. Atomic scattering factors and dispersion corrections were from standard listings [60]. Residuals quoted are $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$ and $R_w = \{\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2\}^{1/2}$. During initial refinement, the isotropic temperature factors of the two non-hydrogen atoms of the formaldehyde group adopted dissimilar values, and thereafter, the atom with the smaller temperature factor was assumed to be the oxygen. Its form-factor identifier was altered accordingly.

During the process of refinement all non-hydrogen atoms except the phenyl carbons were assigned anisotropic thermal parameters. Hydrogen atoms associated with the phenyl rings were included in calculated positions (C—H 1.0 Å) and were given isotropic temperature factors 10% greater than those of the carbon atoms to which they were bonded. After several cycles, the residual, R, was 0.048.

Attempts were then made to locate the two hydrogen atoms of the formaldehyde ligand. The procedure adopted was one found to be successful in previous cases and makes use of the fact that hydrogen atoms only contribute significantly to the intensities of low θ reflections [61]. Two separate difference electron density maps were calculated, one with an upper limit on $\sin\theta/\lambda$ of 0.3 Å^{-1} (727 reflections), and one including all data. Hydrogen atoms were omitted from the calculations. In order to assess the reliability of the procedure, the phenyl hydrogens were examined first. On comparison of the two difference maps there was found to be a close correlation between the calculated positions of the phenyl hydrogen atoms and the positions of common high electron density. Thus encouraged, the area around the formaldehyde ligand was closely examined and found to contain only two possible peaks of electron density, of heights similar to those of the phenyl hydrogen atoms. They existed as distinct peaks 1.07 and 1.14 Å from the carbon atom of the formaldehyde and no peaks were near to the atom assigned as the oxygen. Thus the result of the electron density syntheses enabled the unambiguous location of the formaldehyde hydrogen atoms and confirmed the original assignment of carbon and oxygen atoms.

In view of the success of the above exercise, the same process was applied to attempt to locate the hydrogen atoms of the water dimer. Two well-defined peaks of relatively high electron density were found close to the oxygen atom, and a third more diffuse elongated peak was situated on the centre of symmetry. Such an arrangement of electron density is consistent with a disordered model for the water dimer.



With all atoms included in the structure factor calculations two further full-matrix least-squares refinement cycles were computed. A subsequent weighting

