Hydrido-complexes of Osmium(II) and Osmium(IV)

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The preparations of $[OsH_4L_3]$ (L = tertiary phosphine or arsine) are described. Many neutral ligands L′ (but not dinitrogen) will displace dihydrogen yielding complexes *cis*-$[OsH_2L_3L']$. The hydrido-complexes are Lewis bases. They are also catalysts for olefin isomerisation and polymerisation.

IN view of the ready displacement of dihydrogen from the complexes $[MH_4(PR_3)_4]$ (M = Fe [1] or Ru; [2] PR_3 = tertiary phosphine) by dinitrogen, we have attempted an analogous displacement from a number of osmium analogues which have been reported briefly.[3] During the course of this work a detailed account of *mer*-$[OsH_4(PMe_2Ph)_3]$ and some related compounds appeared.[4] We have therefore restricted this report to detailing only new tetrahydrido-complexes, and discussing the reactions of tetrahydrido-osmium complexes with ligands, L′, to yield complexes of the type $[OsH_2(PR_3)_3L']$, by displacement of dihydrogen. Dinitrogen does not displace dihydrogen, in contrast to its behaviour towards the iron † and ruthenium analogues, but $[OsH_2(N_2)(PMe_2Ph)_3]$ was obtained indirectly.

The complexes $[OsH_4L_3]$ (L = tertiary phosphine or arsine) were prepared by the reduction of *mer*-$[OsCl_3L_3]$ with sodium borohydride in alcohol.[3,4] They are air-stable, crystalline, colourless solids, each characterised by three bands in its i.r. spectrum between 2050 and 1850 cm^{-1}, assignable to ν(Os–H). The phosphine complexes have a quintet (1 : 4 : 6 : 4 : 1) at about τ 19 in the ^1H n.m.r. spectrum, indicating a fluxional structure, and the arsine complexes have the expected corresponding singlet.

Many bases, such as carbon monoxide, tertiary phosphines, and dinitrogen displace dihydrogen from polyhydrido-complexes. Although such displacements from, for example, ruthenium,[2] and iridium [5] are quite facile, none has been reported from $[OsH_4L_3]$. We find that the displacement of H_2 from $[OsH_4L_3]$ is a general reaction.[6]

Tetrahydrido-complexes, $[OsH_4L_3]$.—Hitherto unreported tetrahydrido-complexes were prepared from $[OsCl_3L_3]$ (L = $PMePh_2$, $PEtPh_2$, $AsEt_2Ph$, or $AsEtPh_2$, see the Table), and we also prepared $[OsH_4(PMe_2Ph)_3]$ in high yield by the reduction of $[OsCl_2(PMe_2Ph)_4]$ with sodium borohydride.

The i.r. and ^1H n.m.r. spectra of the new compounds in the metal-hydride regions (see Table) are similar to those reported for analogous complexes by Douglas and Shaw.[4]

The quintet in the ^1H n.m.r. spectrum of the phosphine complexes is due to coupling of the hydrido-protons to three equivalent tertiary phosphines in a non-rigid system,[7,8] and the apparent equivalence of the phosphine ligands is a phenomenon found in most transition metal polyhydrido-complexes. Alternatively, the apparent equivalence could arise from strong phosphorus–phosphorus coupling.[3,4] We attempted to 'freeze' a tetrahydrido-complex in a single configuration by cooling a solution of $[OsH_4(AsEtPh_2)_3]$ in dichloromethane to −60°. The hydride resonance remained a singlet, but broadened somewhat as the temperature was lowered. The spectrum of the ethyl groups was a well-defined quartet and a triplet at higher temperatures (+90°) but these changed to broad symmetrical singlets at −60°. The spectra of the alkyl groups in $[OsH_4(PR_3)_3]$ are more complex owing to P–H coupling.

The i.r. assignments to osmium–hydrogen vibrations were confirmed by comparison of the spectra of $[OsH_4(PMe_2Ph)_3]$ and $[OsD_4(PMe_2Ph)_3]$. The latter was obtained by adding D_2O to a slightly acid solution of the former in thf. The ^1H n.m.r. spectrum showed that deuteriation of the phenyl groups did not occur.

Dihydrido-complexes, $[OsH_2L_4]$.—Osmium tetrahydrido-complexes react with an excess of the tertiary phosphine or tertiary arsine during 20 h in refluxing toluene. A pure product is not obtained when L =

$$[OsH_4L_3] + L \longrightarrow cis\text{-}[OsH_2L_4] + H_2$$

PPh_3. We also found that the diphosphine, $Ph_2PCH_2CH_2PPh_2$, reacts with $[OsH_4(PEtPh_2)_3]$ to yield $[OsH_2(PEtPh_2)_2(Ph_2PCH_2CH_2PPh_2)]$, but no $[OsH_2(Ph_2PCH_2CH_2PPh_2)_2]$.[9]

Our new dihydrido-complexes (Table) all have two poorly resolved bands in the 1950—2050 cm^{-1} region of the i.r. spectrum, assignable to ν(Os–H). In contrast, complexes $[OsH_2(PP)_2]$ (PP = a ditertiary phosphine) have a single band at about 1720 cm^{-1} assignable to ν(Os–H).[8] The latter probably have *trans*-configurations but our new complexes are *cis*, as shown by the ^1H n.m.r. spectra.

A complex *trans*-$[OsH_2(PR_3)_4]$ should have a ^1H n.m.r. spectrum in the metal hydride region consisting of a

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† The formulation of the iron tetrahydrido-complexes (though not that of their reaction products with N_2) has been questioned; see A. T. T. Hsieh, J. D. Ruddick, and G. Wilkinson, *J.C.S. Dalton*, 1972, 1966.

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[2] W. H. Knoth, *J. Amer. Chem. Soc.*, 1968, **90**, 7172; T. Ito, S. Kitazume, A. Yamamoto, and S. Ikeda, *ibid.*, 1970, **92**, 3011.

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[5] M. J. Mays, R. N. F. Simpson, and F. P. Stefanini, *J. Chem. Soc.* (*A*), 1970, 3000.

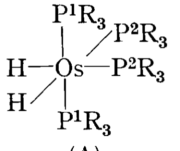
[6] B. Bell, J. Chatt, and G. J. Leigh, *Chem. Comm.*, 1970, 576.

[7] See, for example, E. L. Muetterties, *Accounts. Chem. Res.*, 1970, **3**, 266.

[8] F. N. Tebbe, P. Meakin, J. P. Jesson, and E. L. Muetterties, *J. Amer. Chem. Soc.*, 1970, **92**, 1068; P. Meakin, L. J. Guggenberger, J. P. Jesson, D. H. Gerlach, F. N. Tebbe, W. G. Peet, and E. L. Muetterties, *ibid.*, p. 3482; P. Meakin, E. L. Muetterties, F. N. Tebbe, and J. P. Jesson, *ibid.*, 1971, **93**, 4701.

[9] J. Chatt and R. G. Hayter, *J. Chem. Soc.*, 1961, 2605.

1 : 4 : 6 : 4 : 1 quintet. The observed resonance spectrum is of type $AA'PP'X_2$[7] (see Figure 1), consistent with structure (A), in which P^1 and P^2 distinguish the two (geometrical) kinds of tertiary phosphine.


