Metal Nitrido- and Oxo-complexes. Part II.[1] Osmium and Ruthenium Nitrido-complexes with Group 5 Ligands and their Reactions

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Reactions of $Y[Os(N)X_4]$ and $Y[Ru(N)Cl_4]$ ($Y = Ph_4As$ or $Bu^n{}_4N$; X = Cl or Br) with arsines, stibines, and 2,2'-bipyridyl (bipy) give the nitrido-complexes $[Os(N)X_3L_2]$ and $[Ru(N)Cl_3(QPh_3)_2]$ ($L = QPh_3$, $AsEt_3$, or ½bipy; Q = As or Sb), but tertiary phosphines give reduced species. Reaction of tertiary phosphines with $[M(N)Cl_3(AsPh_3)_2]$ (M = Os or Ru) give the phosphine imidato-complexes $[M(NPR_3)Cl_3(PR_3)_2]$ ($PR_3 = PPh_3$, PPh_2Et, $PPhEt_2$, PEt_3, or PPh_2Me), and with dimethylphenylphosphine the intermediates $[M(NPPhMe_2)Cl_3(AsPh_3)_2]$ have been isolated. Using $[Os(N)Br_3(AsPh_3)_2]$ the complexes $[Os(NPR_3)Br_3(PR_3)_2]$ ($PR_3 = PPh_3$, PPh_2Et, or $PPhEt_2$) were obtained. Oxidation of $[Os(NPR_3)Cl_3(PR_3)_2]$ by chlorine gave the nitrides $[Os(N)Cl_3(PR_3)_2]$. Other new complexes which have been obtained are $[Os(NHPPh_3)Cl_4(PPh_3)]$, $[Ph_4As][OsCl_4(PPh_3)_2]$, $[OsCl_4(PPh_3)_2]$, $[Ph_4As][OsCl_5(PPh_3)]$, and $[Os(OMe)_2Cl_2(PPh_3)_2]$. The formation and reactions of these complexes are discussed.

As part of a systematic study of platinum metal nitrido-complexes, we recently prepared[1] the five-co-ordinate species $Y[M(N)X_4]$ ($Y = Ph_4As$ or $Bu^n{}_4N$; M = Os or Ru; X = Cl or Br), and *X*-ray studies of the isostructural salts $[Ph_4As][Ru(N)Cl_4]$[2] and $[Ph_4As][Os(N)Cl_4]$[3] show that the anions have square-based pyramidal co-ordination with an apical nitrido-ligand. These salts are readily soluble in polar organic solvents, and we were therefore able to study their reactions with tertiary phosphines under mild conditions in attempts to prepare M^{VI} nitrido-complexes with phosphine ligands analogous to the stable Re^V species.[4] We have also investigated the reactions of $Y[M(N)X_4]$ with amines and tertiary arsines and stibines.

In preliminary communications[5] we have reported the unusual reactions of tertiary phosphines with Os≡N and Ru≡N bonds to form complexes with tertiary phosphine imidate ligands $[R_3PN]^-$; the *X*-ray crystal structure of one such product, $[Ru(NPPhEt_2)Cl_3(PPhEt_2)_2]$,[6] has been described. Here we give a fuller account of these and other studies.

[1] Part I, W. P. Griffith and D. Pawson, *J.C.S. Dalton*, 1973, 1315.
[2] F. L. Phillips and A. C. Skapski, unpublished work.
[3] W. P. Griffith, D. Pawson, F. L. Phillips, and A. C. Skapski, *Inorg. Nuclear Chem. Letters*, 1973, **9**, 1117.
[4] J. Chatt, C. D. Falk, G. J. Leigh, and R. J. Paske, *J. Chem. Soc.* (*A*), 1969, 2288.
[5] W. P. Griffith and D. Pawson, *J.C.S. Chem. Comm.*, 1973, 418; *Inorg. Nuclear Chem. Letters*, 1974, **10**, 253.
[6] F. L. Phillips and A. C. Skapski, *J.C.S. Chem. Comm.*, 1974, 49.

RESULTS AND DISCUSSION

Preparation of Complexes.—The main types of reaction are illustrated in Scheme 1 for $[Ph_4As][Os(N)Cl_4]$.

(a) *Nitrido-arsine, -stibine, and -amine complexes*, $[M(N)X_3L_2]$. Reaction of warm solutions of $[Bu^n_4N][Os(N)X_4]$ and $[Bu^n_4N][Ru(N)Cl_4]$ (X = Cl or Br) in methanol with an excess of triphenyl-arsine or -stibine in boiling acetone gave $[Os(N)X_3(QPh_3)_2]$ and $[Ru(N)Cl_3(QPh_3)_2]$ (Q = As or Sb) in high yield. The same products were obtained replacing methanol with acetone