TABLE 8

ATOMIC POSITIONS FOR $Os(\eta^2\text{-}CH_2O)(CO)_2(PPh_3)_2 \cdot H_2O$

Atom	*x/a*	*y/b*	*z/c*	Atom	*x/a*	*y/b*	*z/c*
Os	0.24011(2)	−0.00175(4)	0.46909(5)	C(41)	0.3568(6)	0.219(1)	0.331(1)
P(1)	0.1421(1)	−0.2001(3)	0.4624(3)	C(42)	0.4288(7)	0.305(1)	0.329(1)
P(2)	0.3400(1)	0.2098(3)	0.5044(3)	C(43)	0.4392(9)	0.313(2)	0.194(2)
C(1)	0.3138(7)	−0.023(1)	0.628(1)	C(44)	0.3786(8)	0.240(1)	0.068(2)
O(1)	0.2725(6)	0.088(1)	0.702(1)	C(45)	0.3092(7)	0.156(1)	0.070(1)
C(2)	0.2517(6)	−0.120(1)	0.269(1)	C(46)	0.2985(6)	0.147(1)	0.201(1)
O(2)	0.2580(5)	−0.1891(9)	0.152(1)	C(51)	0.4351(5)	0.241(1)	0.600(1)
C(3)	0.1638(6)	0.059(1)	0.409(1)	C(52)	0.4787(7)	0.173(1)	0.521(1)
O(3)	0.1212(5)	0.0910(9)	0.367(1)	C(53)	0.5512(8)	0.192(1)	0.593(2)
O(S)	0.4860(9)	−0.037(1)	0.103(1)	C(54)	0.5767(7)	0.278(1)	0.747(2)
C(11)	0.1232(5)	−0.160(1)	0.652(1)	C(55)	0.5346(7)	0.344(1)	0.826(2)
C(12)	0.1333(6)	−0.239(1)	0.722(1)	C(56)	0.4633(7)	0.329(1)	0.756(1)
C(13)	0.1213(7)	−0.199(1)	0.869(2)	C(61)	0.3238(6)	0.379(1)	0.622(1)
C(14)	0.0972(7)	−0.091(1)	0.941(1)	C(62)	0.2980(6)	0.398(1)	0.754(1)
C(15)	0.0871(7)	−0.015(1)	0.874(1)	C(63)	0.2882(7)	0.530(1)	0.851(2)
C(16)	0.1001(6)	−0.048(1)	0.728(1)	C(64)	0.3031(8)	0.633(1)	0.812(2)
C(21)	0.0488(5)	−0.2561(9)	0.341(1)	C(65)	0.3296(9)	0.617(2)	0.682(2)
C(22)	−0.0172(7)	−0.271(1)	0.387(1)	C(66)	0.3395(7)	0.485(1)	0.583(2)
C(23)	−0.0875(9)	−0.317(2)	0.286(2)	H(1)	0.3550	−0.0390	0.6900
C(24)	−0.0884(8)	−0.353(1)	0.135(2)	H(2)	0.2982	−0.1073	0.6668
C(25)	−0.0230(7)	−0.338(1)	0.088(1)	H(S1)	0.5443	0.0344	0.1614
C(26)	0.0456(6)	−0.292(1)	0.190(1)	H(S2)	0.4333	−0.0239	0.0956
C(31)	0.1550(5)	−0.372(1)	0.385(1)	H(S3)	0.5	0.0	0.0
C(32)	0.2236(6)	−0.383(1)	0.348(1)				
C(33)	0.2307(7)	−0.520(1)	0.281(1)				
C(34)	0.1712(7)	−0.639(1)	0.256(1)				
C(35)	0.1043(7)	−0.631(1)	0.291(1)				
C(36)	0.0946(6)	−0.496(1)	0.357(1)				

scheme analysis showed minimal variation in the function $\langle \Sigma w(\Delta F^2)/N \rangle$ throughout ranges of F_o, indicating that the p factor of 0.04 was well-chosen. The maximum shift/error for the parameters of the heavier atoms was 0.04, and for the carbon atoms 0.16, and as the sign of the shifts appeared to be random refinement was deemed to be complete. The final residuals were 0.047 and 0.061 for R and R_w, respectively.

Final atomic positions are listed in Table 8. The atomic numbering scheme is outlined in Fig. 1. Tables of thermal parameters, calculated hydrogen positions, and observed and calculated structure factors are available on request from the authors (G.R.C.).

$Os(CHO)H(CO)_2(PPh_3)_2$

(a) $Os(\eta^2\text{-}CH_2O)(CO)_2(PPh_3)_2 \cdot H_2O$ (2.0 g) was heated at ~75°C for several hours (8—12 h, completion of reaction was determined by IR spectrum of crude product). The crude product was purified by column chromatography on florisil using dichloromethane as eluent; the pale yellow band was collected and on addition of ethanol pale yellow needles crystallised (1.24 g, 63.4%). Recrystallization from dichloromethane/ethanol gave pale yellow crystals containing 0.67 mol dichloromethane of solvation. ^1H NMR (τ, $CDCl_3$) 4.73 (s, 1.33 H, CH_2Cl_2). M.p. 193—195°C. Anal. Found: C, 55.48; H, 4.28; P, 7.31%. $C_{39}H_{32}O_3OsP_2 \cdot (CH_2Cl_2)_{0.67}$ calcd.: C, 55.59; H, 3.92; P, 7.23%.

(b) $[OsH(CO)_3(PPh_3)_2]ClO_4$ [56] (0.20 g) was dissolved in dichloromethane (15 ml) and a filtered solution of sodium borohydride (0.10 g) in ethanol (10 ml) was added. After 5 min. stirring the dichloromethane was removed under reduced pressure without the application of heat. The pale yellow crystals were collected and washed with water and ethanol (0.15 g, 84.2%). The product was characterized by comparison with a sample produced by method (a).

