Oxidative Addition Reactions of Triphenylphosphine with Dodecacarbonyltriosmium

By **C. W. Bradford,*** Johnson Matthey & Co. Ltd., Wembley, Middlesex HA9 0HW
(the late) **Ronald S. Nyholm**, Chemistry Department, University College, 20 Gordon Street, London WC1H 0AJ

Reaction of $Os_3(CO)_{12}$ with PPh_3 in the mole ratio of 1 : 2 gave a mixture of nine products among which were the unusual new compounds $HOs_3(CO)_9(PPh_3)(PPh_2C_6H_4)$, $HOs_3(CO)_8(PPh_3)(PPh_2C_6H_4)$, $HOs_3(CO)_7(PPh_2)(PPh_3)(C_6H_4)$, $Os_3(CO)_8(PPh_2)(Ph)(PPhC_6H_4)$, and $Os_3(CO)_7(PPh_2)_2(C_6H_4)$. Decomposition of $Os_3(CO)_{10}(PPh_3)_2$ led to a similar mixture which also included the compound $HOs_3(CO)_7(PPh_2)(PPh_2C_6H_4C_6H_3)$. Some analogous $AsPh_3$ and $P(C_6H_4Me)_3$ derivatives and the new protonated species $[HOs_3(CO)_9(PPh_3)_3]^+Br^-$ were also prepared, the latter to assist in n.m.r. studies. The general properties, structures, and i.r., high field n.m.r., and mass spectra of the new compounds are described.

REACTION of $Os_3(CO)_{12}$ with an excess of PPh_3 in xylene under reflux gives good yields of the trisubstituted derivative $Os_3(CO)_9(PPh_3)_3$.[1] The mono- and di-substituted derivatives were first obtained as by-products during the reaction of the dodecacarbonyl with $(Ph_3P)AuCl$.[2] Mixtures of all three derivatives $Os_3(CO)_{12-x}L_x$ ($x = 1—3$, L = $PMePh_2$, PEt_2Ph, and PEt_3) were later obtained by direct reaction of the dodecacarbonyl with the phosphine.[3]

In an attempt to prepare a mixture of all three PPh_3

---

[1] C. W. Bradford and R. S. Nyholm, *Chem. Comm.*, 1967, 384.

[2] C. W. Bradford and R. S. Nyholm, *Chem. Comm.*, 1968, 867; C. W. Bradford, W. van Bronswijk, R. J. H. Clark, and R. S. Nyholm, *J. Chem. Soc.* (*A*), 1970, 2889.

[3] A. J. Deeming, B. F. G. Johnson, and J. Lewis, *J. Organometallic Chem.*, 1969, **17**, P40; *J. Chem. Soc.* (*A*), 1970, 897.

derivatives by direct reaction with the phosphine, the dodecacarbonyl and PPh_3 were reacted together in the mole ratio of 1 : 2 (*i.e.* sufficient phosphine to substitute carbonyl groups on average on only two of the three osmium atoms). The three compounds expected were obtained, but in a mixture with six other derivatives.

The nine compounds were separated by fractional crystallisation and chromatography on alumina columns. The general properties and i.r. spectra of the new compounds are given in Table 1 and analytical data in Table 2. The numbering of the compounds (I)—(X) follows that used in the two preliminary communications [4,5] to avoid confusion. The tenth compound (X) was obtained together with a mixture of compounds (I)—(VI) on heating the disubstituted derivative $Os_3(CO)_{10}(PPh_3)_2$ in xylene under reflux. Some similar Ph_3As and $(C_6H_4Me)_3P$ derivatives were also prepared, the former on reaction of the dodecacarbonyl with an excess of arsine. For these two ligands the new mono- and di-substituted derivatives are included in the Tables.

In the previous communications [4,5] the preliminary results were given of *X*-ray crystallographic investigations by R. Mason and co-workers of the structures of six of the compounds. These are shown diagrammatically in the Figure. In the case of compound (III) crystals suitable for *X*-ray studies were not obtained and consequently this is the only compound for which the true formula is not known. It is very likely that as with the other compounds there has been loss of an *ortho*-hydrogen atom from one of the phenyl groups and to indicate this possibility when writing the formula of (III) the phenyl groups have been enclosed in inverted commas.