Analytical and i.r. data for osmium and ruthenium complexes with Group 5 ligands

	Colour	Yield (%)	M.p. (θ/°C)	Analyses [a] (%) C	H	N	X	I.r. assignments (cm^{-1}) $\bar{\nu}$(M≡N)	$\bar{\nu}$(M–X)
(*a*) $[M(N)X_3L_2]$ (arsines, stibines, and amines)									
$[Os(N)Cl_3(AsPh_3)_2]$	Pink-brown	90	257	47·0 (46·9)	3·4 (3·3)	1·7 (1·5)	11·4 (11·5)	1 059s	325s, 251m, 243m
α-$[Os(N)Br_3(AsPh_3)_2]$	Brown	85	221	40·9 (40·9)	2·9 (2·9)	1·5 (1·3)	22·8 (22·7)	1 068s, 1 035s [b]	202s
β-$[Os(N)Br_3(AsPh_3)_2]$	Brown	50		41·1 (40·9)	3·0 (2·9)	1·5 (1·3)	22·7 (22·7)	1 062s, 1 030s [b]	200s
$[Os(N)Cl_3(AsEt_3)_2]$	Red	50	140 (decomp.)	22·4 (22·7)	4·9 (4·8)	2·0 (2·2)		1 070s	340(sh), 328s, 302(sh), 230s
$[Os(N)Cl_3(SbPh_3)_2]$	Orange	85	170	42·6 (42·5)	2·9 (3·0)	1·5 (1·4)	10·4 (10·5)	1 065s, 1 032s [b]	327s, 306m, 237m
$[Os(N)Br_3(SbPh_3)_2]$	Orange	85	171	37·4 (37·6)	2·6 (2·6)	1·4 (1·2)	20·7 (20·8)	1 061s	Obscured
$[Os(N)Cl_3(bipy)]$	Deep red	60	355	25·8 (25·7)	2·1 (1·7)	8·9 (9·0)	22·7 (22·8)	1 086s	340s, 326s, 240m
$[Os(N)Br_3(bipy)]$	Purple	50				6·9 (7·0)	39·0 (40·0)	1 090s	Obscured
$[Ru(N)Cl_3(AsPh_3)_2]$	Yellow	80	169	51·5 (51·9)	3·8 (3·6)	1·7 (1·7)	12·5 (12·8)	1 023s	335s, 323s, 240m
$[Ru(N)Cl_3(SbPh_3)_2]$	Orange	90	165	47·3 (46·6)	3·3 (3·3)	1·4 (1·5)	11·8 (11·5)	1 029s	338s, 286s, 239s
(*b*) $[M(NPR_3)Cl_3L_2]$ (phosphines, arsines, and bipy)								$\bar{\nu}$(P=N)	
$[Os(NPPh_3)Cl_3(PPh_3)_2],Me_2CO$ [c]	Orange	90	136	59·4 (59·3)	4·2 (4·5)	1·3 (1·2)	9·0 (9·2)	1 127vs, 1 104vs [b]	309s, 294s, 285m
$[Os(NPPh_3)Br_3(PPh_3)_2],Me_2CO$ [d]	Brown		122	53·3 (53·1)	4·0 (4·0)	1·1 (1·1)	18·8 (18·6)	1 125vs	212s
$[Os(NPPh_2Et)Cl_3(PPh_2Et)_2],Me_2CO$	Orange	80	132	53·6 (53·4)	5·3 (5·6)	1·4 (1·4)	10·7 (10·5)	1 085vs	309s, 285s, 269s
$[Os(NPPh_2Et)Br_3(PPh_2Et)_2],Me_2CO$	Orange	50	154 (decomp.)				21·3 (20·9)	1 090vs	213s
$[Os(NPPhEt_2)Cl_3(PPhEt_2)_2]$	Orange	50	134	44·5 (44·5)	5·8 (5·6)	1·8 (1·7)	13·5 (13·1)	1 204vs	300s, 290s, 276m
$[Os(NPPhEt_2)Br_3(PPhEt_2)_2]$	Orange	50					25·3 (25·4)	1 160vs	205s
$[Os(NPPh_2Me)Cl_3(PPh_2Me)_2]$	Orange	80	165d	51·5 (51·4)	4·4 (4·3)	1·7 (1·5)	11·5 (11·7)	1 128vs	309s, 296s
$[Os(NPPhMe_2)Cl_3(PPhMe_2)_2]$	Orange		95d	39·0 (39·8)	4·7 (4·6)	1·7 (1·9)	14·8 (14·7)	1 165vs	299s, 286s, 270s
$[Os(NPPhMe_2)Cl_3(AsPh_3)_2]$	Pink	90	156	49·8 (50·2)	3·9 (3·9)	1·4 (1·3)	10·0 (10·1)	1 081vs	323s, 294m
$[Os(NPEt_3)Cl_3(PEt_3)_2]$	Orange	50		32·7 (32·5)	6·9 (6·8)	2·1 (2·1)	16·1 (16·0)	1 125vs	292s, 269m
$[Ru(NPPh_3)Cl_3(PPh_3)_2],Me_2CO$	Brown	90	150 (decomp.)	63·9 (64·2)	4·7 (4·8)	1·3 (1·3)	10·0 (10·0)	1 108s	325s, 301s, 280m
$[Ru(NPPh_2Et)Cl_3(PPh_2Et)_2],Me_2CO$	Brown	85	114	58·8 (58·7)	5·4 (5·6)	1·5 (1·5)	12·0 (11·5)	1 063s	317s, 290s, 269s
$[Ru(NPPhEt_2)Cl_3(PPhEt_2)_2]$	Brown	80	134 (decomp.)	50·7 (50·0)	6·6 (6·3)	1·5 (1·9)	14·6 (14·8)	1 165s	320m, 302s, 290s
$[Ru(NPPh_2Me)Cl_3(PPh_2Me)_2]$	Brown	70	145	57·2 (57·0)	4·7 (4·8)	1·9 (1·7)	12·6 (12·9)	1 114s	317s, 297m
$[Ru(NPPhMe_2)Cl_3(AsPh_3)_2]$	Green	60		54·5 (54·8)	4·4 (4·3)	1·3 (1·5)	10·7 (11·0)	1 055vs	325s, 310m, 286m
$[Ru(NPEt_3)Cl_3(PEt_3)_2]$	Brown	50		36·9 (37·5)	7·3 (7·9)	2·2 (2·4)	18·8 (18·5)	1 099vs	311s, 291m
(*c*) $[M(N)Cl_3(PR_3)_2]$								$\bar{\nu}$(M≡N)	
$[Os(N)Cl_3(PPh_3)_2]$	Brown	60	145 (decomp.)	51·6 (51·8)	3·8 (3·6)	1·8 (1·7)	12·9 (12·7)	1 058s, 1 026s [b]	327s, 252m
$[Os(N)Cl_3(PPh_2Et)_2]$	Brown	60	176	45·2 (45·5)	4·0 (4·1)	1·8 (1·9)	14·7 (14·4)	1 062s	321s, 240m
$[Os(N)Cl_3(PPhEt_2)_2]$	Brown	70	129	37·5 (37·4)	4·7 (4·7)	2·1 (2·2)	16·7 (16·6)	1 070s, 1 063s	325s
$[Os(N)Cl_3(PPh_2Me)_2]$	Brown	70	160	43·6 (43·9)	3·8 (3·7)	1·9 (2·0)	14·9 (15·0)	1 072s, 1 063s	330s, 244m
$[Os(N)Cl_3(PPhMe_2)_2]$	Yellow	65	158	32·9 (32·7)	4·0 (3·8)	2·3 (2·4)	19·1 (18·1)	1 068s	325s, 238ms
$[Os(N)Cl_3(PEt_3)_2]$	Brown	50		26·4 (26·3)	5·4 (5·5)	2·5 (2·6)	20·2 (19·6)	1 070s	319s, 245ms