(A)

The resonance spectrum of the methyl protons of [$OsH_2(PMe_2Ph)_4$] is also consistent with (A). A *trans*-structure should give rise to a single broad line, as observed for *trans*-[$ReCl(CO)(PMe_2Ph)_4$],[10] *trans*-[$ReCl(N_2)(PMe_2Ph)_4$],[11] and *trans*-[$OsCl_2(PMe_2Ph)_4$]. The spectrum observed consists of a doublet and a triplet in the ratio 1 : 1. According to Harris,[12] the triplet arises from strong coupling of the mutually *trans* phosphine ligands (P^1R_3), the separation of the outer lines being $|{}^2J_{PCH} + {}^4J_{POsPCH}|$. The *cis* phosphines ($P^2R_3$) are only weakly coupled and each methyl group is split by its own phosphorus. The spectrum of *cis*-[$OsH_2(PEtPh_2)_4$] may be interpreted on this basis, but is complicated by additional H–H coupling in the ethyl groups. The spectrum of *cis*-[$OsH_2(AsEtPh_2)_4$] in the ethyl region consists of two quartets and two triplets in the ratios 2 : 2 : 3 : 3, indicating that two kinds of tertiary arsine are present.

The structures were confirmed by phosphorus decoupling experiments on the proton spectrum of *cis*-[$OsH_2(PMePh_2)_4$]. The phosphorus atoms in P^1R_3 and P^2R_3 each decouple at a different frequency, and the methyl protons on either then give rise to a singlet. Broad band phosphorus decoupling reduces the hydride resonance to a singlet. The osmium dihydrido-complexes resemble their ruthenium analogues in having rigid structures at 30° whereas the iron analogues are labile.

Carbonyldihydrido-complexes, [$OsH_2(CO)L_3$].—Iron and ruthenium analogues of these osmium complexes have already been obtained from [$FeH_2(N_2)(PEt_2Ph)_3$] [1,13] and [$RuH_2(N_2)(PPh_3)_3$] [14] by the action of carbon monoxide.

New complexes of osmium

Complex	M.p. (°C)	Analyses (%) [a]			Yield (%)	I.r. spectra/cm^{-1} [b]		Hydride n.m.r spectra [c]	
		C	H	Other		ν(Os–H)	δ(Os–H)	τ	^2J(POsH)/Hz
[$OsH_4(PMePh_2)_3$]	147—150	58·8 (58·9)	5·7 (5·45)	P, 11·1 (10·7)	73	2070w, 1995m, 1873s [d]	818s [d]	18·80 (q)	9·0
[$OsH_4(PEtPh_2)_3$]	130—133	60·2 (60·3)	6·05 (5·9)	P, 10·3 (11·1)	82	2068w, 2001m, 1893m [d]	827s [d]	18·84(q)	8·8
[$OsH_4(AsEt_2Ph)_3$] [e]	Oil				*ca.* 35	2095w, 2022s, 1990m, 1850s	810s	19·66(s)	
[$OsH_4(AsEtPh_2)_3$]	97—99	52·1 (52·1)	5·3 (5·1)		67	2070m, 2050sh, 1892w, 1851s, 1809sh [d]	814s [d]	20·36(s)	
[$OsD_4(PMePh_2)_3$]						1352s, 1320s [f]	Not assignable		
cis-[$OsH_2(PMe_2Ph)_4$]	104—108	52·5 (51·6)	6·6 (6·2)		43	1950sh, 1920s	830s	20·35	See Figure 1
cis-[$OsH_2(PEt_2Ph)_4$]	155—160	56·8 (56·6)	7·4 (7·3)		81	1960s 1890s,	830s	20·33	See Figure 1
cis-[$OsH_2(PMePh_2)_4$]	194—197	63·5 (62·9)	5·8 (5·4)		78	2015m, 1975s	875s	20·06	See Figure 1
cis-[$OsH_2(PEtPh_2)_4$]	153—158	63·9 (64·1)	6·05 (6·0)	P, 11·1 (11·8)	62	2020m, 2005s	875s	20·25	See Figure 1
cis-[$OsH_2(AsEt_2Ph)_4$] [e]	Oil					1985s, 1950sh	845s		
cis-[$OsH_2(AsEtPh_2)_4$]	158—160	55·4 (55·9)	5·5 (5·1)		37	1992sh, 1975s	845m	23·74(s)	
[$OsH_2(PEtPh_2)_2(Ph_2PCH_2CH_2PPh_2)$]	208—210	63·6 (63·7)	5·65 (5·5)	P, 11·7 (12·2)	87	2000sh, 1978s	817s	Not detected	
[$OsH_2(CO)(PMe_2Ph)_3$]	79—82	47·3 (47·3)	5·2 (5·6)		52	1835m	840m	17·83 (qd) (H^1) 19·25 (dtd) (H^2)	22·7 59·0 (P^2), 26·5 (P^{-1}) [g]
[$OsH_2(CO)(PEt_2Ph)_3$]	69—72	52·2 (51·8)	6·6 (6·85)	P, 12·9 (12·9)	49	1835m	815m	18·87 (qd) (H^1) 20·37 (dtd) (H^2)	22·7 58·5 (P^2), 26·5 (P^1) [g]
[$OsH_2(CO)(PMePh_2)_3$]	184—186	58·7 (58·5)	5·2 (5·0)	P, 11·2 (11·3)	67	1840m	810m	17·42 (qd) (H^1) 18·86 (dtd) (H^2)	22·6 59·0 (P^2), 26·0 (P^1) [g]
[$OsH_2(CO)(PEtPh_2)_3$]	168—170	60·5 (60·0)	5·8 (5·5)		73	1830m	810m	18·12 (qd) (H^1) 19·62 (dtd) (H^2)	22·1 58·8 (P^2), 27·1 (P^1) [g]
[$OsH_2(CO)(AsEtPh_2)_3$]	126—130	52·4 (51·9)	5·05 (4·8)		61	1925sh	829m	18·28 (d) (H^1) 21·57 (d) (H^2) [g]	
[$OsD_2(CO)(PMePh_2)_3$]						1403m, 1348w [f,h]	584w [f,h]		
[$OsH_2(N_2)(PEtPh_2)_3$]	85—89 (d.)	57·1 (58·4)	5·65 (5·45)	N, 2·8 (3·2) [i]	33	2085s,[j] 1925m	Not observable	Too unstable in solution	
[$OsHCl(CO)(PMePh_2)_3$]	151—155	55·9 (56·2)	4·85 (4·7)	P, 10·8 (10·9) [k]	65	1903m [l]	Not observable	16·60 (dt) [m]	84·0 (P^2), 22·0 (P^1) [g]
[$OsCl_2(CO)(PMe_2Ph)_3$]	181—184	63·1 (62·7)	4·9 (4·7)	P, 12·5 (13·2) [n]	48				
trans-[$OsCl_2(PMe_2Ph)_4$]	252—258	47·6 (47·2)	5·6 (5·45)		81				
cis-[$OsCl_2(PMe_2Ph)_4$]	233—238	48·5 (47·2)	5·7 (5·45)		63				
mer-[$OsCl_3(AsEt_2Ph)_3$]	190—194	39·1 (38·9)	5·15 (4·9)		40				
mer-[$OsCl_3(AsEtPh_2)_3$]	173—177	46·7 (47·1)	4·3 (4·2)	Cl, 9·9 (9·1)	75				
[$OsH_3(PEt_2Ph)_4$][BPh_4]	199—203	65·4 (65·3)	7·1 (7·2)	P, 9·5 (10·5) [o]	52	Not observable	842w (?)	21·09 (dt) [p]	16·1
[$OsD_3(PEtPh_2)_4$][BPh_4]	231—237	68·4 (70·0)	6·3 (6·3) [q]		59	Not observable	Not observable		
[$OsH(HgCl)(CO)(PEtPh_2)_3$]	171—175 (d.)	46·8 (47·0)	4·5 (4·2)	P, 7·8 (8·5) [r]	67	1900m	Not observable	18·91 (dt)	58·0 (P^2), 24·5 (P^1)
[$Os(HgCl)_2(CO)(PMe_2Ph)_3$]	90—93 (d.)	28·1 (28·2)	3·3 (3·4)		41				
[$Os(HgCl)_2(CO)(PEt_2Ph)_3$]	162—163 (d.)	31·1 (31·0)	3·7 (3·8)	Cl, 5·7 (5·9)	62				