TABLE 1

General properties and infrared spectra of the new phosphine and arsine derivatives of $Os_3(CO)_{12}$

No.	Compound	Colour	Melting point °C	Infrared bands in the region 2200—1650 cm^{-1} (in CCl_4 solution)
(I)	$Os_3(CO)_8(PPh_2)(Ph)(PPhC_6H_4)$	Orange	195	2074s, 2046s, 2023ms, 2000ms, 1993m, 1973ms, 1942m
(II)	$Os_3(CO)_7(PPh_2)_2(C_6H_4)$	Red	238	2058ms, 2010m, 1999s, 1992sh, 1951m, 1937mw
(III)	$Os_3(CO)_8$‘ $(PPh_3)(PPh_2)$ ’	Yellow	217	2068s, 2036s, 2006s, 2000sh, 1968m, 1959sh, 1943mw
(IV)	$HOs_3(CO)_8(PPh_3)(PPh_2C_6H_4)$	Orange-red	198	2120vw, 2086vw, 2070s, 2027s, 2010ms, 1998mw, 1988mw, 1974m, 1960m, 1947m, 1938sh
(V)	$HOs_3(CO)_9(PPh_3)(PPh_2C_6H_4)$	Yellow	199	2087vw, 2047mw, 2013sh, 2007s, 1994sh, 1969mw, 1944mw
(VI)	$HOs_3(CO)_7(PPh_2)(PPh_3)(C_6H_4)$	Yellow	d. 210—220	2058s, 2016m, 1995s, 1985sh, 1976sh, 1955mw, 1922m
(VII)	$Os_3(CO)_8[P(C_6H_4Me)_2][C_6H_4Me][P(C_6H_4Me)(C_6H_3Me)]$	Orange	204	2073s, 2045s, 2020ms, 1998ms, 1991m, 1970ms, 1938m
(VIII)	$Os_3(CO)_7(AsPh_2)_2(C_6H_4)$	Red	238	2055ms, 2007m, 1995s,b, 1950m, 1935mw
(IX)	$[HOs_3(CO)_9(PPh_3)_3]^+Br^-$	Orange	146	* 2097w, 2064m, 2021vs, 2007sh, 1985w, 1965wb
(X)	$HOs_3(CO)_7(PPh_2)(PPh_2C_6H_4C_6H_3)$	Yellow	d. 243	2056s, 2017ms, 2001s, 1983m, 1958m, 1929m
(XI)	$Os_3(CO)_{11}[P(C_6H_4Me)_3]$	Yellow	181	2104m, 2052s, 2032ms, 2016s, 1997m, 1986m, 1974m, 1954mw
(XII)	$Os_3(CO)_{10}[P(C_6H_4Me)_3]_2$	Orange	d. 180—190	2083mw, 2028s, 2010m, 1997s, 1968m, 1951sh
(XIII)	$Os_3(CO)_{10}(AsPh_3)_2$	Orange	187	2085mw, 2030s, 2013m, 1998s, 1969m, 1947mw

* In $CHCl_3$ solution. d. = Decomposition.