TABLE (*Continued*)

	Colour	Yield (%)	M.p. (θ/°C)	Analyses (%) C	H	N	X	I.r. assignments (cm^{-1}) ν(M≡N)	ν(M–X)
(*d*) $[Os(NHPPh_3)Cl_4(PPh_3)],Me_2CO$ [e]	Red	75	163	53·3 (53·1)	4·1 (4·0)	1·8 (1·5)	15·1 (15·3)	924vs 906vs [b]	333s, 320s 303s, 289s
(*e*) Miscellaneous halogenophosphine complexes									
$[Ph_4As][OsCl_5(PPh_3)]$	Red	80		50·4 (49·8)	3·5 (3·5)		**17·5** (17·5)		318s, 270m
$[Ph_4As][OsCl_4(PPh_3)_2],Me_2CO$	Yellow	60		57·1 (58·3)	4·7 (4·4)		11·2 (10·9)		298vs
$[OsCl_4(PPh_3)_2]$	Brown	90		50·3 (50·5)	3·9 (3·5)		16·6 (16·6)		330s, 323s
$[Ph_4As][OsCl_4(PPhEt_2)_2]$	Yellow	50		51·0 (50·4)	4·8 (4·8)		13·2 (13·5)		298vs
$[Bu^n{}_4N][OsBr_4(PPhEt_2)_2]$	Yellow	60				1·6 (1·5)	15·3 (15·7)		
$[Os(OMe)_2Cl_2(PPh_3)_2]$	Red			53·5 (53·8)	4·3 (4·3)		8·5 (8·4)		324s, 313s

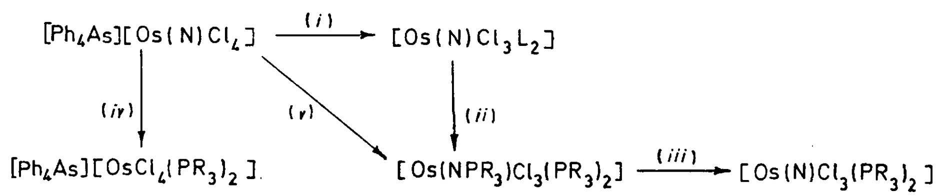
[a] Calculated values are given in parentheses. [b] ^{15}N-Substituted frequency. [c] Also O, 1·6 (1·4); P, 8·0 (8·0)%. [d] Also P, 7·1 (7·2)%. [e] Also P, 7·2 (6·7)%.

but much longer reaction times were needed, possibly because the displaced halide ion is better solvated by methanol or because methanol co-ordinates more strongly than does acetone in the position *trans* to the nitride, with resultant weakening of the M–X bonds.[1] Using methanol–acetone and acetone respectively, two isomers of $[Os(N)Br_3(AsPh_3)_2]$ were obtained. Their i.r. spectra had Os≡N stretching bands differing by 6 cm^{-1}, and there were also minor differences in the positions of some of the lower-frequency arsine modes. These may be geometrical isomers or perhaps 'distortional' isomers of the type recently described for some molybdenum oxophosphine complexes.[7] Using solutions of $[Bu^n{}_4N][Os(N)X_4]$ and the appropriate ligand in acetone we isolated the diamagnetic complexes $[Os(N)X_3(bipy)]$, $[Os(N)Cl_3(AsEt_3)_2]$, and other amine complexes (bipy = 2,2′-bipyridine).

The complexes $[Os(N)X_3(QPh_3)_2]$ and $[Ru(N)Cl_3(QPh_3)_2]$ are diamagnetic. They are sparingly soluble in organic solvents, but we were able to show that they are non-conductors in acetone and dichloromethane and that their molecular weights measured osmometrically in benzene are approximately half their formula weights. It is therefore likely that one arsine or stibine ligand dissociates in solution from the very crowded co-ordination sphere. All these complexes had sharp bands in their i.r. spectra between 1 030 and 1 070 cm^{-1}, characteristic of an M≡N stretching mode in nitrido-species [1] (see Table).

(b) *Phosphine imidate complexes* $[M(NPR_3)X_3(PR_3)_2]$ *and* $[M(NPMe_2Ph)Cl_3(AsPh_3)_2]$. The reaction of triphenylphosphine with solutions of $[Ph_4As][Os(N)X_4]$ in cold acetone gave paramagnetic species of empirical formula $[Os(N)X_3(PPh_3)_3],Me_2CO$ which we have formulated as osmium(IV) triphenylphosphine imidato-complexes, $[Os(NPPh_3)X_3(PPh_3)_2],Me_2CO$, on the basis of their chemical and spectroscopic properties.[5] The corresponding reaction using $[Ph_4As][Ru(N)Cl_4]$ gave only $[Ph_4As][RuCl_4(PPh_3)_2]$, while other tertiary phosphines and $[Ph_4As][Os(N)X_4]$ normally gave analogous Os^{III} species. An exception was the PMe_2Ph–$[Ph_4As][Os(N)Cl_4]$ reaction in ice-cold acetone, when $[Os(NPPhMe_2)Cl_3(PPhMe_2)_2]$ was isolated, probably by virtue of its unusual insolubility.