$\overline{OsH(C_6H_4P}Ph_2)(CO)_2(PPh_3)$

(a) $Os(\eta^2\text{-}CH_2O)(CO)_2(PPh_3)_2 \cdot H_2O$ (1.0 g) was heated under reflux in ethanol (25 ml) for 5 h. The resulting suspension was cooled on ice. Filtration gave white crystals which were recrystallized from dichloromethane/ethanol to afford white microcrystals of the title compound (0.68 g, 72.2%). M.p. 188—190°C. Anal. Found: C, 59.42; H, 3.73. $C_{38}H_{30}O_2OsP_2$ calcd.: C, 59.21; H, 3.92%.

(b) $Os(\eta^2\text{-}C_2H_4)(CO)_2(PPh_3)_2$ [8,9] (1.0 g) was heated under reflux in t-butanol suspension (40 ml). After 12 h the suspension was allowed to cool to room temperature and the white crystals were collected (0.75 g, 77.7%). The product was characterized by comparison of the IR spectrum with that of a sample produced by method (a).

$Os(CO)_2(PPh_3)_3$

(a) $Os(\eta^2\text{-}CH_2O)(CO)_2(PPh_3)_2 \cdot H_2O$ (0.15 g) was suspended in methanol (20 ml) and triphenylphosphine (0.10 g) was added. The suspension was heated under reflux for 12 h and the yellow crystals were collected and washed with methanol (0.16 g, 84.5%). Characterization was by comparison with an authentic sample [8,9].

(b) $\overline{\mathrm{OsH(C_6H_4P}}\mathrm{Ph_2)(CO)_2(PPh_3)}$ (0.10 g) was treated as above to afford yellow crystals (0.12 g, 89.6%) which were characterized in a similar manner.

$OsHCl(CO)_2(PPh_3)_2$

$\overline{\mathrm{OsH(C_6H_4P}}\mathrm{Ph_2)(CO)_2(PPh_3)}$ (0.10 g) was dissolved in a solution comprised of dichloromethane (10 ml), ethanol (5 ml) and concentrated hydrochloric acid (0.1 ml) and heated under reflux for 30 min. Removal of the dichloromethane effected complete crystallization and the white crystals were filtered and washed with ethanol (0.10 g, 95.5%). The product was characterized by comparison of the IR spectrum with that of an authentic sample [56].

$Os(CH_2OH)Cl(CO)_2(PPh_3)_2$

$\mathrm{Os(\eta^2\text{-}CH_2O)(CO)_2(PPh_3)_2 \cdot H_2O}$ (1.0 g) was stirred in a solution consisting of dichloromethane (25 ml), ethanol (5 ml) and concentrated hydrochloric acid (0.11 ml, 1.05 equiv.) until solution had been effected. The solvent volume was reduced to afford white needles which were collected and washed with ethanol (0.76 g, 74.3%). Recrystallization from dichloromethane/n-hexane yielded crystals of the solvate $\mathrm{Os(CH_2OH)Cl(CO)_2(PPh_3)_2 \cdot (CH_2Cl_2)_{0.25}}$. ^{1}H NMR ($\tau$, $CDCl_3$) 4.76 (s, 0.5 H, CH_2Cl_2). M.p. 164—166°C. Anal. Found: C, 54.99; H, 4.02. $\mathrm{C_{39}H_{33}ClO_3OsP_2 \cdot (CH_2Cl_2)_{0.25}}$ calcd.: C, 54.91; H, 3.93%.

$Os(CH_2OH)Br(CO)_2(PPh_3)_2$

$\mathrm{Os(\eta^2\text{-}CH_2O)(CO)_2(PPh_3)_2 \cdot H_2O}$ (1.0 g) was stirred in a solution comprised of dichloromethane (30 ml), ethanol (3 ml) and hydrobromic acid (ca. 49%, 0.12 ml, 1.04 equiv.) until solution had been effected. Removal of the dichloromethane yielded a white crystalline product which was filtered and washed with ethanol (0.77 g, 71.5%). Recrystallization from dichloromethane/n-hexane yielded white needles. M.p. 180—183°C. Anal. Found: C, 52.68; H, 4.11. $\mathrm{C_{39}H_{33}BrO_3OsP_2}$ calcd.: C, 53.13; H, 3.77%.