TABLE 2

Analytical data for the new phosphine and arsine derivatives of $Os_3(CO)_{12}$

		Analytical data [a]					(By osmometry)	
No.	Compound	C	H	O	Os	P (or As)	*M* [a]	Concn. M
(I)	$Os_3(CO)_8(PPh_2)(Ph)(PPhC_6H_4)$	36·7 (36·8)	2·2 (2·0)	10·0 (10·3)	45·2 (46·0)	5·2 (5·0)	1232 (1241)	0·006 [b]
(II)	$Os_3(CO)_7(PPh_2)_2(C_6H_4)$	36·6 (36·6)	2·2 (2·0)	9·2 (9·2)	45·7 (47·0)	4·9 (5·1)	1364 (1213)	0·003 [b]
(III) [c]	$Os_3(CO)_8$‘ $(PPh_3)(PPh_2)$ ’	37·5 (36·8)	2·3 (2·0)	10·8 (10·3)	(46·0)	4·6 (5·0)	(1241)	
(IV)	$HOs_3(CO)_8)PPh_3)(PPh_2C_6H_4)$	40·1 (40·1)	2·4 (2·3)	9·8 (9·7)	41·5 (43·2)	4·6 (4·7)	1224 (1319)	0·009 [d]
(V)	$HOs_3(CO)_9(PPh_3)(PPh_2C_6H_4)$	40·0 (40·1)	2·4 (2·2)	10·4 (10·7)	(42·3)	4·4 (4·6)	1392 (1347)	0·006 [d]
(VI)	$HOs_3(CO)_7(PPh_2)(PPh_3)(C_6H_4)$	39·8 (40·0)	2·3 (2·3)	8·7 (8·7)	(44·2)	4·5 (4·8)	1243 (1291)	0·002 [d]
(VII)	$Os_3(CO)_8[P(C_6H_4Me)_2][C_6H_4Me][P(C_6H_4Me)(C_6H_3Me)]$	40·4 (39·4)	2·9 (2·6)	(9·8)	(43·5)	4·6 (4·7)	1350 (1311)	0·001 [b]
(VIII)	$Os_3(CO)_7(AsPh_2)_2(C_6H_4)$	34·4(34·2)	2·3 (1·9)	(8·6)	(43·9)	(11·5)	(1301)	
(IX) [e]	$[HOs_3(CO)_9(PPh_3)_3]^+Br^-$	44·9 (44·8)	2·7 (2·7)	8·4 (8·5)	(33·8)	5·2 (5·5)	(1690)	
(XI)	$Os_3(CO)_{11}[P(C_6H_4Me)_3]$	32·9 (32·5)	1·8 (1·8)	(14·9)	(48·2)	(2·6)	1110 (1183)	0·010 [d]
(XII)	$Os_3(CO)_{10}[P(C_6H_4Me)_3]_2$	43·2 (42·8)	3·2 (2·9)	10·6 (11·0)	(39·1)	4·3 (4·2)	1640 (1459)	0·004 [b]
(XIII)	$Os_3(CO)_{10}(AsPh_3)_2$	38·5 (37·8)	2·2 (2·1)	10·3 (10·9)	(39·0)	(10·2)	1671 (1463)	0·005 [b]

[a] Calculated values in parentheses. [b] In benzene solution. [c] Calculated assuming loss of one hydrogen atom. [d] In chloroform solution. [e] %Br: Found 4·5, Calc. 4·7%.

As mentioned above compounds (I)—(VI) and (X) can be obtained by the decomposition of $Os_3(CO)_{10}(PPh_3)_2$. The yields of the hydrides (IV) and (V) decrease as the reaction time is increased suggesting that the decomposition proceeds *via* these hydrides. This was confirmed by heating (IV) under similar conditions; compounds (II), (III), and (X) were identified in the reaction mixture. It seems likely that (V) is first formed by reaction of a C–H bond of one triphenylphosphine ligand with a second osmium atom