However, the complexes $[M(NPR_3)Cl_3(PR_3)_2]$ (M = Os or Ru; PR_3 = PPh_3, PPh_2Et, $PPhEt_2$, PEt_3, or PPh_2Me) were prepared in high yield by the action of excess of PR_3 on a suspension of $[M(N)Cl_3(AsPh_3)_2]$ in cold acetone. When using dimethylphenylphosphine, the intermediates $[M(NPPhMe_2)Cl_3(AsPh_3)_2]$ were isolated. The complexes with more bulky phosphines (PPh_3 or PPh_2Et) were obtained as acetone adducts (as indicated by a strong i.r. absorption at 1 710 cm^{-1}), a feature of some other triphenylphosphine complexes.[8] All these complexes were paramagnetic, having effective magnetic moments at room temperature typical of these metals in their quadrivalent states,[9] near 1·8 B.M. for osmium species and 2·8 B.M. for ruthenium species.* They are either sparingly soluble or give somewhat



SCHEME 1 Main reactions studied: (*i*), L (= $AsPh_3$, $SbPh_3$, $AsEt_3$, or ½bipy); (*ii*), PR_3 for L = $AsPh_3$; (*iii*), Cl_2; (*iv*), PR_3; (*v*), PPh_3

* 1 B.M. ≃ 9·27 × 10^{-24} A m^2.

[7] J. Chatt, L. Manojlovic-Muir, and K. W. Muir, *Chem. Comm.*, 1971, 655.

[8] J. V. McArdle, A. J. Schultz, B. J. Corden, and R. Eisenberg, *Inorg. Chem.*, 1973, **12**, 1676.

[9] H. P. Gunz and G. J. Leigh, *J. Chem. Soc.* (*A*), 1971, 2229; B. N. Figgis and J. Lewis, *Progr. Inorg. Chem.*, 1965, **6**, 37.

unstable solutions in organic solvents, the more soluble stable species being monomeric in benzene and non-conductors in dichloromethane.

Nitridoamine complexes of osmium $[Os(N)Cl_3L_2]$ ($L = \frac{1}{2}$bipy, $\frac{1}{2}$phen, or py) gave $[Os(NPPh_3)Cl_3L_2]$ with triphenylphosphine in acetone (phen = 1,10-phenanthroline); these and other reactions with phosphines and phosphites are being further investigated.

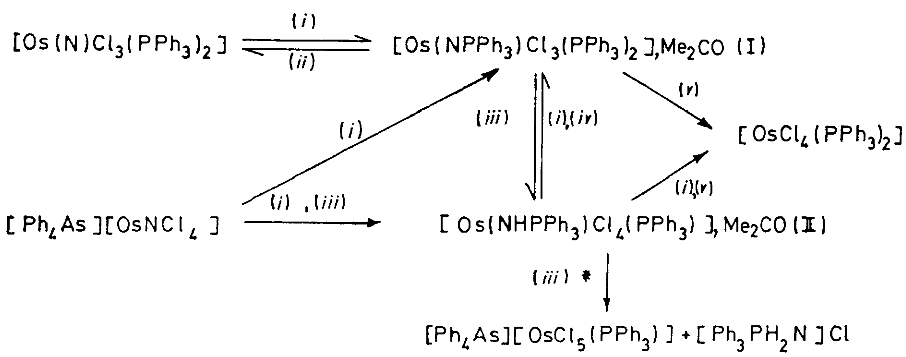
(c) *Nitridophosphine complexes* $[M(N)X_3(PR_3)_2]$. Oxidation of a methanolic suspension of $[Os(NPR_3)Cl_3(PR_3)_2]$ with chlorine gave the nitrides $[Os(N)Cl_3(PR_3)_2]$ in high yield ($PR_3 = PPh_3$, PPh_2Et, $PPhEt_2$, PEt_3, PPh_2Me, or $PPhMe_2$), but bromine oxidation of the corresponding bromides gave no similar products, except the complex $[Os(NPPh_3)Br_3(PPh_3)_2]$ from which an imperfectly characterised material [ν(OsN) at 1 062 cm^{-1}], probably $[Os(N)Br_3(PPh_3)_2]$, was obtained. An impure sample of $[Ru(N)Cl_3(PPh_3)_2]$ was made by chlorine oxidation of $[Ru(NPPh_3)Cl_3(PPh_3)_2]$ [ν(RuN) 1 026 cm^{-1}], but other ruthenium nitrides could not be obtained in this way. Solutions of $[Os(N)Cl_3(PR_3)_2]$ are normally rather unstable, but the more stable diethylphenyl- and methyldiphenyl-phosphine complexes were found to be monomeric in benzene. With triphenylphosphine in acetone, $[Os(N)Cl_3(PPh_3)_2]$ regenerates $[Os(NPPh_3)Cl_3(PPh_3)_2]$, indicating that the instability in solution of some of these nitrides may be due to dissociation of a phosphine ligand which subsequently attacks the nitrido-ligand.

(d) *Triphenylphosphine imide complex*, $[Os(NHPPh_3)Cl_4(PPh_3)],Me_2CO$. The reaction of $[Ph_4As][Os(N)Cl_4]$ with triphenylphosphine in acetone in the presence of tetraphenylarsonium hydrochloride (a convenient source of small quantities of hydrochloric acid in non-aqueous solvents; it is in fact $[Ph_4As][H_5O_2]Cl_2$ [10]) gave a bright red protonated species $[Os(NHPPh_3)Cl_4(PPh_3)],Me_2CO$. This is paramagnetic ($\mu_{eff.}$ 1·6 B.M.), a non-conductor in dichloromethane and acetone, and has an i.r. spectrum consistent with the given formulation (see below). On treatment of this product with one equivalent of $[Ph_4As][H_5O_2]Cl_2$ in boiling acetone, $[Ph_4As][OsCl_5(PPh_3)]$ and $[Ph_3PNH_2]Cl$ were obtained in stoicheiometric quantities.

(e) *Halogenophosphine complexes*. Treatment of $[Ph_4As][Os(N)X_4]$ (X = Cl or Br) with alkylarylphosphines, PR_3, in cold acetone, or with triphenylphosphine in boiling acetone, gave $[Ph_4As][OsX_4(PR_3)_2]$, probably *via* $[R_3PN]^-$ intermediates. We isolated the PPh_3 and $PPhEt_2$ species, which are 1 : 1 electrolytes in dichloromethane. Likewise, reaction of $[Ph_4As][Ru(N)Cl_4]$ with PPh_3 in cold acetone gave $[Ph_4As][RuCl_4(PPh_3)_2]$. Salts of the type $[Ph_4As][MCl_4(PR_3)_2]$ (M = Os [11] or Ru [12]) have been made by other methods, and are thought to have *trans*-configurations.

