Multihydrido-complexes of Osmium and Related Complexes

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A new route to tetrachloro-complexes of the type *trans*-$[OsCl_4L_2]$ from *mer*-$[OsCl_3L_3]$ (L = tertiary phosphine or tertiary arsine) is described, which involves treatment with chlorine in the presence of light. The tetrachloro-osmium(III) complex *trans*-$[OsCl_4(PMe_2Ph)_2]$ reacts with tertiary phosphines, tertiary arsines, alkyl phosphites, or alkyl phosphonites (≡L') to give $[OsCl_3(PMe_2Ph)_2L']$. Reduction of *mer*-$[OsCl_3L_3]$ or $[OsCl_3(PMe_2Ph)_2L']$ with either sodium borohydride or lithium aluminium hydride gives tetrahydrido-osmium complexes of types $[OsH_4L_3]$ or $[OsH_4(PMe_2Ph)_2L']$. Similar reduction of *trans*-$[OsCl_4(PMe_2Ph)_2]$ gives a mixture of $[OsH_6(PMe_2Ph)_2]$ and $[OsCl_4(PMe_2Ph)_2]^-$. The tetrahydrides of type $[OsH_4L_3]$ react with hydrogen chloride to give *fac*-$[OsCl_3L_3]$. The tetrahydrides also react slowly with EtOD in benzene to give the corresponding tetradeuterides. The hydrogen–deuterium exchange is catalysed by strong acids and is completely inhibited by a strong base such as tetrabutylammonium hydroxide. In benzene solution the high-field resonance (hydride) splittings due to coupling with phosphorus nuclei collapse immediately to a singlet resonance on adding $CF_3 \cdot CO_2H$, because of rapid exchange. Conductimetric titration shows that in the presence of a strong acid $[OsH_4L_3]$ is converted into $[OsH_5L_3]^+$. I.r. and n.m.r. data are given and discussed.

SEVERAL multihydrido-complexes of rhenium containing tertiary phosphines or tertiary arsines as ligands are known. The main ones are of type $[ReH_5L_3]$ and $[ReH_7L_2]$ (L = tertiary phosphine or tertiary arsine).[1-4] For this paper a multihydrido-complex is defined as one where more than three hydrogen ligands are bonded to a metal atom. Until recently rhenium was unique in forming such multihydrido-species but we have described the complex $[WH_6(PMe_2Ph)_3]$.[5] We now show that osmium also forms similar multihydrido-complexes.[6]

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† No reprints available.

[1] A. P. Ginsberg, *Transition Metal Chem.*, 1965, **1**, 111.

[2] M. L. H. Green and D. J. Jones, *Adv. Inorg. Chem. Radiochem.*, 1965, **7**, 115.

[3] J. Chatt and R. S. Coffey, *Chem. Comm.*, 1966, 545.

[4] L. Malatesta, M. Freni, and V. Valenti, *Gazzetta*, 1964, **94**, 1278.

[5] J. R. Moss and B. L. Shaw, *Chem. Comm.*, 1968, 632.

[6] P. G. Douglas and B. L. Shaw, *Chem. Comm.*, 1969, 624.

Others have recently described some tetrahydrido-complexes of osmium of this type.[7]