[a] Required values in parentheses. [b] Nujol mulls, unless otherwise stated. [c] In benzene solution, unless otherwise stated. [d] In benzene solution. [e] Dried at 0·1 mmHg; identity confirmed by ^1H n.m.r. spectroscopy. [f] ν(Os–D) and δ(Os–D). [g] H^1, H^2, P^1, P^2, *etc.* refer to the formulae in the text; in all these spectra, where relevant, $^2J|H^1OsH^2|$ is *ca.* 5·5 Hz. [h] Mull in hexachlorobutadiene. [i] S Analysis: found 0·0%. [j] Assigned to ν(N_2). [k] Cl Analysis: found, 4·7, requires 4·2%. [l] In methylene chloride solution. [m] In deuteriochloroform solution. [n] Cl Analysis: found, 10·7, requires 10·1%. [o] Cl Analysis: found, 0·1, requires 0·1%. [p] In perdeuterioacetone solution. [q] Analysis for H and D combined. [r] Cl Analysis: found, 3·1, requires 3·2%.

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[10] P. G. Douglas and B. L. Shaw, *J. Chem. Soc.* (*A*), 1969, 1491.

[11] J. Chatt, J. R. Dilworth, and G. J. Leigh, *J.C.S. Dalton*, 1973, 612.

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

[13] K. C. Dewhurst, W. Keim, and C. A. Reilly, *Inorg. Chem.*, 1968, **7**, 546; see also D. H. Gerlach, W. G. Peet, and E. L. Muetterties, *J. Amer. Chem. Soc.*, 1972, **94**, 4545.

[14] T. Eliades, R. O. Harris, and M. Zia, *Chem. Comm.*, 1970, 1709.

Carbon monoxide also converts $[RuH_2(PMePh_2)_4]$ to $[RuH_2(CO)(PMePh_2)_3]$.[13] The complex $[OsH_2(CO)(PPh_3)_3]$ has been synthesised by reduction of $[OsHCl(PPh_3)_3]$ with alcoholic potassium hydroxide.[15] Related species are $[OsH_2(CO)_2(PPh_3)_2]$,[16] $[OsH_2(CO)_3(PPh_3)]$,[17] and $[OsClH(CO)(PR_3)_3]$.[18] We have synthesised $[OsH_2(CO)L_3]$ by the action of carbon monoxide on $[OsH_4L_3]$ or *cis*-$[OsH_2L_4]$ in boiling toluene, or by the interaction of $[OsH_4L_3]$ and boiling 2-methoxyethanol.

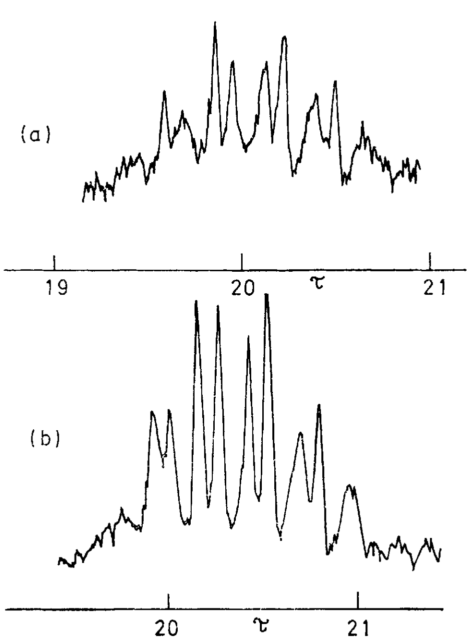
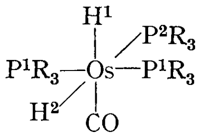


FIGURE 1 ^1H N.m.r. spectra of (a) *cis*-$[OsH_2(PMePh_2)_4]$ and (b) *cis*-$[OsH_2(PMe_2Ph)_4]$ in the metal-hydride region, showing the $AA'PP'X_2$ pattern

Of the $[OsH_4L_3]$ investigated, $[OsH_4(PPh_3)_3]$ gave a mixture of products with carbon monoxide, presumably because carbon monoxide reacts with $[OsH_2(CO)(PPh_3)_3]$ to yield $[OsH_2(CO)_2(PPh_3)_2]$.[16] All other complexes yield $[OsH_2(CO)L_3]$ (see Table) of configuration (B) in which the superscripts distinguish geometrically different kinds of H and P.



(B)

The i.r. spectra of $[OsH_2(CO)(PR_3)_3]$ show a strong band at 1925—1970 cm^{-1} [ν(CO)] and a weaker absorption at 1830—1840 cm^{-1}. These bands are found at 1345—1350 cm^{-1} in $[OsD_2(CO)(PEtPh_2)_3]$ although an extra unexplained band appears at 1403 cm^{-1}. δ(Os–H) is found at 810—840 cm^{-1} (584 cm^{-1} in the deuteride). The deuterides were obtained generally by the slow exchange of hydridic hydrogen using acid D_2O in *thf* solution. Two ν(Os–H) bands would be expected for *cis* hydrogen ligands, but one of these is evidently masked by ν(CO). The masked band, on the basis of the deuterido-spectrum, would be expected at about 1925 cm^{-1}. The ^1H n.m.r. spectrum of $[OsH_2(CO)(PEtPh_2)_3]$ in the metal-hydride region is a quartet of doublets (intensities 1 : 3 : 3 : 1) due to H^1 [see (B)] and a more complex quintet consisting of four outer doublets (ratio 1 : 2 : 2 : 1) and a central triplet (total ratio 2) due to H^2 (see Figure 2). Very similar spectra are shown by $[IrClH_2(PEtPh)_3]$ [19] and $[RuH_2(CO)(PMePh_2)_3]$.[13] These are consistent with configuration (B).

The spectra of the alkyl protons are generally too complex to analyse, but the methyl groups in $[OsH_2(CO)(PEtPh_2)_3]$ give rise to a quintet and two overlapping triplets, intensity ratio 1 : 2, which confirms the *meridional* arrangement of the tertiary phosphine ligands.