Using methanol rather than acetone as a solvent, $[Ph_4As][Os(N)Cl_4]$ and triphenylphosphine gave a red methoxo-complex which is probably $[Os(OMe)_2Cl_2(PPh_3)_2]$, and this was also isolated by stirring $[Os(NPPh_3)Cl_3(PPh_3)_2]$ in methanol. With aqueous HCl and acetone, the methoxo-species yields $[OsCl_4(PPh_3)_2]$, also made from triphenylphosphine and $[Ph_4As][Os(N)Cl_4]$ in acetone–aqueous HCl. Similarly, treatment of $[Os(NPPh_3)Cl_3(PPh_3)_2]$ or $[Os(NHPPh_3)Cl_4(PPh_3)]$ with one equivalent of phosphine in acetone with aqueous HCl gave $[OsCl_4(PPh_3)_2]$. Analogues of $[OsCl_4(PPh_3)_2]$ have been prepared with other tertiary phosphines.[13]

Chemical and Spectroscopic Properties of the Complexes.—(i) *Chemical reactions*. The principal chemical reactions of the phosphine imidato-complex $[Os(NPPh_3)Cl_3(PPh_3)_2],Me_2CO$, (I), and the phosphine imide complex $[Os(NHPPh_3)Cl_4(PPh_3)],Me_2CO$, (II), are summarised in Scheme 2, and these support the suggested formulations.



SCHEME 2 Some reactions of osmium nitrido-complexes: (*i*), PPh_3; (*ii*), Cl_2; (*iii*), $[Ph_4As][H_5O_2]Cl_2$; (*iv*), Et_3N; (*v*), HCl(aq). The reactions were carried out in acetone at 25 or 60 °C (*)

Of particular note is the reversible protonation of (I) to give (II), protonation being accomplished with $[Ph_4As][H_5O_2]Cl_2$, and deprotonation with triethylamine in the presence of triphenylphosphine. Furthermore, treatment of (II) with one equivalent of $[Ph_4As][H_5O_2]Cl_2$ yielded $[Ph_3PNH_2]Cl$ in essentially quantitative yield [equation (1)]. (Triphenylphosphine imide, Ph_3PHN, is

$$[Os(NHPPh_3)Cl_4(PPh_3)] + [Ph_4As][H_5O_2]Cl_2 \longrightarrow [Ph_3PNH_2]Cl,H_2O + [Ph_4As][OsCl_5(PPh_3)] + H_2O \quad (1)$$

[10] H. E. LeMay, *Inorg. Nuclear Chem. Letters*, 1969, **5**, 941; K. M. Hammon and R. R. Lake, *Inorg. Chem.*, 1968, **7**, 1921.
[11] P. G. Douglas and B. L. Shaw, *J. Chem. Soc.* (*A*), 1970, 334.
[12] T. A. Stephenson, *J. Chem. Soc.* (*A*), 1970, 889.
[13] J. Chatt, G. J. Leigh, D. M. P. Mingos, and R. J. Paske, *J. Chem. Soc.* (*A*), 1968, 2636.

known to form $[Ph_3PNH_2]Cl$ with HCl.[14]) Further evidence for the oxidation state IV in (I) and (II) is provided by their ready conversion to $[OsCl_4(PPh_3)_2]$.

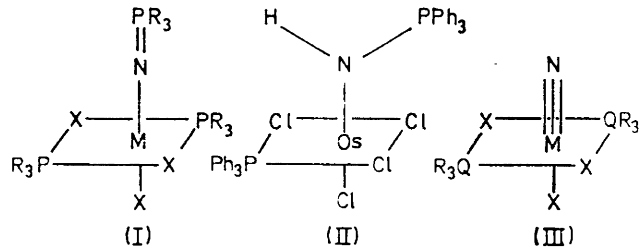
The intermediate species $[Os(NPPhMe_2)Cl_3(AsPh_3)_2]$ [see (*b*) above], prepared from $[Os(N)Cl_3(AsPh_3)_2]$ and $PPhMe_2$, can be oxidised quantitatively back to the starting nitride, showing that in the reactions of tertiary phosphines with these nitrides, attack on the nitrido-ligand is the first step [equation (2)]. The oxidation of

$$[Os(N)Cl_3(AsPh_3)_2] \underset{Cl_2}{\overset{PPhMe_2}{\rightleftharpoons}} [Os(NPPhMe_2)Cl_3(AsPh_3)_2] \quad (2)$$

osmium(IV) phosphine imidato-complexes to osmium(VI) nitrides seems to be a characteristic reaction [see (*c*) above].

(ii) *I.r. and n.m.r. spectra*. The principal i.r. absorptions of these complexes down to 200 cm^{-1} are listed in the Table. The nitrido-complexes each have a strong sharp absorption near 1 060 or 1 030 cm^{-1} for osmium and ruthenium respectively. They are metal–nitrogen stretches, $\nu(M{\equiv}N)$, identified in these rather complex spectra by ^{15}N substitution of selected complexes [$\nu(M{\equiv}N)$ decreases by 33—36 cm^{-1}]. In $[M(NPR_3)X_3L_2]$ the phosphorus–nitrogen stretching mode is assigned to a strong broad band in the region 1 050—1 200 cm^{-1}, which decreases in frequency by 20 cm^{-1} on ^{15}N substitution. Similar bands and shifts were observed in N-substituted phosphine imides[15] and in other phosphine imidato-complexes previously known in which the ligand functions as a bridge.[16] The complex $[Os(NHPPh_3)Cl_4(PPh_3)]$ has a somewhat lower P–N stretching frequency at 924 cm^{-1}, decreasing to 906 cm^{-1} on ^{15}N substitution, a frequency similar to those of some other Ph_3PNH complexes.[17] It also has bands at 3 299 and 1 243 cm^{-1} which shifted to 2 445 and 979 cm^{-1} on deuteriation and 3 291 and 1 240 cm^{-1} on ^{15}N substitution. These were not seen in the phosphine imidato-complexes and we assign them to the N–H stretching and deformation frequencies respectively. A band at 586 cm^{-1}, which shifted to 572 cm^{-1} on deuteriation and 579 cm^{-1} on ^{15}N substitution, is assigned to a principally Os–N stretching mode.