TABLE 1

Some new tertiary phosphine and tertiary arsine complexes

Complex	Colour	Yield (%)	Analyses (%) [a] C	H or H + D	Cl	M.p.	*M* [a]
mer-$[OsCl_3(AsEt_2Ph)_3]$	Red	60	39·0(38·85)	4·95(4·9)	11·3(11·5)	185—194° [d]	—
trans-$[OsCl_4(PEt_2Ph)_2]$	Brown	85	36·6(36·15)	4·6(4·55)	20·9(21·35)	179—181	—
trans-$[OsCl_4(AsEt_2Ph)_2]$	Brown	55	31·75(31·95)	4·05(4·0)	19·1(18·85)	163—165	—
$[OsCl_3(PMe_2Ph)_2(PEt_2Ph)]$	Red	67	42·4(42·25)	5·1(5·05)	14·95(14·4)	186—193 [d]	709(739)
$[OsCl_3(PMe_2Ph)_2(PPh_3)]$	Orange	56	49·1(48·9)	4·45(4·45)	12·5(12·75)	179—182 [d]	720(835)
$[OsCl_3(PMe_2Ph)_2(Ph_2PCH_2)_2]$	Orange	31	52·3(51·95)	5·15(4·8)	11·6(10·95)	140 [d]	—
$[OsCl_3(PMe_2Ph)_2(AsMe_2Ph)]$	Red	45	38·4(38·2)	4·55(4·4)	14·3(14·1)	182—187 [d]	705(755)
$[OsCl_3(PMe_2Ph)_2\{P(OMe)_2Ph\}]$	Red	65	38·6(38·75)	4·3(4·5)	14·5(14·35)	178—186 [d]	—
$[OsCl_3(PMe_2Ph)_2\{P(OEt)_2\}]$	Red	45	35·8(35·75)	5·25(5·05)	14·5(14·4)	198—204 [d]	—
$[OsH_4(PMe_2Ph)_3]$	White	50	47·5(47·35)	6·2(6·15)	—	80—80·5	572(608) [b]
$[OsH_4(PMe_2Ph)_3]$	White	66	52·15(52·0)	7·2(7·15)	—	79—80	661(692) [b]
$[OsH_4(PMe_2Ph)_2(PEt_2Ph)\}$	White	67	48·4(49·05)	6·55(6·5)	—	92—93	647(637) [b]
$[OsH_4(PMe_2Ph)_2(AsMe_2Ph)]$	White	41	55·35(55·57)	5·7(5·64)	—	135—138 [d]	—
$[OsH_4(PMe_2Ph)_2(AsMe_2Ph)]$	White	65	44·5(44·2)	5·85(5·7)	—	57—59	624(652) [b]
trans-$[OsCl_4(PMe_2Ph)_2][AsPh_4]$	Yellow	39	48·2(48·45)	4·4(4·25)	13·75(14·3)	200—204 [d]	—
trans-$[OsCl_4(PEt_2Ph)_2][AsPh_4]$	Yellow	84	50·35(50·5)	4·95(4·8)	13·15(13·55)	198—202	—
fac-$[OsCl_3(PMe_2Ph)_3]$	Carmine	25	40·45(40·5)	5·05(4·60)	15·05(15·00)	197—201	—
fac-$[OsCl_3(PEt_2Ph)_3]$	Pink	49	45·6(45·25)	6·0(5·85)	13·65(13·35)	171—174	757(796)
fac-$[OsCl_3(AsEt_2Ph)_3]$	Orange	13	39·3(38·85)	5·1(5·0)	11·65(11·45)	173—177	—
$[OsD_4(PMe_2Ph)_3]$	White	50	47·2(47·05)	2·801(2·755)		82—82·5	
$[OsD_4(PEt_2Ph)_3]$	White	74	51·55(51·7)	3·154(3·172)		76—77	
fac-$[OsCl_3(AsMe_2Ph)_3]$	Yellow	21	34·3(34·2)	4·35(4·05)	12·35(12·65)	195—197 [d]	837(843) [c]

Required values in parentheses. Analyses for H + D are quoted as the weight (mg.) of $D_2O + H_2O$ together with the calculated weight in parentheses. [b] In benzene solution. [c] In chloroform solution. [d] With decomposition.

Some new chloro-complexes of osmium were required and we describe these first. Compounds of the type *mer*-$[OsCl_3L_3]$ (L = tertiary phosphine or tertiary arsine) were prepared as described previously,[8,9] only the compound with L = $AsEt_2Ph$ is new (Table 1). Compounds of the type $[OsCl_4L_2]$ have been prepared by the prolonged action of carbon tetrachloride on the compounds $[OsCl_3L_3]$ [7] but in our hands this method gives very poor yields. However, we find that these trichloro-compounds when treated with chlorine in a mixture of dichloromethane and carbon tetrachloride in the presence of light from a fluorescent lamp, readily give the required tetrachloro-complexes. Two new complexes $[OsCl_4L_2]$ with L = PEt_2Ph or $AsEt_2Ph$ are described. These tetrachloro-complexes have the *trans*-configuration.[10]