Dinitrogendihydrido-complexes, $[OsH_2(N_2)L_3]$.—The complexes $[OsH_4L_3]$ (L = $PEtPh_2$ or $PMePh_2$) do not react with dinitrogen at 150 atm during 48 h at 20°, and even at 100° $[OsH_4L_3]$ is recovered essentially quantitatively. *p*-Toluenesulphonyl azide has been used to transform an active methylene group to a diazo-group,[20]

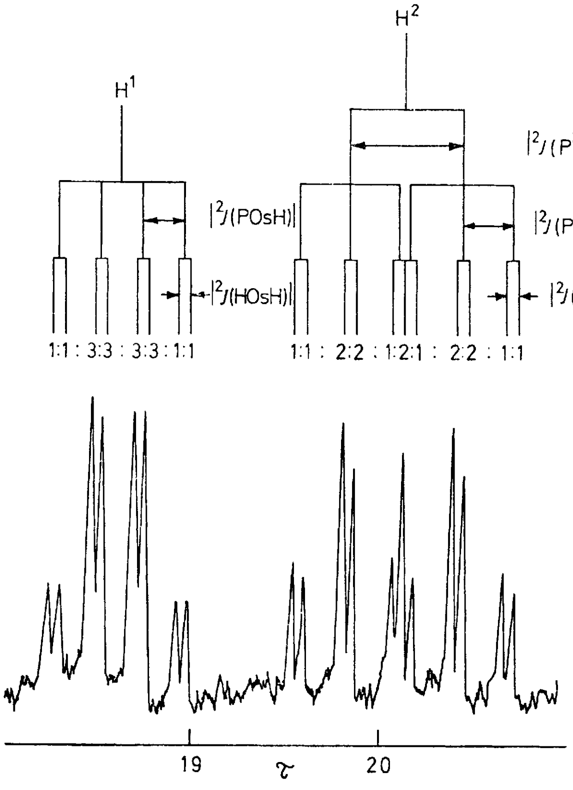


FIGURE 2 ^1H N.m.r. spectrum of *cis*-$[OsH_2(CO)(PEtPh_2)_3]$ in the metal-hydride region, showing how the observed pattern arises

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[15] L. Vaska, *J. Amer. Chem. Soc.*, 1966, **88**, 4100.

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[18] J. Chatt, D. P. Melville, and R. L. Richards, *J. Chem. Soc.* (*A*), 1971, 895, 1169.

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[20] M. Rigitz, *Angew. Chem.*, 1967, **79**, 786.

and we have applied this reaction to the tetrahydrido-osmium complexes.

$$p\text{-}CH_3C_6H_4SO_2N_3 + {>}CH_2 \longrightarrow p\text{-}CH_3C_6H_4SO_2NH_2 + {>}CN_2$$

The reaction of *p*-toluenesulphonyl azide (1 mol) with $[OsH_4L_3]$ at low temperatures is irreproducible, and only infrequently does the product have an i.r. spectrum consistent with the presence of $[OsH_2(N_2)L_3]$. On one occasion $[OsH_2(N_2)(PEtPh_2)_3]$ was obtained relatively pure and free from sulphur-containing contaminants. The i.r. spectrum showed a band at 2085 cm^{-1}, assigned to $\nu(N_2)$ and a further band at 1925 cm^{-1}, which is attributable to ν(Os–H). We also obtained i.r. evidence for the impure $[OsH_2(N_2)(PEt_2Ph)_3]$. Evidently, the complexes $[OsH_2(N_2)L_3]$ are not very stable.

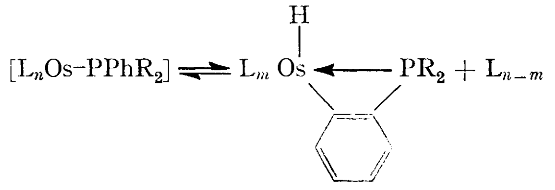
This lack of stability is emphasised by the reaction of $[OsH_2(N_2)(PEtPh_2)_3]$ with $PEtPh_2$ in benzene at reflux, which gives *cis*-$[OsH_2(PEtPh_2)_4]$ in less than 1 h. This compares with the complexes $[OsCl_2(N_2)(PR_3)_3]$,[21] for which the displacement of N_2 by a neutral ligand requires the refluxing of a toluene solution of the reactants for several hours. Thus the replacement of two chloride ligands by two hydride ligands produces a much less stable complex. Evidently, the stability in the hydride series $[MH_2(N_2)(PR_3)_3]$ falls in the order Fe > Ru > Os, whereas the stability in the halogeno-series $[MCl_2(N_2)(PR_3)_3]$ increases Fe < Ru < Os. For comparison the carbonyl hydrido-complexes $[MH_2(CO)_4]$ also fall in stability in the order Fe > Ru > Os, but carbonyl halogeno-complexes show the reverse sequence of stabilities.

When the metal atom in a class of dinitrogen complexes is changed, $\nu(N_2)$ is no guide to relative stabilities, compare $[FeH_2(N_2)(PEtPh_2)_3]$, 2058 cm^{-1};[1] $[RuH_2(N_2)(PPh_3)_3]$, 2147 cm^{-1};[2] $[OsH_2(N_2)(PEtPh_2)_3]$, 2085 cm^{-1}. However, when phosphines only are changed, then the more basic phosphines lower $\nu(N_2)$ and tend to give less stable complexes.[22] This is not necessarily so when ligands other than phosphines are changed. For example, replacement of H by Cl in $[OsXY(N_2)(PEtPh_2)_3]$ [$X = Y = H$, $\nu(N_2) = 2085$ cm^{-1}; $X = H$, $Y = Cl$, $\nu(N_2) = 2050$ cm^{-1};[18] $X = Y = Cl$, $\nu(N_2) = 2090$ cm^{-1}][21] produces a stability series $Cl_2 \sim HCl \gg H_2$. The i.r. spectra in this case probably reflect not stability, but the high *trans*-influence of H. The bonding of dinitrogen to a metal involves a delicate balance of σ- and π-effects, and the prediction of the effects of changing metal and ligands can only be based on experience.

Acetonitrile Complexes, $[OsH_2(CH_3CN)L_3]$.—Complexes containing methyl cyanide are apparently formed from $[OsH_4L_3]$ and methyl cyanide, but they decompose during work-up.

Reactions of Osmium Hydrido-complexes.—(a) *With olefins in the absence of dihydrogen.* The tetrahydride $[OsH_4(PEtPh_2)_3]$ reacts with four equivalents of cyclo-octa-1,5-diene (cod) at 100° in toluene during 65 h to give, after treatment with ethanol, a 50% yield of cyclo-octene, unreacted cyclo-octadiene, and a compound analysing for $Os(cod)(PEtPh_2)_3(EtOH)$. The reaction with 12 equivalents of oct-1-ene under the same conditions produces various octenes, two equivalents of octane, and an uncharacterised olefin complex of osmium. Tolane (4 equivalents) reacts under these conditions during 24 h to yield about 40% 1,2-diphenylethylene and an unidentified acetylene-free olefin complex.

cis-$[OsH_2(PEtPh_2)_4]$ isomerises and hydrogenates oct-1-ene. The amount of octane formed indicates that more than two atoms of hydrogen per osmium atom are transferred to the octane. This probably means that further hydrogen atoms are made available by the kind of mechanism invoked by Schunn[23] to explain his observations of hydrogenation of ethylene and but-1-ene by cobalt hydrides.