In the metal–chlorine stretching region (240—350 cm^{-1}), two or three bands which may reasonably be assigned to $\nu(MCl)$ were observed for $[M(N)Cl_3L_2]$ and $[M(NPR_3)Cl_3L_2]$. In the former, the lowest-frequency band appeared at *ca.* 240 cm^{-1}, which may well arise from the stretching mode of the ligand *trans* to the nitride [assuming structure (III), Scheme 3]. In $[Re(N)Cl_2(PR_3)_3]$, bands near 220 cm^{-1} have been assigned to the *trans* Re–Cl stretch.[4] In complexes with the less *trans*-influential ligands $[R_3PN]^-$, the lower-frequency band disappears. The complex $[Os(NHPPh_3)Cl_4(PPh_3)]$ has four absorptions in the osmium–chlorine stretching region, consistent with a *cis*-arrangement of phosphine and phosphine imide ligands [structure (II), Scheme 3]. The i.r. spectra of $[OsCl_4(PR_3)_2]^-$ and $[OsCl_4(PPh_3)_2]$ show only one broad metal–chlorine



SCHEME 3 Structure of $[M(NPR_3)X_3(PR_3)_2]$, (I); proposed structures of $[Os(NHPPh_3)Cl_4(PPh_3)]$, (II), and $[M(N)X_3(QR_3)_2]$, (III)

absorption, providing some evidence for a *trans*-configuration, as proposed[11,12] or shown[18] for some analogues of these species. The complex $[Ph_4As][OsCl_5(PPh_3)]$ has two well separated absorptions, the lower-frequency one being assigned to the stretch of the chloro-ligand *trans* to the phosphine. Since our measurements did not extend below 200 cm^{-1}, we cannot make complete assignments for metal–bromine stretching modes in any of these complexes. However, we assign one strong band seen near 210 cm^{-1} to $\nu(MBr)$.

Preliminary ^1H n.m.r. spectral studies were carried out on some of these complexes, but the spectra were difficult to measure and assign due to the low solubility or instability of most of them in solution. Of the more stable nitrido-complexes, $[Os(N)Cl_3(PPh_2Me)_2]$ has a 1 : 2 : 1 triplet resonance centred on τ 7·51 [apparent J(P–H) 4·5 Hz] of methyl protons. Such a pattern is suggestive of virtual coupling,[19] which normally indicates a *trans*-configuration of phosphine ligands. This would then also indicate that there was no loss of a phosphine ligand in solution, in agreement with the molecular-weight data.

Although the osmium and ruthenium(IV) complexes are apparently paramagnetic, they exhibited sharp ^1H n.m.r. spectra with the resonances having unusually large chemical shifts. Similar effects have been noted for other d^4 complexes of osmium(IV) and rhenium(III).[13,20] We are planning a complete study of the ^1H and ^{31}P n.m.r. spectra of these complexes over a wide temperature range, in conjunction with further studies on their magnetic properties.

Structure and Bonding in the Complexes.—The *X*-ray crystal structure of $[Ru(NPPhEt_2)Cl_3(PPhEt_2)_2]$ confirms the presence of a phosphine imidate ligand in this species,[6] and shows that the complex has the overall geometry (I), Scheme 3. The similar spectral properties of the other phosphine imidate species indicate that these too have this configuration The ready conversion of $[Os(NPR_3)Cl_3(PR_3)_2]$ to $[Os(N)Cl_3(PR_3)_2]$, together

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with the ^1H n.m.r. and i.r. spectra of the latter, support structure (III), Scheme 3, in which there has been minimal dislocation of the co-ordination sphere from (I). The other nitrido-species with bulky arsine and stibine ligands probably also prefer this configuration for steric reasons, although the bipy complexes require the chloro-ligands *cis* to the nitride to be in a *cis*-configuration. A *trans*-arrangement of phosphine ligands has been found in a variety of complexes of the type $[M(Z)Cl_3(PR_3)_2]$ (Z = O,[21] NO,[22] NR,[23] N_2R,[8] and NPR_3 [6]). The i.r. spectrum of $[Os(NHPPh_3)Cl_4(PPh_3)]$ supports the structure (II) for this complex, and this would require the minimum of rearrangement in its reversible deprotonation to give a phosphine imidate species.

It would appear that the nitrido-ligands in the complexes studied here are unusually reactive in that they undergo nucleophilic attack by tertiary phosphines, PR_3, to give complexes with $[R_3PN]^-$ ligands. Such behaviour has not been previously observed for nitrido-complexes, although somewhat similar reactions between metal oxo-complexes and phosphines are known, forming phosphine oxides with concomitant reduction of the metal oxidation state by two, *e.g.* equation (3).[24]

$$[Mo^{VI}O_2(S_2CNR_2)_2] + PPh_3 \longrightarrow [Mo^{IV}O(S_2CNR_2)_2] + Ph_3PO \quad (3)$$

This behaviour is in contrast to that shown by $[Re(N)Cl_2(PR_3)_3]$ complexes which are stable in the presence of good nucleophiles such as phosphines [4] and phenyl-lithium [25] and behave as Lewis bases towards acceptor molecules such as boron halides.[26] It may be that the difference in reactivity between the isoelectronic rhenium(V) and osmium(VI) nitrides is due to the greater ability of the more electronegative osmium to draw electron density away from the nitrogen atom in the M≡N bond, *i.e.* the osmium is more easily reduced. Since other nucleophiles, some of which are also reducing agents, *e.g.* halide ion, amines, tertiary arsines and stibines, do not attack the nitrogen atom under similar conditions, the strength of the resultant P–N bond may be an important factor favouring the formation of $[R_3PN]^-$ ligands. In this context it is interesting to note that the P–N distance in $[Ru(NPPhEt_2)Cl_3(PPhEt_2)_2]$ is only 1·571 Å,[6] comparable to the corresponding distance in phosphonitrilic halides, in other N-substituted phosphazene compounds,[27] and to the P=O distance in tertiary phosphine oxide complexes.[28]

EXPERIMENTAL

Tetraphenylarsonium and tetra-n-butylammonium salts of $[Os(N)Cl_4]^-$, $[Os(N)Br_4]^-$, and $[Ru(N)Cl_4]^-$ were prepared as described previously.[1] All manipulations involving air-sensitive tertiary phosphine ligands were carried out in dried, deoxygenated, solvents under an atmosphere of nitrogen.