We find that the complex *trans*-$[OsCl_4(PMe_2Ph)_2]$ reacts with ligands L (2·5 mol.) in benzene to give trichloro-complexes of type $[OsCl_3(PMe_2Ph)_2L]$, where L = PMe_2Ph, PEt_2Ph, PPh_3, $P(OEt)_3$, $P(OMe)_2Ph$, $AsMe_2Ph$, or $Ph_2P{\cdot}CH_2{\cdot}CH_2PPh_2$. Under similar conditions to those with which $[OsCl_4(PMe_2Ph)_2]$ reacted with L the complexes $[OsCl_4(PEt_2Ph)_2]$ or $[OsCl_4(AsEt_2Ph)_2]$ did not react and we have been unable to prepare complexes of the type $[OsCl_3L'_2L]$ (L′ = PEt_2Ph or $AsEt_2Ph$). Osmium–chlorine stretching frequencies for the various complexes are in Table 2. Osmium–chlorine stretching frequencies for similar compounds have been reported.[11]

TABLE 2

Far-i.r. frequencies (±2 cm.$^{-1}$) for some osmium complexes

Complex	ν(Os–Cl) [a]	Other bands (400—200 cm.$^{-1}$)
mer-$[OsCl_3(PMe_2Ph)_3]$	308vs, 266s	346w
mer-$[OsCl_3(PEt_2Ph)_3]$	308vs, 262s	
mer-$[OsCl_3(PBu^n{}_3)_3]$	306vs, 256vs	388m
$[OsCl_3(PMe_2Ph)_2(PEt_2Ph)]$	305s, 260s	343m, 317m [b]
$[OsCl_3(PMe_2Ph)_2(PPh_3)]$	308vs, 266m	345w, 275m,[b] 236w
$[OsCl_3(PMe_2Ph)_2\{P(OMe)_2Ph\}]$	312vs, 274s	347w, 354m [b]
$[OsCl_3(PMe_2Ph)_2(AsMe_2Ph)]$	308vs, 268s	347m, 278w [b]
fac-$[OsCl_3(PMe_2Ph)_3]$	296vs, 254vs	345w, 314w, 243s
fac-$[OsCl_3(PEt_2Ph)_3]$	292vs, 252vs [c]	379m, 325m
fac-$[OsCl_3(PBu^n{}_3)_3]$	291vs, 262s [c]	
fac-$[OsCl_3(AsMe_2Ph)_3]$	296s,[d] 260s [d]	307s, 279s, 246s
fac-$[OsCl_3(AsEt_2Ph)_3]$	294s,[d] 264s [d]	362w, 338s, 244m [c]
trans-$[OsCl_4(PMe_2Ph)_2][AsPh_4]$	305, 288s	361m, 347m
trans-$[OsCl_4(PEt_2Ph)_2][AsPh_4]$	298s [c]	358s, 353s, 345s

[a] The assignments are somewhat tentative, since the corresponding bromides or iodides were not made. However, similar assignments have been made for some closely related compounds.[11] [b] Shoulder. [c] Broad. [d] Very tentative asasignment.

Complexes of type $[OsCl_3L_3]$ are reduced smoothly by either sodium borohydride in ethanol or by lithium aluminium hydride in tetrahydrofuran to tetrahydrido-complexes of type $[OsH_4L_3]$. Compounds of the type $[OsH_4(PMe_2Ph)_2L]$ were prepared similarly. The complexes are stable in air and are readily recrystallised from methanol. Some properties are given in Table 1. Treatment of the tetrachloro-complex $[OsCl_4(PMe_2Ph)_2]$ with sodium borohydride in ethanol gave a mixture of two products: (1) a benzene-soluble pale yellow oil, identified by its n.m.r. spectrum as $[OsH_6(PMe_2Ph)_2]$ (see below),

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[7] G. J. Leigh, J. J. Levison, and S. D. Robinson, *Chem. Comm.*, 1969, 705.

[8] J. Chatt, G. J. Leigh, D. M. P. Mingos, and R. J. Paske, *J. Chem. Soc.* (*A*), 1968, 2636.

[9] J. Chatt and B. L. Shaw, *Chem. and Ind.*, 1961, 290.

[10] R. Mason and A. G. Wheeler, unpublished work.

[11] J. Chatt, G. J. Leigh, and D. M. P. Mingos, *J. Chem. Soc.* (*A*), 1969, 1674.

and (2) a water-soluble product, which on addition of tetraphenylarsonium chloride gave the tetraphenylarsonium salt of *trans*-tetrachlorobis(dimethylphenylphine)osmate(III). (The water-soluble product was probably therefore the corresponding sodium salt.) An alternative route to the hexahydrido-complex is to treat this salt with lithium aluminium hydride. $[AsPh_4]$-$[OsCl_4(PEt_2Ph)_2]$ was also prepared by the above method.