$[OsH_2(CO)(PEtPh_2)_3]$ isomerises octenes in boiling toluene without formation of octane, the isomerisation of oct-2-ene being much slower than that of oct-1-ene. The dihydridocarbonyl is recovered unchanged at the end of the reaction.

(b) *With olefins in the presence of dihydrogen.* Oct-1-ene is catalytically hydrogenated by $[OsH_4(PEtPh_2)_3]$ to octane (1 atm, boiling toluene). There is also considerable isomerisation, and the catalyst is recovered unchanged at the end of the reaction. *cis*-$[OsH_2(PEtPh_2)_4]$ catalyses hydrogenation, although isomerisation is much more rapid. The tetrahydrido-complex was also recovered from this reaction mixture. Only traces of hydrogenation are effected by $[OsH_2(CO)(PEtPh_2)_3]$, and the rate of isomerisation is about as fast as without dihydrogen. In contrast $[RhH(CO)(PPh_3)_3]$ isomerises hex-1-ene, and also hydrogenates it readily.[24] The dihydrido-carbonyl was recovered at the end of the reaction.

It is not possible to discuss the mechanism of these reactions in any detail. The carbonyl species is the least efficient catalyst, both for isomerisation and hydrogenation, and all three are evidently much less efficient than the catalysts based upon rhodium or ruthenium. The hydrogenation and isomerisation appear to be selective, the former occurs primarily at the terminal position and the latter produces principally the terminal olefin.

(c) *With proton acids.* The reactions of metal hydrido-

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[21] J. Chatt, G. J. Leigh, and R. L. Richards, *J. Chem. Soc.* (*A*), 1970, 2243.

[22] J. Chatt, D. P. Melville, and R. L. Richards, *J. Chem. Soc.* (*A*), 1969, 2841.

[23] R. A. Schunn, *Inorg. Chem.*, 1970, **9**, 2567.

[24] C. O'Connor, G. Yagupsky, D. Evans, and G. Wilkinson, *Chem. Comm.*, 1968, 420; M. Yagupsky and G. Wilkinson, *J. Chem. Soc.* (*A*), 1970, 941.

complexes with proton acids have often been investigated. In some cases, simple protonation occurs,[25] *e.g.*:

$$[ReH_3(Ph_2PCH_2CH_2PPh_2)(PPh_3)_2] \xrightarrow{HCl} [ReH_4(Ph_2PCH_2CH_2PPh_2)(PPh_3)_2]^+$$

In other cases, dihydrogen is evolved,[18] *e.g.*

$$[OsCl_2H_2(PR_3)_3] + HCl \longrightarrow [OsCl_3H(PR_3)_3] + H_2$$

and $[OsCl_3H(PR_3)_3]$ spontaneously decomposes to *fac*-$[OsCl_3(PR_3)_3]$.[18] Douglas and Shaw showed[4] that $[OsH_4(PR_3)_3]$ reacts with hydrochloric acid to yield, finally, *fac*-$[OsCl_3(PR_3)_3]$, *via* an intermediate, protonated species, $[OsH_5(PR_3)_3]^+$. It seems probable that protonation is always a preliminary to dihydrogen evolution, and our complexes were investigated with this in mind.

Hydrochloric acid reacts with $[OsH_2(CO)(PR_3)_3]$ in stepwise manner, yielding first $[OsClH(CO)(PR_3)_3]$ and and then $[OsCl_2(CO)(PR_3)_3]$. Compounds of each type have been isolated before,[18] and the ^1H n.m.r. spectra show that, in both cases, the tertiary phosphines are *meridional* and that chlorine is *trans* to CO.

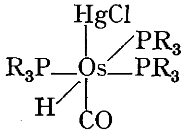
The reactions of *cis*-$[OsH_2(PR_3)_4]$ depend upon PR_3, and are not stepwise. Thus *cis*-$[OsH_2(PMe_2Ph)_4]$ reacts with hydrogen chloride during 48 h at 20° to give only *cis*-$[OsCl_2(PMe_2Ph)_4]$. Under the same conditions, $[OsH_2(PEt_2Ph)_4]$ yields $[OsH_3(PEt_2Ph)_4]^+$, which has been isolated as the tetraphenylborate, but which, for no obvious reason, shows no bands assignable to ν(Os–H) in its i.r. spectrum. The ^1H n.m.r. spectrum of this salt in $[^2H_6]$acetone solution is consistent with a non-rigid structure, and the high field protons produce a quintet. We investigated the ^1H n.m.r. spectrum of *cis*-$[OsH_2(PMe_2Ph)_4]$ as a function of added fluoroboric acid, and found that the high field protons gave rise to a quintet which reached a maximum intensity with an acid : osmium ratio of 2 : 1. Thereafter, increased proportions of acid caused a decrease of intensity. The intensity of the quintet also decreased with time. The spectrum is consistent with the formation in solution of $[OsH_5(PMe_2Ph)_4]^+$ and the cation is fairly stable in the absence of co-ordinating anions.

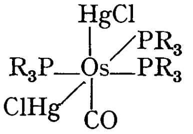
There is no hydride exchange between *cis*-$[OsH_2(PEtPh_2)_4]$ and D_2O in thf solution. Traces of acid or base (*e.g.*, triethylamine) do not catalyse exchange. However, one mole of acid in D_2O in thf rapidly forms $[OsH_2D(EtPh_2)_4]^+$ which exchanges with D_2O during 16 days to give $[OsD_3(PEtPh_2)_4]^+$ which was isolated as its tetraphenylborate. The ^1H n.m.r. spectrum is consistent with a non-rigid structure, because there is only one kind of ethyl resonance. There are no bands assignable to ν(Os–D) or δ(Os–D) in the i.r. spectrum.

The cation $[OsH_{2\cdot1}D_{0\cdot9}(PEtPh_2)_4]^+$ (H : D ratio obtained from the ^1H n.m.r. spectrum) reacts with one mole of NaOD in thf to give $[OsH_{1\cdot4}D_{0\cdot6}(PEtPh_2)_4]$ in 50% yield. The removal of the proton or deuteron by base is thus apparently statistical, supporting the idea of rapid intramolecular rearrangement.

Addition of fluoroboric acid to $[OsH_2(PEt_2Ph)_2(Ph_2PCH_2CH_2PPh_2)]$ produces a very stable cation which gives rise to a septet in the ^1H n.m.r. spectrum. This reached a maximum intensity also at an acid : osmium ratio of 2 : 1 (compare $[OsH_2(PMe_2Ph)_4]$), but an excess of acid did not diminish this intensity, nor did the intensity diminish with time. This suggests that $[OsH_3(PEt_2Ph)_2(Ph_2PCH_2CH_2PPh_2)]^+$ is stable, but the acid : osmium ratio for maximum intensity, and the septet, are difficult to explain. The rhenium analogue, $[ReH_4(PPh_3)_2(Ph_2PCH_2CH_2PPh_2)]^+$, is stable, and its ^1H n.m.r. spectrum contains a quintet arising from the hydride protons.[25]

(d) *With mercury*(II) *chloride*. Both $[OsH_4(PEtPh_2)_3]$ and $[OsH_2(PEtPh_2)_4]$ react with mercury(II) chloride to give products which show no ν(Os–H) bands in the i.r. spectra, and which contain as many as 9 moles of mercury(II) chloride per osmium. The products are crystalline, yellow, and light-sensitive, and could not be properly characterised. However, $[OsH_2(CO)(PR_3)_3]$ (PR_3 = PMe_2Ph or $PEtPh_2$) react stepwise to form two kinds of complex, which are white, air-stable, and not light sensitive. Analysis and i.r. spectra suggest the structures shown below.