(a) *Trihalogenonitrido-arsine, -stibine, and -bipyridyl Complexes*, $[M(N)X_3L_2]$.—$[Os(N)Cl_3(AsPh_3)_2]$, α-$[Os(N)Br_3(AsPh_3)_2]$, $[Os(N)Cl_3(SbPh_3)_2]$, $[Os(N)Br_3(SbPh_3)_2]$, $[Ru(N)Cl_3(AsPh_3)_2]$, *and* $[Ru(N)Cl_3(SbPh_3)_2]$. These complexes were prepared by adding $[Bu^n_4N][M(N)X_4]$ (0·1 g) in methanol (2 cm³) to a rapidly stirred solution of triphenyl-arsine or -stibine (1·0 g) in boiling acetone (6 cm³). The immediately formed precipitate of the *product* was filtered off, washed with acetone, and air-dried on the filter. ^{15}N-Substituted complexes were made from $[Bu^n_4N][Os(^{15}N)X_4]$. Another isomer of $[Os(N)Br_3(AsPh_3)_2]$, the β form, was made from a solution of triphenylarsine (1 g) and $[Bu^n_4N][Os(N)Br_4]$ (0·15 g) in cold acetone (12 cm³). The mixture was left for 2 d and the brown microcrystalline *precipitate* filtered off, washed with acetone, and air-dried.

$[Os(N)Cl_3(AsEt_3)_2]$. Triethylarsine (1 cm³) was added to a solution of $[Bu^n_4N][Os(N)Cl_4]$ (0·5 g) in deoxygenated acetone (2 cm³). The mixture was poured onto a watch glass and the solvent allowed to evaporate until a sticky mass of red microcrystals remained. The precipitate was washed onto a sinter with the minimum amount of acetone (1 cm³), filtered off, triturated with a further portion of acetone (1 cm³), and air-dried on the filter to give the red microcrystalline *product*.

$[Os(N)X_3(bipy)]$. The chloro- and bromo-complexes were made from solutions of 2,2′-bipyridyl (1·0 g) and $[Bu^n_4N][Os(N)X_4]$ (0·2 g) in acetone (5 cm³). The mixture was set aside for 24 h and the microcrystalline *precipitate* filtered off and washed with a little acetone.

(b) *Trihalogeno(phosphine imidato)-bis(phosphine) and -bis(arsine) Complexes*, $[M(NPR_3)X_3(PR_3)_2]$ *and* $[M(NPPhMe_2)Cl_3(AsPh_3)_2]$.— $[Os(NPPh_3)X_3(PPh_3)_2]$,Me_2CO (X = Cl *or* Br). To a stirred solution of triphenylphosphine (0·2 g) in dry cold acetone (4 cm³) was added $[Bu^n_4N][Os(N)X_4]$ (0·1 g). Orange *crystals* (90%) precipitated from the solution after 1 min and were filtered off and washed with acetone. The ^{15}N-substituted form of the chloro-complex was made using $[Bu^n_4N][Os(^{15}N)Cl_4]$.

$[Os(NPR_3)X_3(PR_3)_2]$ (X = Cl *or* Br) and $[Ru(NPR_3)Cl_3(PR_3)_2]$. The preparation of all these complexes followed the same outline. We report below the method and generally used quantities of reagents. In some cases the method was varied slightly because of the particular solubilities of the complexes concerned and this is noted below.

To a suspension of $[M(N)X_3(AsPh_3)_2]$ (0·3 g), in cold dried deoxygenated acetone (5 cm³) in a reaction vessel sealed under nitrogen, was added PR_3 (0·7 g, 0·6 cm³) and the solution stirred until all the starting material had dissolved. This gave an orange (M = Os) or dark brown (M = Ru) solution (30 s). This solution was injected into ice-cold deoxygenated light petroleum (b.p. 60—80 °C) (100 cm³), also sealed under nitrogen. The mixture was set aside at 0 °C for up to 1 h, and the orange (M = Os) or

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dark brown (M = Ru) *precipitate* filtered off and air-dried. The yields were 60—90%. If a fluffy yellow precipitate formed when the reaction mixture was injected into the light petroleum, dry acetone (up to 10 cm^3) had to be added to redissolve it.

$[Os(NPPhEt_2)Cl_3(PPhEt_2)_2]$. This complex is particularly sensitive to water in the reaction solution; for isolation of $[Os(NPPhEt_2)Br_3(PPhEt_2)_2]$ the quantity of light petroleum was increased to 200 cm^3 and the resulting solution cooled to −10 °C; $[Ru(NPPh_3)Cl_3(PPh_3)_2],Me_2CO$ is insoluble and does not need precipitation by light petroleum. Special procedures were used for the triethylphosphine derivatives.

$[Os(NPEt_3)Cl_3(PEt_3)_2]$. All the reaction solutions must be very carefully deoxygenated. $[Os(N)Cl_3(AsPh_3)_2]$ (1·0 g), acetone (2 cm^3), PEt_3 (1·5 cm^3), and light petroleum (250 cm^3) were used to prepare the orange crystalline *complex*, which is extremely soluble and air and moisture sensitive.