The ^1H n.m.r. spectra of the tetrahydrido-complexes of type $[OsH_4L_3]$, where L = PMe_2Ph, PEt_2Ph, or PBu_3, at high field consisted of a 1 : 3 : 3 : 1 quartet showing equivalence of the hydrogens with respect to the phosphines; a similar behaviour is shown by rhenium complexes of type $[ReH_5L_3]$.[3,4] This equivalence may be due to a rapid intramolecular process which makes all the hydrogens apparently couple equally with all the phosphines or might be due to strong phosphorus–phosphorus coupling, giving a deceptively simple ^1H n.m.r. pattern (compare the pattern for two mutually trans PMe_2Ph ligands).[12,13]

TABLE 3

N.m.r. and i.r. data (cm.$^{-1}$ ± 2 cm.$^{-1}$) for some osmium hydride complexes.

Complexes of type $[OsH_xL_y]$

	Hydride resonance		Ligand resonances		ν(Os–H) [a]	
	τ	*J*(PH)			KCl	C_6H_6 solution
$[OsH_4(PMe_2Ph)_3]$	18·81q	9·8	P-*Me*	8·37i	2051w, 1988m, 1864m	2033, 1970, 1861, 1806 [a]
$[OsH_4(PEt_2Ph)_3]$	19·52q	9·4	P-*Et*	8·46c, 9·15c	2031w, 1982m, 1949w,[a] 1864m, 1817w [a]	2041,[a] 1984, 1961,[a] 1885, 1802 [a]
$[OsH_4(PBu^n{}_3)_3]$ [c]	20·39q	9·5	P-*Bu*	8·47c, 9·09c		2049,[a] 1990, 1883, 1764
$[OsH_4(AsMe_2Ph)_3]$ [c] ...	19·68s	—	As-*Me*	8·53s		2033, 1974, 1833
$[OsH_4(AsEt_2Ph)_3]$ [c]	20·34s	—	As-*Et*	7·94c, 9·04c		2041, 1986, 1813
$[OsH_6(PMe_2Ph)_2]$ [c]	18·60t	3·5	P-*Me*	8·34i		2028, 1980, 1869

Complexes of type $[OsH_4(PMe_2Ph)_2L]$

	Hydride resonance			Resonance of PMe_2Ph methyls		ν(Os–H)	
L =	τ	*J*(PMe_2Ph–H)	*J*(P_L–H)	τ	*J*(PH) [b]	KCl	C_6H_6 solution
PPh_3	18·48	6·9	13·8	8·53d	7·4	2056w, 1982m, 1867m	2049, 1986, 1969,[a] 1874, 1802
PEt_2Ph	19·13	8·1	12·9	8·49d	7·6	2053w, 1984m, 1874m, 1818 [a]	2037, 1976, 1871, 1805 [a]
$P(OEt)_3$ [c]	19·22	8·1	14·0	8·81	*d*		2041, 1946, 1880, 1815 [a]
$P(OMe)_2Ph$ [c] ...	18·93	9·2	9·2	8·36i	7·0		2088, 1992, 1960,[a] 1878
$AsMe_2Ph$	19·07	12·6	—	8·24t	6·7	2037w, 1962m, 1862m, 1843m	2041, 1972, 1852, 1813 [a]

[a] Shoulder. [b] Separation of outer peaks, see refs. 12 and 13. [c] Obtained as colourless oils. [d] Partly obscured.

N.m.r. spectra recorded at 60 MHz. and *ca.* 34° in benzene (*J* values ±0·2 Hz., τ-values ±0·02); s = singlet, d = doublet, t = triplet, i = intermediate pattern, c = complex multiplet

The two arsine complexes $[OsH_4L_3]$, where L = $AsMe_2Ph$ or $AsEt_2Ph$, gave high-field singlet resonances (Table 2). The hydrides of type $[OsH_4(PMe_2Ph)_2L]$ gave a doublet of triplets at high field with L = a tertiary phosphine or phosphite but one triplet with L = $AsMe_2Ph$ (Table 3). The methyl groups of PMe_2Ph ligands gave complex patterns corresponding to intermediate values of *J*(P–P).[12,13]

Integration of the high-field resonance against the resonances due to the organic ligands confirmed the presence of four hydrogen ligands per osmium atom. The high-field resonance pattern of the hexahydrido-complex is a well-defined 1 : 2 : 1 triplet and integration confirmed the presence of six hydrogens per osmium atom. Therefore, although this compound was only isolated as an oil, there can be little doubt that it has been correctly formulated as $[OsH_6(PMe_2Ph)_2]$.