Neither of these complexes reacts with hydrogen chloride produced in the reaction, nor does the dimercurio-complex with an excess of mercury(II) chloride. It is not clear why not, because $[OsH_4(PR_3)_4]$ forms polymercury derivatives readily.

EXPERIMENTAL

Carbon, hydrogen, chlorine, nitrogen, and phosphorus analyses were carried out by the Microanalytical Department of the University of Sussex, or by Dr. A. Bernhardt, West Germany. M.p.s were determined *in vacuo* on an Electrothermal apparatus. Conductivities were measured, in nitrobenzene or nitromethane, by use of a Portland–Electronics conductivity bridge. I.r. spectra in the range 4000—400 cm^{-1} were recorded on a Perkin-Elmer 337, or a Pye–Unicam SP 1200 spectrophotometer. Spectra in the range 400—40 cm^{-1}, of samples compressed with Polythene, were measured on a R.I.I.C. FS620 interferometer, with an on-line FTS 100/7 Fourier Transform Computer. Spectra in the range 500—200 cm^{-1}, of Nujol mulls between Polythene plates, were measured on a Grubb–Parsons D.M.4 spectrometer.

^1H N.m.r. spectra were measured on a Varian Associates HA-100 spectrometer using tetramethylsilane as internal lock, or on a Varian Associates T60 spectrometer. Variable temperature ^1H n.m.r. spectra and phosphorus decoupling experiments were recorded on a JEOL C60-HL n.m.r. spectrometer. ^{31}P N.m.r. spectra were recorded on a

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[25] J. Chatt and R. S. Coffey, *J. Chem. Soc.* (*A*), 1969, 1963; M. Freni, R. Demichalis, and D. Giusto, *J. Inorg. Nuclear Chem.*, 1967, **29**, 1433.

Perkin-Elmer R10 spectrometer by Mr. G. G. Mather; P_4O_6 was used as an internal lock. In all cases, integration of peak areas of ^{1}H n.m.r. spectra was in agreement with the proposed formulations. τ-Values are accurate to $\pm 0{\cdot}01$ p.p.m. and coupling constants are accurate to $\pm 0{\cdot}2$ Hz.

Mass spectra were recorded using an A.E.I. MS 10 spectrometer. G.l.c. analyses were carried out on a Pye-Unicam chromatograph, series 104, with a flame ionisation detector.

Solvents were dried by published techniques and were distilled in an atmosphere of dinitrogen before use. Tertiary phosphines and tertiary arsines were prepared by standard Grignard methods. Osmium tetraoxide was obtained, on loan, from Johnson, Matthey and Co. Ltd.

trans-*Dichlorotetrakis*(*dimethylphenylphosphine*)*osmium*(II).— (a) *mer*-Trichlorotris(dimethylphenylphosphine)-osmium(III) (2·2 g), dimethylphenylphosphine (0·9 g), and amalgamated zinc (3·2 g) were shaken in thf (40 ml) for 1·5 h to give a clear yellow solution, which was filtered and evaporated to 8 ml at 0·1 mmHg. Ethanol (20 ml) was added and the resulting solution cooled to 0° to yield yellow *prisms*, which were dried at 100°, 0·01 mmHg.

(b) Osmium tetroxide (1·0 g), concentrated hydrochloric acid (1·5 ml), and dimethylphenylphosphine (4·0 g) in boiling ethanol (30 ml) for 10 min gave a yellow solution which, on cooling to 0°, yielded the *complex* (1·06 g, 30·2%). The product was filtered off, washed with methanol (3 × 5 ml), and dried at 100°, 0·01 mmHg.

cis-*Dichlorotetrakis*(*dimethylphenylphosphine*)*osmium*(II).—Hydrogen chloride (0·014 g, $3{\cdot}9 \times 10^{-4}$ mol) in methanol (2·8 ml) was added to a solution of *cis*-tetrakis(dimethylphenylphosphine)dihydrido-osmium(II) (0·138 g, $1{\cdot}88 \times 10^{-4}$ mol) in benzene (5 ml). After 18 h at room temperature, the solvent was evaporated off at 0·1 mmHg to leave an oily residue, which crystallised from hot ethanol (5 ml) as colourless *prisms*. The i.r. spectrum shows no ν(Os–H) or δ(Os–H).

mer-*Trichlorotris*(*ethyldiphenylarsine*)*osmium*(III).— Osmium tetroxide (2·3 g), concentrated hydrochloric acid (11 ml), and ethyldiphenylarsine (12 g) in boiling ethanol (120 ml) for 3 h gave an orange solution, which deposited the *complex* as an orange powder on cooling to 0°.

Preparation of the Complexes $[OsH_4L_3]$.—These were prepared as illustrated below. In general the complexes were not recrystallised but were repeatedly washed with methanol or ethanol and dried at 80°, 0·01 mmHg. Analyses, i.r., and ^{1}H n.m.r. data are recorded in the Table.

Tris(*ethyldiphenylphosphine*)*tetrahydrido-osmium*(IV).— Ethanol (65 ml) was added to a mixture of *mer*-trichlorotris-(ethyldiphenylphosphine)osmium(III) (2·76 g) and sodium borohydride (0·85 g). The resulting suspension was stirred at room temperature for 2 h when water (5 ml) was added, and then the stirring was continued for a further 2 h. The solvent was evaporated from the reaction mixture at 0·1 mmHg, and the residue was extracted with benzene (3 × 10 ml). The benzene was evaporated from the combined extracts at 0·1 mmHg to leave an oil, which on stirring with ethanol (20 ml) for 2 h at room temperature yielded *tris*(*ethyldiphenylphosphine*)*tetrahydrido-osmium*(IV) as a white powder.

Preparation of Complexes of Type cis-$[OsH_2L_4]$.—The hydrides *cis*-$[OsH_2L_4]$ were prepared as illustrated below for *cis*-tetrakis(diethylphenylphosphine)dihydrido-osmium(II). In all cases the complexes were purified by repeated washing with ethanol followed by drying at 80°, 0·01 mmHg.

cis-*Tetrakis*(*diethylphenylphosphine*)*dihydrido-osmium*(II).—Tris(diethylphenylphosphine)tetrahydrido-osmium(IV) (0·61 g) was boiled with diethylphenylphosphine (0·3 ml) in toluene (14 ml) for 22 h. The solvent was evaporated off at 0·1 mmHg to leave a pale yellow oil which, on stirring with methanol (20 ml) for 4 h at room temperature, yielded the *product*.

Preparation of Complexes of Type $[OsH_2(CO)L_3]$(B).—The hydridocarbonyl complexes $[OsH_2(CO)L_3]$(B) were prepared as illustrated below for carbonyltris(ethyldiphenylphosphine)dihydrido-osmium(II). The complexes were purified by washing with ethanol or methanol followed by thorough drying at 80°, 0·01 mmHg. Analyses, i.r. and ^{1}H n.m.r. data are tabulated in the Table.