$Os(CH_2OH)(\eta^1\text{-}OC[O]CF_3)(CO)_2(PPh_3)_2$

$\mathrm{Os(\eta^2\text{-}CH_2O)(CO)_2(PPh_3)_2 \cdot H_2O}$ (0.50 g) was stirred in a solution of benzene (10 ml) and trifluoroacetic acid (0.05 ml, 1.10 equiv.) until solution had been effected. n-Hexane was added to afford a white crystalline product which was collected and washed with n-hexane (0.39 g, 69.8%). M.p. 148—150°C. Anal. Found: C, 53.54; H, 3.92. $\mathrm{C_{41}H_{33}F_3O_5OsP_2}$ calcd.: C, 53.83; H, 3.64%.

$Os(CH_2OH)H(CO)_2(PPh_3)_2$

$\mathrm{Os(CH_2OH)Cl(CO)_2(PPh_3)_2 \cdot (CH_2Cl_2)_{0.25}}$ (0.25 g) was dissolved in dichloromethane (20 ml) and a filtered solution of sodium borohydride (0.1 g) in ethanol (10 ml) was added. After 5 min. stirring the dichloromethane was removed under reduced pressure without the application of heat. The white crystalline product was washed with water and ethanol (0.15 g, 64.2%). Recrystallization of an analytical sample from dichloromethane/n-hexane afforded white crystals containing 0.33 mol dichloromethane of solvation. ^{1}H NMR (τ, $CDCl_3$) 4.76 (s, 0.67 H, CH_2Cl_2). M.p. 191—192°C. Anal. Found: C, 56.70; H, 4.28. $\mathrm{C_{39}H_{34}O_3OsP_2 \cdot (CH_2Cl_2)_{0.33}}$ calcd.: C, 56.85; H, 4.21%.

$Os(CH_2Cl)Cl(CO)_2(PPh_3)_2$

(a) $Os(\eta^2\text{-}CH_2O)(CO)_2(PPh_3)_2 \cdot H_2O$ (1.0 g) was stirred in a solution comprised of dichloromethane (30 ml), ethanol (5 ml) and concentrated hydrochloric acid (0.5 ml) for 45 min. Removal of the dichloromethane afforded white crystals which were collected and washed with ethanol. Recrystallization from dichloromethane/n-pentane afforded white needles (0.98 g, 93.8%). M.p. 233—235°C. Anal. Found: C, 55.00; H, 4.04; P, 7.17. $C_{39}H_{32}Cl_2O_2OsP_2$ calcd.: C, 54.74; H, 3.77; P, 7.24%.

(b) $Os(CH_2OH)Cl(CO)_2(PPh_3)_2 \cdot (CH_2Cl_2)_{0.25}$ (0.20 g) was stirred in a solution of dichloromethane (25 ml), ethanol (5 ml) and concentrated hydrochloric acid (0.5 ml) for 1 h. The solvent volume was reduced to yield white needles which were collected and washed with ethanol (0.18 g, 90.3%). The product was characterized by comparison of the IR spectrum with that of an authentic sample prepared by method (a).

$Os(CH_2Br)Br(CO)_2(PPh_3)_2$

(a) $Os(\eta^2\text{-}CH_2O)(CO)_2(PPh_3)_2 \cdot H_2O$ (1.0 g) was stirred in a solution comprised of dichloromethane (30 ml), ethanol (5 ml) and hydrobromic acid (ca. 49%, 1 ml) for 20 min. Upon reduction of the solvent volume white crystals deposited which were collected and washed with ethanol (1.10 g, 95.3%). Recrystallization from dichloromethane/n-hexane yielded white needles which contained 1 mol n-hexane of solvation. ^1H NMR (τ, $CDCl_3$) 8.73, 9.10 (2m, 14 H, C_6H_{14}). M.p. 178—180°C. Anal. Found: C, 52.33; H, 4.54. $C_{39}H_{32}Br_2O_2OsP_2 \cdot C_6H_{14}$ calcd.: C, 52.43; H, 4.50%.

(b) $Os(CH_2OH)Br(CO)_2(PPh_3)_2$ (0.20 g) was stirred in a solution of dichloromethane (30 ml), ethanol (5 ml) and hydrobromic acid (ca. 49%, 0.5 ml) for 45 min. Removal of the dichloromethane yielded white needles (0.2 g, 93.3%) which were characterized by comparison with an authentic sample.