The tetrahydride $[OsH_4(PMe_2Ph)_3]$ when treated with an excess of hydrogen chloride in methanol gave *fac*-$[OsCl_3(PMe_2Ph)_3]$ as carmine crystals. Corresponding PEt_2Ph and $AsMe_2Ph$ complexes were also made and shown to be monomeric. The *mer*-isomers $[OsCl_3L_3]$ are well established so that the new compounds are formulated as *fac*-isomers; their i.r. spectra are virtually identical to those of the corresponding iridium complexes of type *fac*-$[IrCl_3L_3]$.[14,15] Far-i.r. data are in Table 2. *fac*-$[OsCl_3(PBu_2Ph)_3]$ has recently been reported [11] and gives similar values of ν(Os–Cl) to our compounds.

When the complex $[OsH_4(PMe_2Ph)_3]$ was dissolved in an 0·25M solution of EtOD in benzene at 34°, slow hydrogen–deuterium exchange took place giving $[OsD_4$-$(PMe_2Ph)_3]$. The reaction had a half-life of 12 hr. The exchange was strongly catalysed by trifluoroacetic acid (5 moles %) in the presence of which exchange was complete in less than 10 min. (probably in a few seconds). In the presence of tetrabutylammonium hydroxide, however, exchange was completely inhibited, none being detected after several days. The complex $[OsH_4$-$(PEt_2Ph)_3]$ showed similar effects with an exchange half-lifetime of 20 hr. in neutral solution and less than 10 min. in the presence of trifluoroacetic acid: again no exchange was detected in the presence of tetrabutylammonium hydroxide. The deuterides $[OsD_4L_3]$ with L = PMe_2Ph or PEt_2Ph were readily prepared in this

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[12] R. K. Harris, *Canad. J. Chem.*, 1964, **42**, 2275.

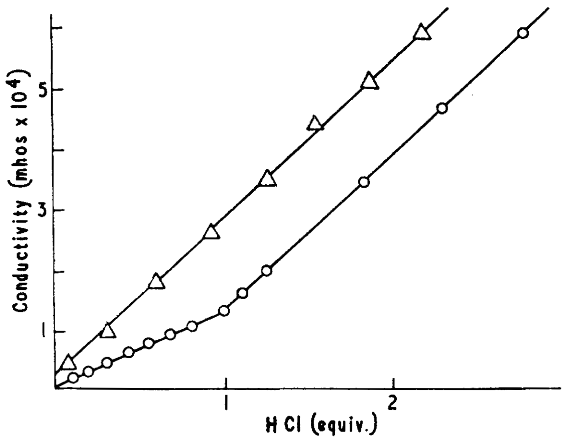
[13] B. L. Shaw and A. C. Smithies, *J. Chem. Soc.* (*A*), 1968, 2784, and references therein.

[14] P. R. Brookes and B. L. Shaw, *Chem. Comm.*, 1968, 919.

[15] J. Chatt, N. P. Johnson, and B. L. Shaw, *J. Chem. Soc.*, 1963, 3371.

way and both were converted back into the tetrahydrides by treatment with a mixture of C_6H_6–EtOH and trifluoroacetic acid.

This strongly acid-catalysed reaction suggests that a protonated species is involved as intermediate. We have confirmed this by conductimetric titration of $[OsH_4(PMe_2Ph)_3]$ or $[OsH_4(PEt_2Ph)_3]$ with methanolic hydrogen chloride at 0°, when a sharp end point is found after the addition of one mol. of the acid (Figure). Thus the tetrahydrides can act as bases and in the presence of strong acids very probably give the pentahydrido-species $[OsH_5L_3]^+$. Titration of $[OsH_4(PMe_2Ph)_3]$ with methanolic hydrogen chloride at 25° caused slow hydrogen evolution and the conductivity tended to decrease with time without further addition of the acid. At 0° however the hydrogen evolution was negligibly slow in comparison with the time required to complete a titration.