Carbonyltris(*ethyldiphenylphosphine*)*dihydrido-osmium*(II).—Carbon monoxide was bubbled through a boiling solution of tris(ethyldiphenylphosphine)tetrahydrido-osmium(IV) (0·52 g) in toluene (20 ml) for 18 h. The solution was cooled to room temperature, evaporated to dryness at 0·1 mmHg, and the pale yellow residue was stirred with ethanol (10 ml) for 3 h to give the *product* as a white powder.

Subsequently, $[OsH_2(CO)L_3]$(B) was prepared by two other routes.

(a) Tris(ethyldiphenylphosphine)tetrahydrido-osmium-(IV) (0·45 g) was boiled in 2-methoxyethanol (10 ml) for 19 h. On cooling the solution to 0°, *carbonyltris*(*ethyldiphenylphosphine*)*dihydrido-osmium*(II) crystallised as colourless plates.

(b) Carbon monoxide was bubbled through a boiling solution of *cis*-tetrakis(diethylphenylphosphine)dihydrido-osmium(II) (0·2 g) in toluene (15 ml) for 19 h. After cooling the solution to room temperature, the solvent was evaporated off at 0·1 mmHg to leave a pale yellow oil, which yielded *carbonyltris*(*diethylphenylphosphine*)*dihydrido-osmium*(II) as a white *powder* on stirring with methanol (5 ml).

(*Dinitrogen*)*tris*(*ethyldiphenylphosphine*)*dihydrido-osmium*(II).—*p*-Toluenesulphonyl azide (0·052 g, $2{\cdot}62 \times 10^{-4}$ mol) in thf (10 ml) was added slowly to a stirred solution of tetrahydridotris(ethyldiphenylphosphine)osmium(IV) (0·21 g, $2{\cdot}47 \times 10^{-4}$ mol) in thf (15 ml) at −78°. The resulting solution was allowed to warm to 10—15 °C and was maintained at this temperature for 1 h, during which time some darkening occurred. The solvent was evaporated off at 10 °C, 0·1 mmHg to leave a dirty brown solid which was washed with ethanol (2 × 3 ml) and pentane (2 × 5 ml) to yield the *complex* (0·07 g, 33%). The i.r. spectrum shows $\nu(N_2)$ at 2085 cm^{-1}, and ν(Os–H) at 1925 cm^{-1} (Nujol).

Reactions of Osmium Hydrido-complexes with Olefins.—Usually the reactants were charged into a flask containing toluene solvent, heated for the required time and then samples were withdrawn for g.l.c. analysis. When reactions were carried out *in vacuo*, analysis of the gaseous products showed no dihydrogen. In all cases when carbonyltris(ethyldiphenylphosphine)dihydrido-osmium(II) was used as the catalyst it was recovered essentially unchanged at the end of the reaction. Tris(ethyldiphenylphosphine)tetrahydrido-osmium(IV) was recovered unchanged when it was used to isomerise and hydrogenate olefins in the presence of dihydrogen. Attempts to isolate other residual osmium species are reported below.

(*Cyclo-octa*-1,5-*diene*)*tris*(*ethyldiphenylphosphine*)*osmium*(0).—Tetrahydridotris(ethyldiphenylphosphine)osmium(IV) (0·45 g) and cod (3·0 ml) in toluene (10 ml) were maintained at 100° *in vacuo* for 65 h. After cooling to room temperature, the solvent was evaporated off at 0·1 mmHg, and the residue was stirred with ethanol (15 ml) for 2 h at room temperature to yield a pale grey *powder* (0·23 g, 43%), m.p. 87—93°. The powder was filtered off, washed with methanol (2 × 5 ml), and dried at room temperature, 0·01 mmHg. The powder contained one molecule of ethanol of crystallisation per osmium atom (Found: C, 63·15; H, 6·45. $C_{52}H_{63}OOsP_3$ requires C, 63·3; H, 6·4%). The i.r. spectrum has no absorption assignable to ν(Os–H) or ν(C=C). The ^1H n.m.r. spectrum showed no easily assignable resonances except for those due to ethanol of crystallisation, but it integrates correctly for the proposed formulation.

Reaction of Tetrahydridotris(ethyldiphenylphosphine)osmium(IV) *with Oct-*1*-ene.*—A solution of tetrahydridotris(ethyldiphenylphosphine)osmium(IV) (0·23 g) and oct-1-ene (0·4 g) in toluene (10 ml) was maintained at 100° for 65 h *in vacuo*. After cooling to room temperature, the solvent was evaporated off at 0·1 mmHg to leave a pale yellow oil, which on stirring with ethanol (5 ml) for 5 h at room temperature gave a pale yellow *powder* (0·11 g), m.p. 198—208 °C (d). The powder was filtered off, washed with ethanol (2 × 5 ml), and dried at room temperature, 0·01 mmHg (Found: C, 65·7; H, 6·05, which corresponds to $[Os(C_8H_{16})_x(PEtPh_2)_3]$ where x is between 1 and 2). The i.r. spectrum shows no ν(Os–H) or δ(Os–H).

Reaction of cis-*Dihydridotetrakis(ethyldiphenylphosphine)osmium*(II) *with Oct-*1*-ene.*—A toluene solution (5 ml) of *cis*-dihydridotetrakis(ethyldiphenylphosphine)osmium(II) (0·35 g) and oct-1-ene (1·0 ml) was boiled for 16·5 h. After cooling to room temperature, the solvent was evaporated off at 0·1 mmHg to leave a pale yellow oil, which on stirring with ethanol (10 ml) for 24 h yielded a pale yellow *powder* (0·18 g), m.p. 183—197° (d.). This powder was similar to the product of the reaction of tetrahydridotris(ethyldiphenylphosphine)osmium(IV) and oct-1-ene, and could not be purified by recrystallisation from mixtures of benzene and ethanol.

In the presence of dihydrogen, an essentially similar reaction yields tetrahydridotris(ethyldiphenylphosphine)osmium(IV).

Chlorohydridocarbonyltris(methyldiphenylphosphine)osmium(II).—Hydrogen chloride (0·016 g, 4·4 × 10^{-4} mol) in methanol (3·2 ml) was added to a solution of dihydridocarbonyltris(methyldiphenylphosphine)osmium(II) (0·36 g, 4·4 × 10^{-4} mol) in benzene (10 ml). A vigorous evolution of gas occurred. After 21 h the solvent was evaporated off at 0·1 mmHg, and then the residue was stirred with ethanol (10 ml) for 18 h to yield the *complex*, which was filtered off, washed with ethanol (2 × 5 ml), and dried at 80°, 0·01 mmHg.

Dichlorocarbonyltris(dimethylphenylphosphine)osmium(II).—Hydrogen chloride (0·025 g, 6·9 × 10^{-4} mol) in methanol (2·4 ml) was added to a solution of dihydridocarbonyltris(dimethylphenylphosphine)osmium(II) (0·21 g, 3·3 × 10^{-4} mol) in benzene (10 ml). There was a slow evolution of gas, and after 44 h at room temperature the solvent was evaporated off at 0·1 mmHg to leave a pale orange oil. The oil was dissolved in hot methanol (13 ml) and, on cooling to −20°, the solution deposited colourless *prisms*.