$Os(CH_2I)I(CO)_2(PPh_3)_2$

$Os(\eta^2\text{-}CH_2O)(CO)_2(PPh_3)_2 \cdot H_2O$ (2.0 g) was dissolved in a solution comprised of dichloromethane (75 ml), isopropanol (5 ml) and hydroiodic acid (ca. 55%, 1 ml). Removal of the dichloromethane gave white needles which were filtered, washed with isopropanol and hexane and recrystallized from dichloromethane/isopropanol (2.47 g, 97.4%). M.p. 245—248°C. Anal. Found: C, 45.07; H, 3.48. $C_{39}H_{32}I_2O_2OsP_2$ calcd.: C, 45.10; H, 3.11%.

$Os(CH_2Br)Cl(CO)_2(PPh_3)_2$

$Os(CH_2OH)Cl(CO)_2(PPh_3)_2 \cdot (CH_2Cl_2)_{0.25}$ (0.20 g) was dissolved in a solution of dichloromethane (30 ml), ethanol (5 ml) and hydrobromic acid (ca. 49%, 0.5 ml). After stirring for 45 min. removal of the dichloromethane afforded a white crystalline product which was washed with ethanol (0.185 g, 88.2%). Recrystallization from dichloromethane/n-hexane yielded white needles. M.p. 178—181°C. Anal. Found: C, 52.27; H, 4.04. $C_{39}H_{32}BrClO_2OsP_2$ calcd.: C, 52.04; H, 3.58%.

$Os(CH_2I)Cl(CO)_2(PPh_3)_2$

$Os(CH_2OH)Cl(CO)_2(PPh_3)_2 \cdot (CH_2Cl_2)_{0.25}$ (0.20 g) was stirred in a solution comprised of dichloromethane (30 ml), isopropanol (5 ml) and hydroiodic acid (ca. 55%, 0.5 ml) for 30 min. Reduction of the solvent volume gave white crystals (0.20 g, 90.6%). An analytical sample was recrystallized from dichloromethane/n-hexane to afford white needles. M.p. 175—177°C. Anal. Found: C, 49.52; H, 3.70. $C_{39}H_{32}ClIO_2OsP_2$ calcd.: C, 49.45; H, 3.41%.

$[Os(CH_2OMe)(H_2O)(CO)_2(PPh_3)_2]CF_3SO_3$

(a) $Os(\eta^2\text{-}CH_2O)(CO)_2(PPh_3)_2 \cdot H_2O$ (0.50 g) was suspended in benzene (10 ml) and methyl triflate (0.2 ml) was added. After stirring for 15 min n-hexane was added and the white crystalline solid collected and washed with n-hexane. Recrystallization from dichloromethane/ethanol/cyclohexane afforded white needles (0.55 g, 91.6%). M.p. 177—179°C. Anal. Found: C, 49.94; H, 4.20; P, 6.16. $C_{41}H_{35}F_3O_6OsP_2S$ calcd.: C, 50.10; H, 3.79; P, 6.30%.

(b) $Os(CHO)H(CO)_2(PPh_3)_2 \cdot (CH_2Cl_2)_{0.67}$ (0.15 g) was dissolved in benzene (5 ml) and methyl triflate (0.1 ml) was added. The solution was stirred for 10 min; addition of n-hexane gave a white crystalline product (0.165 g, 96.0%) which was characterized by comparison of the IR spectrum with that of a sample produced by method (a).

$Os(CH_2OMe)Cl(CO)_2(PPh_3)_2$

$[Os(CH_2OMe)(H_2O)(CO)_2(PPh_3)_2]CF_3SO_3$ (0.20 g) and lithium chloride (0.10 g) were heated under reflux in methanol solution (20 ml) for 5 min. The white needles were collected and washed with methanol (0.17 g, 98.1%). An analytical sample was recrystallized from dichloromethane/methanol. M.p. 212—214°C. Anal. Found: C, 56.11; H, 3.61; P, 7.08. $C_{40}H_{35}ClO_3OsP_2$ calcd.: C, 56.44; H, 4.14; P, 7.28%.