Plot of conductivity against HCl added for a solution of $[OsH_4(PMe_2Ph)_3]$ in methanol. ○ $1\cdot3 \times 10^{-2}$M-$[OsH_4(PMe_2Ph)_3]$, △ blank, *i.e.* no complex present

On addition of a little trifluoroacetic acid to $[OsH_4(PMe_2Ph)_3]$ in benzene the high-field quartet collapsed to a singlet. This singlet gradually broadened and the quartet gradually re-formed so that after *ca.* 80 min. at 34° it was virtually as sharp as the original quartet and only slightly weaker in intensity. In benzene–ethanol mixtures addition of $CF_3 \cdot CO_2H$ caused the hydride resonance to disappear, probably because of exchange with the hydroxyl protons of the ethanol. Again the resonance gradually reappeared, and was virtually identical with the original after 2 hr. at 34°. These experiments show that the reversible protonation of $[OsH_4(PMe_2Ph)_3]$ takes place very rapidly and the protonated species gradually breaks down, thereby removing acid from the solution. Very probably hydrogen and a fluoroacetate complex of osmium are formed.

Attempts to isolate salts of the protonated species of type $[OsH_5L_3]^+$ were unsuccessful; *e.g.*, the addition of $NaBPh_4$ to an OsH_4L_3–HCl–MeOH mixture at 0° gave a precipitate which rapidly became an oil and evolved hydrogen.

The hydrides of types $[OsH_4L_3]$, $[OsH_6(PMe_2Ph)_2]$, and $[OsH_4(PMe_2Ph)_2L]$ showed several medium or weak i.r. absorption bands within the range 1850—2050 cm.$^{-1}$ due to ν(Os–H) and also a strong or medium band due to δ(Os–H) at 805—826 cm.$^{-1}$. These bands were absent from the spectra of the corresponding deuterides (Tables 3 and 4). Some of the osmium–deuterium stretching modes were presumably obscured by absorption bands due to the Nujol or the organic ligands; similarly, some bands due to δ(Os–H) were obscured.

TABLE 4

Some i.r. frequencies (cm.$^{-1}$ ± 2 cm.$^{-1}$) for corresponding hydrido- and deuterido-osmium complexes (Nujol mulls)

	ν(M–H) or ν(M–D)	δ(M–H) or δ(M–D)
$[OsH_4(PMe_2Ph)_3]$	2033w, 2014w, 1970m, 1901w, 1864m	805s
$[OsD_4(PMe_2Ph)_3]$	1340s	578m, 504s
$[OsH_4(PEt_2Ph)_3]$	2033w, 1984m, 1864m	826m
$[OsD_4(PEt_2Ph)_3]$	1367w,* 1344m	586m, 509s, 454m

* Shoulder.

These tetrahydrido-osmium complexes $[OsH_4(PR_3)_3]$ can be considered as part of a series; *i.e.*, $[WH_6(PR_3)_3]$, $[ReH_5(PR_3)_3]$, $[OsH_4(PR_3)_3]$, and $[IrH_3(PR_3)_3]$, although the iridium complexes exist as *fac*- and *mer*-isomers with complex n.m.r. spectra for the *fac*-isomers, which have so far not been fully interpreted.[1,2,16]

N.m.r. data for the PMe_2Ph complexes of W, Re, Os, and Ir are in Table 5 and show regular changes. It has been suggested that the high chemical shift of metal hydrides is mainly due to shielding by electrons in outer *d*-orbitals.[17] In agreement with this (Table 5), there is a large and regular increase in chemical shift in going from $[WH_6(PMe_2Ph)_3]$ (d^0) to $[IrH_3(PMe_2Ph)_3]$ (d^6).