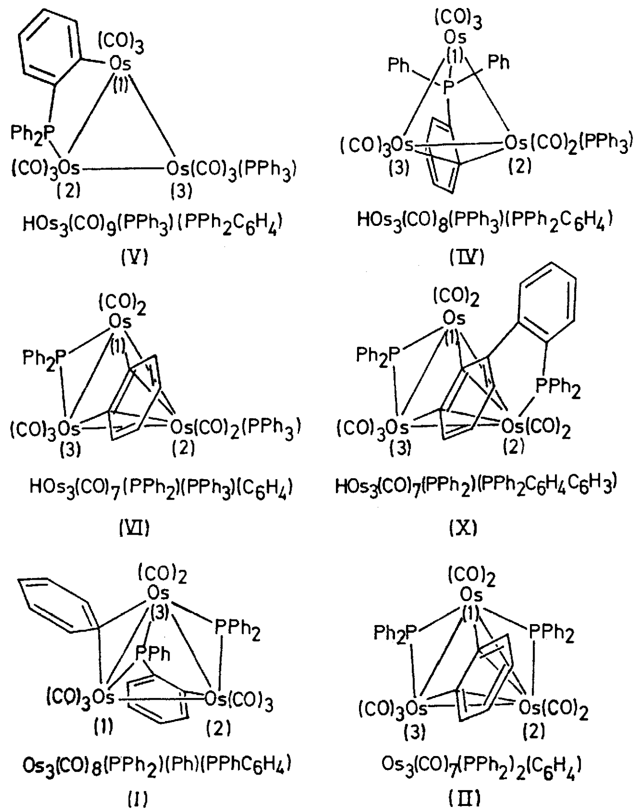
---

[4] C. W. Bradford, R. S. Nyholm, G. J. Gainsford, J. M. Guss, P. R. Ireland, and R. Mason, *Chem. Comm.*, 1972, 87.

[5] G. J. Gainsford, J. M. Guss, P. R. Ireland, R. Mason, C. W. Bradford, and R. S. Nyholm, *J. Organometallic Chem.*, 1972, **40**, C70.

(not the osmium atom to which the phosphine is coordinated) to form an osmium–carbon bond and a five membered chelate ring. Presumably (V) then loses carbon monoxide forming (IV) which in turn decomposes to (I), (II), and (VI). Compound (X) is probably formed from (VI) by elimination of hydrogen from the C_6H_4 ligand and an *ortho*-carbon–hydrogen bond of the terminal phosphine ligand with the formation of a carbon–carbon bond.

The high-field n.m.r. spectrum of (V) shows a hydride signal (1 : 1 doublet) at τ 30·36 (J_{P-H} 10 Hz) while that of (IV) is a 1 : 1 : 1 : 1 quartet at τ 27·31 (J_{P-H} 10, 17 Hz). Integrated intensities of the n.m.r. spectra of mixtures of equal weights of (IV) and (V) and of (V) with $[HOs_3(CO)_9(PPh_3)_3]^+Br^-$ showed that both (IV) and (V) contain one hydride ligand. Whereas the $^1H-^{31}P$ spin-spin coupling pattern of (V) can be interpreted as proton coupling to one ^{31}P nucleus, that of (IV) appears to result from the coupling of a proton to two non-equivalent ^{31}P nuclei. Thus it is likely that the hydride ligand bridges Os(1) and Os(2) in both cases.



$HOs_3(CO)_9(PPh_3)(PPh_2C_6H_4)$ (V)

$HOs_3(CO)_8(PPh_3)(PPh_2C_6H_4)$ (IV)

$HOs_3(CO)_7(PPh_2)(PPh_3)(C_6H_4)$ (VI)

$HOs_3(CO)_7(PPh_2)(PPh_2C_6H_4C_6H_3)$ (X)

$Os_3(CO)_8(PPh_2)(Ph)(PPhC_6H_4)$ (I)

$Os_3(CO)_7(PPh_2)_2(C_6H_4)$ (III)

Structures of the complexes. The Os atoms are numbered as in the preliminary communications [4,5] to avoid confusion. For the positions of the hydride ligands see text

The new protonated species $[HOs_3(CO)_9(PPh_3)_3]^+Br^-$ was prepared by treatment of $Os_3(CO)_9(PPh_3)_3$ in chloroform under reflux with dry hydrogen bromide. Its molar conductivity in nitrobenzene (10^{-3}M solution) is 22·0 Ω^{-1} cm^2 mol^{-1} in agreement with the formulation of the compound as a 1 : 1 electrolyte. The high-field n.m.r. spectrum shows a 1 : 2 : 1 triplet at τ 27·92 (J_{P-H} 7·5 Hz) indicating that the proton is coupling equally to two ^{31}P nuclei, *i.e.* the hydride ligand bridges two osmium atoms. The i.r. spectrum in the CO stretching region and the high-field n.m.r. spectra are very similar to the spectra of one of the isomers of $[HOs_3(CO)_9(PMePh_2)_3]^+[PF_6]^-$.[6]