$[Ru(NPEt_3)Cl_3(PEt_3)_2]$. The quantities used for this very soluble complex were $[Ru(N)Cl_3(AsPh_3)_2]$ (0·5 g), PEt_3 (0·7 cm^3), Me_2CO (2 cm^3), and light petroleum (250 cm^3). The brown air and moisture-sensitive *precipitate* (50%) was filtered off under nitrogen and sealed in an inert dry atmosphere.

$[Os(NPPhMe_2)Cl_3(PPhMe_2)_2]$. Dimethylphenylphosphine (0·5 cm^3) was added to a solution of $[Bu^n{}_4N][Os(N)Cl_4]$ (0·5 g) in ice-cold, dried, deoxygenated acetone (2 cm^3). The orange microcrystalline *precipitate* was filtered off after 2 min, and washed with a small amount of ice-cold acetone.

$[Os(NPPhMe_2)Cl_3(AsPh_3)_2]$ *and* $[Ru(NPPhMe_2)Cl_3(AsPh_3)_2]$. To a rapidly stirred solution of $[M(N)Cl_3(AsPh_3)_2]$ (0·5 g) in cold, dried, deoxygenated acetone (5 cm^3) was added $PPhMe_2$ (0·5 cm^3). The pink (osmium) or green (ruthenium) *complex* was filtered off after 30 s.

(c) *Trichloronitridobis(phosphine)osmium*(IV) *Complexes*, $[Os(N)Cl_3(PR_3)_2]$.—All these were made as follows. Finely ground $[Os(NPR_3)Cl_3(PR_3)_2]$ (0·2 g) was suspended in methanol (2 cm^3), and chlorine gas passed through the solution until all the starting complex had reacted (5—30 s). The brown to yellow *complexes* precipitated from the solution within 1 min and were filtered off and washed with cold methanol (1 cm^3). The complex $[Os(^{15}N)Cl_3(PPh_3)_2]$ was made by chlorine oxidation of $[Os(^{15}NPPh_3)Cl_3(PPh_3)_2]$.

(d) *Tetrachloro(phosphine imide)triphenylphosphine-osmium*(IV)*-Acetone* (1/1), $[Os(NHPPh_3)Cl_4(PPh_3)],Me_2CO$.—An intimate mixture of $[Ph_4As][H_5O_2]Cl_2$ (0·2 g) and $[Bu^n{}_4N][Os(N)Cl_4]$ (0·1 g) was added with rapid stirring to a solution of triphenylphosphine (0·25 g) in acetone (4 cm^3). The bright red *precipitate* was filtered off after 2 min stirring and washed with acetone, then methanol, and air-dried. A deuteriated product was made using $[Ph_4As][D_5O_2]Cl_2$, and a ^{15}N-substituted product using $[Bu^n{}_4N][Os(^{15}N)Cl_4]$.

(e) *Miscellaneous Halogenophosphine Complexes*.—$[Ph_4As][OsCl_4(PPh_3)_2],Me_2CO$. To a hot solution of triphenylphosphine (0·2 g) in acetone (4 cm^3) was added $[Ph_4As][Os(N)Cl_4]$ (0·1 g). The solution was stirred rapidly for 2 min giving a yellow microcrystalline *precipitate*, which was filtered off, washed with acetone, and air-dried.

$[Ph_4As][OsCl_4(PPhEt_2)_2]$. The salt $[Ph_4As][Os(N)Cl_4]$ (0·1 g) was added to a solution of diethylphenylphosphine (0·5 cm^3) in acetone (2 cm^3). The solution was stirred for 2 min giving a yellow microcrystalline *precipitate* which was filtered off, washed with acetone, and air-dried. The salt $[Bu^n{}_4N][OsBr_4(PPhEt_2)_2]$ was made in the same way as the chloro-derivative using $[Bu^n{}_4N][Os(N)Br_4]$ in place of $[Ph_4As][Os(N)Cl_4]$.

$[OsCl_4(PPh_3)_2]$. The salt $[Ph_4As][Os(N)Cl_4]$ (0·1 g) was added to a solution of triphenylphosphine (0·2 g) in acetone (4 cm^3) and concentrated hydrochloric acid (1 cm^3). The light brown *precipitate* was filtered off, washed with acetone, and air-dried.

$[Ph_4As][OsCl_5(PPh_3)]$. *Recovery of* $[Ph_3PNH_2]Cl$ *from* $[Os(NHPPh_3)Cl_4(PPh_3)],Me_2CO$. The following procedure was adopted. A suspension of $[Os(NHPPh_3)Cl_4(PPh_3)],Me_2CO$ (0·186 g) in acetone (5 cm^3) was heated under reflux for 10 min in the presence of tetraphenylarsonium chloride, $[Ph_4As][H_5O_2]Cl_2$ (0·091 g). The solution was cooled and the resulting precipitate filtered off. The precipitate was triturated on the glass sinter with methanol (2 cm^3), and the methanol then collected and evaporated on a watch glass. This left a white *residue* of $[Ph_3PNH_2]Cl,H_2O$ (85%) (Found: C, 64·9; H, 5·3; Cl, 11·7; N, 4·1. Calc. for $C_{18}H_{19}ClNO$: C, 65·1; H, 5·8; Cl, 10·7; N, 4·2%). The red product left on the sinter was $[Ph_4As][OsCl_5(PPh_3)]$. This was filtered off, washed with a little acetone, and dried in air.

$[Os(OMe)_2Cl_2(PPh_3)_2]$. A solution of $[Bu^n{}_4N][Os(N)Cl_4]$ (0·1 g) in methanol (2 cm^3) was added to a warm solution of triphenylphosphine (0·2 g) in acetone (2 cm^3). A red microcrystalline *precipitate* was formed which was filtered off, washed with acetone, and air-dried.

^1H N.m.r. spectra were measured from 223 to 308 K on a Perkin-Elmer R-12B instrument at 60 MHz. I.r. spectra were measured from Nujol mulls between caesium iodide plates using a Perkin-Elmer 325 instrument. Microanalyses were carried out by the Microanalytical Department, Imperial College, and by A. Bernhardt, Munich.

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