TABLE 5

N.m.r. data for some multihydrido-complexes containing PMe_2Ph

	Hydrides		Methyls		5*d*-Electron
Complex	τ	*J*(PH)	τ	*J*(PH)	confign.
$[WH_6(PMe_2Ph)_3]$ ...	11·93q *	36	8·25t	8·2	0
$[ReH_5(PMe_2Ph)_3]$ ...	16·12q	14·2	8·33d	7·2	2
$[OsH_4(PMe_2Ph)_3]$ ...	18·81q	9·8	8·37i	6·2	4
fac-$[IrH_3(PMe_2Ph)_3]$	21·7	†	8·44d	7·0	6
mer-$[IrH_3(PEt_2Ph)_3]$	21·75q	15	—	—	6

* Further coupling with ^{183}W, spin ½, abundance 14·4%, $J(^{183}W–^1H) = 27\cdot8$ Hz. † Six peaks arranged symmetrically about τ 21·7.

τ-Values ± 0·02, *J* values ± 0·2 Hz. In benzene solution. d = 1 : 1 doublet; t = 1 : 2 : 1 triplet, q = 1 : 3 : 3 : 1 quartet, i = intermediate pattern.[12,13]

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[16] J. Chatt, R. S. Coffey, and B. L. Shaw, *J. Chem. Soc.*, 1965, 7391.

[17] A. D. Buckingham and P. J. Stephens, *J. Chem. Soc.*, 1964, 2747.

EXPERIMENTAL

M.p.s were determined on a Kofler hot-stage apparatus and are corrected. Operations involving free tertiary phosphines or tertiary arsines were carried out under nitrogen. Analytical and other data are in Table 3. Molecular weights were determined on an Hitachi–Perkin-Elmer apparatus, model 115.

The complexes *mer*-$[OsCl_3L_3]$ {L = PMe_2Ph, PEt_2Ph, PBu^n_3, $AsMe_2Ph$, or $AsEt_2Ph$ (which is new)} were prepared by the method of Chatt *et al.*[8]

trans-*Tetrachlorobis(dimethylphenylphosphine)osmium*(IV), $[OsCl_4(PMe_2Ph)_2]$.—*Method* 1. A stream of chlorine was passed through a solution of *mer*-trichlorotris(dimethylphenylphosphine)osmium(III) (1·20 g.) in benzene (80 ml.) for 15 hr. Ethanol was then added to the filtered solution when the *product* formed as prisms (0·62 g.).

Method 2. A solution of *mer*-trichlorotris(dimethylphenylphosphine)osmium(III) (1·07 g.) in a mixture of dichloromethane (20 ml.) and carbon tetrachloride (20 ml.) was placed *ca.* 1 cm. from a fluorescent lamp (Mazda, Universal White, 20 w, 2 feet long) for 70 hr. The solvent was then removed under reduced pressure giving an oil which crystallised from ethanol to give the required product (0·816 g.), identified by its i.r. spectrum.

trans-*Tetrachlorobis(diethylphenylphosphine)osmium*(IV), $[OsCl_4(PEt_2Ph)_2]$.—This was prepared by method 2; reaction time 4½ days.

trans-*Tetrachlorobis(diethylphenylarsine)osmium*(IV), $[OsCl_4(AsEt_2Ph)_2]$.—This was similarly prepared with a reaction time of 3½ days, and crystallised from benzene–methanol.

Action of Dimethylphenylphosphine on trans-*Tetrachlorobis(dimethylphenylphosphine)osmium*(IV).—To a solution of *trans*-tetrachlorobis(dimethylphenylphosphine)osmium(IV) (0·20 g., 0·329 mmole) in hot benzene (10 ml.) was added dimethylphenylphosphine (110 μl., 0·785 mmole). The resulting orange solution was diluted with light petroleum (b.p. 60—80°), then cooled to −20° whereupon *mer*-trichlorotris(dimethylphenylphosphine)osmium(III) formed as prisms (0·12 g.).

The complexes $[OsCl_3(PMe_2Ph)_2L]$ (L = $AsMe_2Ph$, PEt_2Ph, PPh_3, $P(OMe)_2Ph$, $P(OEt)_3$, and $Ph_2P{\cdot}CH_2{\cdot}CH_2PPh_2$) were similarly prepared by adding the ligand L (2·5 mol.) to a hot benzene solution of *trans*-$[OsCl_4(PMe_2Ph)_2]$. For L = $P(OEt)_3$ the reaction mixture was refluxed for 1 hr.