$Os(\eta^1\text{-}C[O]CH_3)H(CO)_2(PPh_3)_2$

$Os(CO)_2(PPh_3)_3$ (0.50 g) was dissolved in degassed benzene (50 ml) and acetaldehyde (0.5 ml) was added. The light from a 1000 Watt tungsten-halogen sun-lamp was directed at the reaction flask which was cooled by a constant air flow across the surface. When the solution was quite colourless (8—9 h) the solvent volume was reduced to 5 ml and n-hexane was added to effect complete crystallization. Recrystallization from dichloromethane/ethanol/n-hexane afforded white crystals (0.32 g, 81.1%). M.p. 188—190°C. Anal. Found: C, 58.98; H, 4.57. $C_{40}H_{34}O_3OsP_2$ calcd.: C, 58.96; H, 4.21%.

Trans-$[OsCl(CO)_2(PPh_3)_3]ClO_4$

$Os(CO)_2(PPh_3)_3$ (0.50 g) was stirred in benzene (40 ml) and trichloroacetaldehyde (0.20 ml) was added, followed by $NaClO_4$ (0.25 g) in ethanol (10 ml). n-Hexane was added to effect complete crystallization. Recrystallization from dichloromethane/ethanol/cyclohexane gave white platelets (0.51 g, 90.2%). M.p. >200°C. Anal. Found: C, 57.50; H, 4.01; P, 7.79. $C_{56}H_{45}Cl_2O_6OsP_3$ calcd.: C, 57.59; H, 3.88; P, 7.96%.

$[OsCl(CO)_3(PPh_3)_2]ClO_4$

trans-$[OsCl(CO)_2(PPh_3)_3]ClO_4$ (0.50 g) in dichloromethane (30 ml) was heated under carbon monoxide (60 p.s.i.) at 80°C for 2 h. After cooling to room temperature n-hexane (20 ml) was added and removal of the dichloromethane yielded white crystals (0.38 g, 95.1%) which were characterized by comparison with an authentic sample [55].

Os(CHO)Cl(CO)$_2$(PPh$_3$)$_2$

[OsCl(CO)$_3$(PPh$_3$)$_2$]ClO$_4$ (0.20 g) was dissolved in dichloromethane (10 ml) and a filtered solution of sodium borohydride (0.10 g) in ethanol (10 ml) was added. After 5 min stirring the dichloromethane was removed under reduced pressure without the application of heat. The pale yellow crystals were collected and washed with water and ethanol (0.14 g). IR indicates a mixture of Os(CHO)Cl(CO)$_2$(PPh$_3$)$_2$ and OsHCl(CO)$_2$(PPh$_3$)$_2$ (ca. 70/30), but further purification was not possible.

Os(CHO)Br(CO)$_2$(PPh$_3$)$_2$

[OsBr(CO)$_3$(PPh$_3$)$_2$]ClO$_4$ [55] (0.20 g) was treated as above to afford pale yellow crystals (0.145 g). IR indicates a mixture of Os(CHO)Br(CO)$_2$(PPh$_3$)$_2$ and OsHBr(CO)$_2$(PPh$_3$)$_2$ (ca. 60/40) but further purification was not possible.

Os(CHO)(CH$_3$)(CO)$_2$(PPh$_3$)$_2$

[Os(CH$_3$)(CO)$_3$(PPh$_3$)$_2$]ClO$_4$ [48] (0.20 g) was treated as above to afford pale yellow crystals (0.155 g, 86.9%). Recrystallization from dichloromethane/ethanol/n-hexane afforded pale yellow plates. M.p. 182—186°C. Anal. Found: C, 58.93; H, 4.28. $C_{40}H_{34}O_3OsP_2$ calcd.: C, 58.96; H, 4.21%.

Os(CHO)(CH$_2$OMe)(CO)$_2$(PPh$_3$)$_2$

[Os(CH$_2$OMe)(CO)$_3$(PPh$_3$)$_2$]ClO$_4$ [48] (0.20 g) was treated as above to give a pale yellow crystalline product (0.145 g, 80.9%). Recrystallization from dichloromethane/ethanol/n-hexane yielded pale yellow needles. M.p. 169—174°C. Anal. Found: C, 58.51; H, 4.77. $C_{41}H_{36}O_4OsP_2$ calcd.: C, 58.29, H, 4.30%.

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