Tetrakis(diethylphenylphosphine)trihydrido-osmium(II) *Tetraphenylborate.*—Hydrogen chloride (0·0335 g, 9·17 × 10^{-4} mol) in methanol (6·6 ml) was added to a solution of *cis*-tetrakis(diethylphenylphosphine)dihydrido-osmium(II) (0·390 g, 4·56 × 10^{-4} mol) in benzene (10 ml). The solution was boiled for 5 min, and after 46 h at room temperature was evaporated to dryness at 0·1 mmHg. The resulting oil was dissolved in methanol (10 ml) and to this was added a solution of sodium tetraphenylborate (0·5 g) in methanol (6 ml). On standing white needles separated. These were filtered off, washed with ethanol (2 × 5 ml), water (2 × 5 ml), and then dried at room temperature, 0·01 mmHg. The molar conductivity of the complex was 17·9 Ω^{-1} in nitrobenzene (2·24 × 10^{-3}M), 19·2 Ω^{-1} in nitrobenzene (1·06 × 10^{-3}M), and 62 Ω^{-1} in nitromethane (7·55 × 10^{-4}M). The i.r. spectrum shows no ν(OS–H), but a weak absorption at 842 cm^{-1} may be due to δ(Os–H).

Trideuteridotetrakis(ethyldiphenylphosphine)osmium(II) *Tetraphenylborate.*— *cis*-Tetrakis(ethyldiphenylphosphine)dihydrido-osmium(II) (0·42 g, 5·1 × 10^{-4} mol), deuterium oxide (1·8 ml), and fluoroboric acid (0·2 ml, 6·1M, 1·2 × 10^{-3} mol), in thf (20 ml) were allowed to react at room temperature for 16 days. The solvent was evaporated off at 0·1 mmHg and to a methanol (10 ml) solution of the residue was added sodium tetraphenylborate (0·4 g) in methanol (5 ml). On standing for a few minutes the product separated as white *needles*. The i.r. spectrum shows no bands obviously assignable to ν(Os–D) or δ(Os–D), and bands arising from the Os–H group had disappeared.

In a similar experiment the product was isolated after 6 days. The ^1H n.m.r. spectrum of the product had a quintet hydride resonance of intensity approximately equivalent to one proton, consistent with the formulation dideuteridotetrakis(ethyldiphenylphosphine)hydrido-osmium(II) tetraphenylborate.

Deuteriation of Osmium Hydrido-complexes.—*Tetradeuteridotris(methyldiphenylphosphine)osmium*(IV). Tris(methyldiphenylphosphine)tetrahydrido-osmium(IV) (0·30 g, 3·6 × 10^{-4} mol), fluoroboric acid (2 μl, 6·1M, 1·23 × 10^{-5} mol), and deuterium oxide (0·25 ml) were stirred in thf (5 ml) for 48 h at room temperature. The solvent was evaporated off at 0·1 mmHg to leave a colourless *oil*. The i.r. spectrum shows ν(Os–D) at 1352 and 1330 cm^{-1}, and δ(Os–D) at 595 cm^{-1}. Integration of the ^1H n.m.r. spectrum showed that the ligand phenyl groups had not been deuteriated.

A similar experiment, in the absence of fluoroboric acid, yielded only traces of the deuteride.

Carbonyldideuteridotris(ethyldiphenylphosphine)osmium(II).— Carbonyltris(ethyldiphenylphosphine)dihydrido-osmium(II) (0·14 g, 1·7 × 10^{-4} mol), fluoroboric acid (1·1 μl, 6·1M, 6·7 × 10^{-6} mol), and deuterium oxide (0·3 ml) were stirred in thf (5 ml) for 22 h at room temperature. The solvent was evaporated off at 0·1 mmHg to yield a white solid. The i.r. spectrum shows ν(Os–D) at 1403 and 1348 cm^{-1} and δ(Os–D) at 584 cm^{-1}. Integration of its ^1H n.m.r. spectrum indicated that the solid was carbonyltris(ethyldiphenylphosphine)dihydrido-osmium(II) in which *ca.* 20% of the hydride ligands had been replaced by deuterium. The ligand phenyl groups were not deuteriated.

Deuteriation did not occur during 48 h in the absence of acid.

Reaction of cis-*Tetrakis(diethylphenylphosphine)dihydrido-osmium*(II) *with Mercuric Chloride.*—Tetrahydrofuran (12 ml) was added to a mixture of *cis*-tetrakis(diethylphenylphosphine)dihydrido-osmium(II) (0·11 g, 1·2 × 10^{-4} mol) and mercuric chloride (0·074 g, 2·7 × 10^{-4} mol) and the resulting solution became golden brown during 24 h at room temperature. The solvent was evaporated off at 0·1 mmHg and the residue was extracted with benzene (3 ml). Addition of methanol (4 ml) to the filtered extract caused the product to crystallise as yellow *prisms* (0·07 g), m.p. 190—192° (d.). The i.r. spectrum shows no absorptions due to ν(Os–H) or δ(Os–H). The product became black during 3 h.

Carbonyl(chloromercurio)tris(ethyldiphenylphosphine)-hydrido-osmium(II).—Tetrahydrofuran (10 ml) was added to a mixture of carbonyltris(ethyldiphenylphosphine)dihydrido-osmium(II) (0·25 g, $2·9 \times 10^{-4}$ mol) and mercuric chloride (0·080 g, $3·0 \times 10^{-4}$ mol). After stirring the solution at room temperature for 45 h the solvent was evaporated off at 0·1 mmHg. The residue was stirred with methanol (8 ml) for 4 h to give the product as a white *powder*. The i.r. spectrum shows ν(CO) at 1912 cm^{-1} (methylene chloride).

Carbonylbis(chloromercurio)tris(dimethylphenylphosphine)-osmium(II).—Tetrahydrofuran (10 ml) was added to a mixture of carbonyltris(dimethylphenylphosphine)dihydrido-osmium(II) (0·23 g, $3·7 \times 10^{-4}$ mol) and mercuric chloride (0·20 g, $7·3 \times 10^{-4}$ mol). There was an immediate evolution of gas. After stirring the solution at room temperature for 68 h, the solvent was evaporated off at 0·1 mmHg. Addition of ethanol (5 ml) to the oily residue gave the product as colourless *prisms*. The crystals retained one molecule of ethanol of crystallisation per osmium atom. The i.r. spectrum shows ν(CO) at 1918 cm^{-1} and two strong absorptions at 568 and 579 cm^{-1} which are not present in the starting material.

Carbonylbis(chloromercurio)tris(diethylphenylphosphine)-osmium(II).—Tetrahydrofuran (10 ml) was added to a mixture of carbonyltris(diethylphenylphosphine)dihydrido-osmium(II) (0·22 g, $3·1 \times 10^{-4}$ mol) and mercuric chloride (0·48 g, $1·8 \times 10^{-3}$ mol). There was an immediate evolution of gas and the resulting solution was stirred at room temperature for 68 h. The solution was evaporated to 3 ml at 0·1 mmHg and methanol (10 ml) was added to precipitate a white powder. This was crystallised from a mixture of benzene (3 ml) and methanol (5 ml) to give the product as white *prisms*. The i.r. spectrum shows ν(CO) at 1920 cm^{-1} and a strong absorption at 572 cm^{-1} which is not present in the starting material.

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