The small amount of compound (VI) available made it difficult to obtain good n.m.r. data. In a relatively dilute solution a weak high field signal (1 : 1 : 1 : 1 quartet) was observed at τ 19·55 (J_{P-H} 11, 15 Hz). There was not sufficient material to allow the number of hydride ligands to be established by the method used for (IV) and (V). However, from consideration of the compound's structure, the inert gas rule, and the likely relationship of (VI) to compounds (IV) and (V), it seems very likely that it has only one hydride ligand. The metal stereochemistry suggests that the hydride is terminally bound to Os(1) although this is at variance with the (admittedly weak) n.m.r. data, which suggest coupling of a proton to two non-equivalent ^{31}P nuclei, *i.e.* the hydride ligand bridging Os(1) and Os(2) or Os(2) and Os(3).

The very small amount of (X) available was insufficient to enable any n.m.r. or analytical data to be obtained. Its obvious structural relationship to (VI) and consideration of the inert gas rule and metal stereochemistry suggest that it also has one hydride ligand terminally bound to Os(1).

No high-field n.m.r. signals were obtained with compounds (I) and (II). Insufficient (III) was available for n.m.r. studies but the similarity of its mass spectrum and analysis to (I) and (II), differing only in the number of carbonyl groups, suggest that it is non-hydridic also.

For compounds (I), (II), and (IV—VI) the n.m.r. spectra in the region τ 1—10 were very complex and no interpretation was attempted. Others [7] have since prepared the dimethylphenylphosphine derivative analogous to (II), *i.e.* $Os_3(CO)_7(PMe_2)_2(C_6H_4)$, for which the n.m.r. is simpler and has been interpreted as showing that the C_6H_4 ligand undergoes rapid rotation relative to the Os_3 ring, a process which necessitates a carbonyl transfer between osmium atoms in the complex. Evidence for the migration of carbonyl groups in cluster compounds through the agency of bridge-terminal interconversion has recently been given for $Rh_4(CO)_{12}$.[8]

The only compound for which the parent ion was observed in the mass spectrum was (II). This showed the ions $Os_3(CO)_n(PPh_2)_2(C_6H_4)^+$ (n = 0—7) and fragments of the $Os_3(PPh_2)_2(C_6H_4)$ cluster; the doubly charged ions $Os_3(CO)_n(PPh_2)_2(C_6H_4)^{2+}$ (n = 0—6) were

---

[6] A. J. Deeming, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc.* (*A*), 1970, 2967.

[7] A. J. Deeming, R. S. Nyholm, and M. Underhill, *Chem. Comm.*, 1972, 224.

[8] F. A. Cotton, L. F. Johnson, L. Kruczynski, and B. L. Shapiro, *J. Amer. Chem. Soc.*, 1972, 6191.

also observed. The parent ion had the expected isotopic pattern (see Table 3). The mass spectrum was calibrated against the spectrum of $Os_4O_4(CO)_{12}$.[9] The most abundant isotope in the molecular ion $Os_4O_4(CO)_{12}^+$ occurs at *m/e* 1162 and this was easily located in the spectrum of a mixture of (II) with the oxocarbonyl. The loss of a hydrogen atom from one of the phenyl groups of (II) was detected in the first instance from the mass spectrum, the accurate calibration showing that the most abundant isotope occurred at *m/e* 1214 instead of at *m/e* 1215 as had been expected from the analytical data which indicated seven carbonyl and five phenyl groups.

TABLE 3

Isotopic pattern for the molecular ion $Os_3(CO)_7(PPh_2)_2(C_6H_4)^+$

m/e	*I*(Calc.)	*I*(Obs.)
1204	0·7	
1205	1·9	2·7
1206	5·2	6·3
1207	10·4	11·8
1208	21·5	25·7
1209	33·0	32·8
1210	52·8	52·9
1211	64·8	68·0
1212	90·6	89·3
1213	85·5	84·1
1214	100·0	100·0
1215	73·2	71·3
1216	85·0	80·4
1217	30·0	30·1
1218	38·1	36·3
1219	14·2	13·3
1220	2·8	2·3
1221	0·4	

Note. Abundances (*I*) were calculated using the abundances of the naturally occurring isotopes of osmium and carbon.