Tetrahydridotris(dimethylphenylphosphine)osmium(IV), $[OsH_4(PMe_2Ph)_3]$.—*Method* 1. A suspension of *mer*-trichlorotris(dimethylphenylphosphine)osmium(III) (0·375 g.) and sodium borohydride (0·160 g.) in ethanol (10 ml.) was warmed on a steam-bath until the red complex had dissolved (*ca.* 2 min.), giving a white suspension. The solvent was then removed under reduced pressure and the product isolated with benzene. The resultant yellow oil crystallised from methanol as *prisms* (0·08 g.).

Method 2. To a mixture of *mer*-trichlorotris(dimethylphenylphosphine)osmium(III) (0·195 g.) and lithium aluminium hydride (0·080 g.) was added dry tetrahydrofuran (10 ml.). After 1 min. ethanol (5 ml.) was added: the solvent was then removed under reduced pressure and the required product isolated as in method 1. Other tetrahydrido-complexes were prepared and purified similarly, by method 1 (see Table 1).

Hexahydridobis(dimethylphenylphosphine)osmium(VI), $[OsH_6(PMe_2Ph)_2]$.—To a suspension of tetraphenylarsonium *trans*-tetrachlorobis(dimethylphenylphosphine)osmate(III) (0·140 g.) in dry tetrahydrofuran (10 ml.) was added lithium aluminium hydride (0·070 g.). The mixture was set aside at *ca.* 20° for 2 min. then methanol (5 ml.) was added whilst maintaining the temperature at *ca.* 10°. The solvent was then removed under reduced pressure and the product isolated with benzene (2 × 10 ml.). It was obtained as a pale yellow oil (0·03 g.), identified by its n.m.r. spectrum.

Action of Sodium Borohydride on trans-*Tetrachlorobis(dimethylphenylphosphine)osmium*(IV).—A suspension of *trans*-tetrachlorobis(dimethylphenylphosphine)osmium(IV) (0·240 g.) and sodium borohydride (0·160 g.) in ethanol (10 ml.) was warmed on a steam-bath until the complex had dissolved, giving a yellow suspension (*ca.* 3 min.). The solvent was removed under reduced pressure and the residue extracted with benzene. The extracts were taken to dryness under reduced pressure whereupon a pale yellow oil was obtained (0·075 g.), which was shown by its n.m.r. spectrum to be hexahydridobis(dimethylphenylphosphine)osmium(VI). The benzene-insoluble portion of the residue was extracted with water (10 ml.) giving a yellow solution which, on addition of a solution of tetraphenylarsonium chloride (0·100 g.) in water (3 ml.), gave *tetraphenylarsonium* trans-*tetrachlorobis(dimethylphenylphosphine)osmate*(III) as microprisms (0·150 g.). Conductivity (10^{-3}M solution) in nitrobenzene at 24°, 24·0 mho $cm.^2$.

fac-*Trichlorotris(dimethylphenylphosphine)osmium*(III), $[OsCl_3(PMe_2Ph)_3]$.—Tetrahydridotris(dimethylphenylphosphine)osmium(IV) (0·10 g.) was suspended in methanol (2 ml.). Hydrogen chloride was passed through the suspension, whereupon the solid dissolved. The desired *product* then slowly deposited as prisms (0·30 g.). *fac*-$[OsCl_3(MEt_2Ph)_3]$ (M = P or As) were similarly prepared and recrystallised from chloroform–light petroleum (b.p. 30—40°) (Table 1).

Deuteriation Studies on Hydride Complexes.—The hydride complex (*ca.* 2·5 × 10^{-4} mole) was dissolved in a mixture of C_6H_6 (*ca.* 500 μl.) and C_2H_5OD (*ca.* 7 × 10^{-3} mole) in an n.m.r. tube. Exchange was monitored by integration of the high-field resonance. $CF_3{\cdot}CO_2H$ or Bu^n_4NOH (*ca.* 5 mole %) was added from a microlitre syringe. For the studies on the inhibition by Bu^n_4NOH, the complex was dissolved in C_6H_6; Bu^n_4NOH was then added, followed by C_2H_5OD. The solution was immediately agitated and the n.m.r. spectrum recorded periodically. When the reaction was over the solution was evaporated to dryness under reduced pressure and the product crystallised from C_2H_5OD or C_2H_5OD–D_2O.

We thank the S.R.C. for a maintenance grant (to P. G. D.). We also thank Johnson Matthey Ltd. for the loan of osmium salts.

[9/1316 *Received, August 4th,* 1969]