The mass spectra of (I), (IV), and (V) were very similar to that of (II) although with (IV) and (V) heavier ions were also observed in very low abundance. It therefore seems likely that decomposition was occurring in the heated source. The spectrum of (III) showed a heavier ion corresponding to an extra carbonyl group but it was otherwise identical to that of (II).

The formation of (V) is not surprising as there are a number of cases in the literature of an *ortho*-C–H bond of a triarylphosphine or phosphite complex reacting with the central metal atom to form a metal–carbon bond. Such reactions have been reviewed by Parshall.[10] A typical example is the intramolecular addition and metallation of $(PPh_3)_3IrCl$ to give $[PPh_2(C_6H_4)]IrHCl(PPh_3)_2$.[11] Formation of a metal–carbon bond and a bridging hydrogen atom similar to that in (V) was first observed in the reaction between $Ru_3(CO)_{12}$ and phenyl-lithium when $HRu_3(CO)_9[PhC(C_6H_4)]$ was obtained,[12] and later in the reaction between $Ru_3(CO)_{12}$ and cyclododeca-1,5,9-triene when $HRu_3(CO)_9(C_{12}H_{15})$ was the main product.[13]

The other five structures shown in the Figure display some very unusual features. In particular there are the bridging C_6H_4 groups in (II), (VI), and (X), the bridging C_6H_5 group in (I), the metallation of an *ortho*-carbon–hydrogen bond of a triphenylphosphine ligand by two adjacent osmium atoms in (IV), and the carbon–carbon bond in (X) formed by the elimination of hydrogen from the C_6H_4 ligand and an *ortho*-carbon–hydrogen bond of the terminal phosphine ligand in (VI). These structures will be discussed more fully by R. Mason and co-workers when further details of the *X*-ray investigations are published.

EXPERIMENTAL

Preparations.—The following general points apply to all the preparations and are listed here to avoid repetition. (i) The reactions were carried out under nitrogen. (ii) The high boiling point solvents, xylene and toluene, were removed by distillation under reduced pressure. Only the temperature used is stated. (iii) The mixtures left after removal of the solvent were separated by chromatography on alumina columns and by fractional crystallisation. Solutions of the mixtures for separations on the columns were prepared by dissolution in acetone and evaporation on a water-bath with occasional additions of light petroleum until precipitation was about to occur. Sufficient acetone was then added to prevent precipitation on cooling. (iv) The columns (generally 10 in. long, 11/16 in. diameter) were prepared using alumina, Brockman Activity II, suspended in light petroleum. (v) Light petroleum or acetone–light petroleum mixtures were used to elute the columns. Only in the case of mixed solvents is the eluant stated and then only the acetone concentration (by volume) is given. (vi) Unless otherwise stated the light petroleum used had b.p. 60—80 °C. (vii) The yields given are after recrystallisation, usually from acetone–light petroleum. Where other solvents were used they are specified in brackets together with the yields. (viii) Analytical data are given in Table 2.

Reaction of $Os_3(CO)_{12}$ *with* PPh_3 *in the Mole Ratio* 1 : 2.—$Os_3(CO)_{12}$ (5·0 g) and PPh_3 (2·9 g) were heated under reflux in xylene (1 l) for 1 h. The xylene was removed at 60 °C and the residue leached with acetone. The insoluble orange-red material was compound (IV) [0·76 g, chloroform–light petroleum (b.p. 80—100 °C)].

The acetone solution was evaporated to 50 ml, light petroleum (100 ml) added, the solution again evaporated to 50 ml, and further light petroleum (100 ml) added. The orange-yellow precipitate was coagulated by boiling and filtered from the solution (A). The precipitate was dissolved in hot acetone and set aside to crystallise slowly. Initially red crystals of $Os_3(CO)_{10}(PPh_3)_2$ were deposited (0·49 g; acetone). Subsequently yellow crystals of (V) were deposited and separated mechanically from further $Os_3(CO)_{10}(PPh_3)_2$.

Solution (A) was separated on a large column (E) (18 in. long, 1·5 in. diameter). A red solution (B) (*ca.* 800 ml) was first eluted and then a yellow solution (C) (*ca.* 3·5 l).

On standing for 3 days solution (B) deposited a mixture

---

[9] C. W. Bradford and R. S. Nyholm, *J. Chem. Soc.* (*A*), 1971, **2038**.

[10] G. W. Parshall, *Accounts Chem. Res.*, 1970, **3**, 139.

[11] M. A. Bennett and D. L. Milner, *Chem. Comm.*, 1967, 581; *J. Amer. Chem. Soc.*, 1969, **91**, 6983.

[12] A. W. Parkins, E. O. Fischer, G. Huttner, and D. Regler, *Angew. Chem. Internat. Edn.*, 1970, **9**, 633.

[13] M. I. Bruce, M. A. Cairns, and M. Green, *J.C.S. Dalton*, 1972, 1293; A. Cox and P. Woodward, *J. Chem. Soc.* (*A*), 1971, 3599.

of red and orange crystals and these were separated from the solution (D) by decantation. The red crystals were very light and flaky and dissolved more readily in cold acetone than the larger orange crystals. This property and mechanical separation formed the basis of the purification of the two compounds. Residual mixtures were separated on a second, smaller column. The yields of orange (I) and red (II) were 0·67 and 0·26 g respectively.

Solution (D) was separated on a third column. The yellow band first eluted gave on fractional crystallisation further (I) and then yellow $Os_3(CO)_{11}(PPh_3)$ (0·16 g). Subsequent wash liquors gave on fractional crystallisation further (II) and then yellow (III) (0·034 g). Further elution with 5% acetone gave a solution which deposited yellow (VI) (0·005 g; acetone).

The yellow solution (C) was slowly evaporated and deposited (II) (0·13 g). The solution was then separated on a fourth column. Yellow, orange, and yellow bands were eluted in that order and these deposited further (I), (II), and (VI) respectively. These products were recrystallised together with (I) and (II) from solution (D) and the yields were (I) 0·13 g, (II) 0·06 g, and (VI) 0·036 g.

Further elution of the large column (E) with 5% acetone gave a yellow solution (2·5 l). On slow evaporation this deposited a mixture of red $Os_3(CO)_{10}(PPh_3)_2$, yellow (V), and traces of orange-red (IV). These were separated by fractional crystallisation and mechanical means. Complex (V) was recrystallised together with that obtained earlier (0·47 g total). Recrystallisation of the other products gave $Os_3(CO)_{10}(PPh_3)_2$, 0·51 g and (IV), 0·05 g.

Finally elution of column (E) with 20% acetone gave a red solution which deposited $Os_3(CO)_9(PPh_3)_3$ (0·04 g; acetone).

Thus the overall yields were: $Os_3(CO)_{11}(PPh_3)$, 0·16 g; $Os_3(CO)_{10}(PPh_3)_2$, 1·0 g; $Os_3(CO)_9(PPh_3)_3$, 0·04 g; (I), 0·80 g; (II), 0·45 g; (III), 0·034 g; (IV), 0·81 g; (V), 0·47 g; (VI), 0·041 g.

Decomposition of $Os_3(CO)_{10}(PPh_3)_2$.—(1) $Os_3(CO)_{10}(PPh_3)_2$ (0·5 g) was heated under reflux in xylene (80 ml) for 1 h. Evolution of carbon monoxide was detected by passing a slow stream of nitrogen over the solution, through a carbon bed to remove hydrocarbons, and then through a Dräger CO detection tube. The xylene was removed at 60 °C and the residue separated on a column.

A yellow band was first eluted which gave (I) (0·047 g) and then a red band which gave (II) (0·13 g) and (III) (0·026 g). Elution with 1% acetone gave a yellow solution which deposited (VI) (0·005 g).

Finally elution with 5% acetone gave a yellow solution which deposited (X) (0·012 g) and (IV) (0·002 g).

(2) $Os_3(CO)_{10}(PPh_3)_2$ (0·1 g) was heated under reflux in xylene (25 ml) for 15 min. The xylene was removed at 60 °C and the residue dissolved in acetone and light petroleum added. Fractional crystallisation yielded (IV) (0·020 g) and (V) (0·006 g). The compounds remaining in solution were not separated.

Decomposition of $HOs_3(CO)_8(PPh_3)(PPh_2C_6H_4)$, (IV).—Complex (IV), $HOs_3(CO)_8(PPh_3)(PPh_2C_6H_4)$ (0·1 g) was heated under reflux in xylene (25 ml) for 1 h. Evolution of carbon monoxide was detected during the first 45 min. The xylene was removed at 60 °C and the residue separated on a column. Elution gave initially a small yellow band which did not deposit crystals. Subsequent elution with 1% acetone gave an orange band which deposited (II) (0·025 g) and (III) (0·005 g). Finally elution with 5% acetone gave a solution which yielded (X) (0·007 g).

Reaction of $Os_3(CO)_{12}$ *with* $P(C_6H_4Me)_3$ *in the Mole Ratio* 1 : 2.—$Os_3(CO)_{12}$ (1 g) and $P(C_6H_4Me)_3$ (0·67 g) were heated under reflux in xylene (300 ml) for 1 h. The xylene was removed at 60 °C. The residue was separated on a column.

The first band deposited initially orange (VII) (0·2 g). On further evaporation yellow (XI) (0·030 g) was obtained and separated from traces of the orange compound by mechanical means.

Further elution gave a red band from which no crystalline product was obtained.

Finally elution with 5% acetone gave an orange solution which deposited (XII) (0·01 g; acetone).

In a similar experiment on a 0·3 g scale using toluene as solvent and a reaction time of 16 h the only product isolated was (VII) in low yield.

Reaction of $Os_3(CO)_{12}$ *with* $AsPh_3$ *in the Mole Ratio* 1 : 6.—$Os_3(CO)_{12}$ (1 g) and $AsPh_3$ (2 g) were heated under reflux in xylene (250 ml) for 1 h. The orange solution was evaporated to 30 ml at 60 °C. There was no precipitate. Evaporation was continued to dryness. The residue was separated on a column.

The first yellow band eluted gave $Os_3(CO)_{11}(AsPh_3)$ [2] (0·15 g). Further elution with 5% acetone gave an orange-yellow solution which deposited (XIII) (0·082 g).

In a similar experiment on a 0·3 g scale and reaction time of 7 h, elution of the column gave initially a yellow band and then a red band which deposited (VIII) (0·025 g).

Hydridononacarbonyltris(triphenylphosphine)triosmium bromide, (IX).—Dry hydrogen bromide was bubbled for 1 h through a solution of $Os_3(CO)_9(PPh_3)_3$ (0·25 g) in $CHCl_3$ (25 ml) under reflux. The solution was evaporated to dryness under vacuum at room temperature and the residue recrystallised from acetone–light petroleum. The orange crystalline product contained acetone and was purified by dissolution in $CHCl_3$, evaporation to 5 ml, and addition of light petroleum (100 ml) to give (IX) (0·21 g).

Spectra.—I.r., ^{1}H n.m.r., and mass spectra were recorded on Perkin-Elmer 257, Varian HA-100, and A.E.I. MS12 spectrometers respectively.

Analysis.—Elemental microanalyses and molecular weight determinations were carried out by A. Bernhardt and University College, London, and osmium determinations by Johnson Matthey & Co. Ltd.

We thank Johnson Matthey & Co. Ltd. for the loan of osmium and the provision of research facilities (for C. W. B.).

[2/2237 *Received, 25th September*, 1972]