Osmium Nitrido-complexes with Triphenyl-phosphine, -arsine, and -stibine, with Evidence for Nitrene-like Behaviour of the Phosphine Complex

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Summary The new complexes $[OsNX_3(AsPh_3)_2]$ and $[OsNCl_3(LPh_3)_2]$ (X = Cl or Br, L = P or Sb) have been made; we propose that nucleophilic attack of the nitrogen atom by triphenylphosphine occurs in some of these complexes to give derivatives of triphenylphosphine imine.

ALTHOUGH osmium imido tertiary phosphine complexes are known[1] there are no nitrido-analogues, and no arsine or stibine nitrido-complexes of any metal. We find that the salts $Bu^n_4N[OsNX_4]$, made by addition of Bu^n_4NX to solutions of $[OsNX_5]^{2-}$ in HX (X = Cl or Br),[2] react quickly in methanol at 70° with an excess of triphenylarsine or triphenylstibine to give $[OsNX_3(AsPh_3)_2]$ or $[OsNCl_3(SbPh_3)_2]$. With triphenylphosphine, however, a suspension of $Ph_4As[OsNCl_4]$ in acetone at room temperature yields a paramagnetic species of empirical formula $[OsNCl_3(PPh_3)_3],Me_2CO$ (I) μ_{eff} 1·8 B.M.); a suspension of this in methanol reacts with chlorine to give $[OsNCl_3(PPh_3)_2]$. The bromo-analogue of (I) has also been prepared. The complexes $[OsNX_3(LPh_3)_2]$ are non-conductors in acetone and have properties typical of osmium(VI) nitrido-species:[2] they are diamagnetic and have sharp Os≡N stretching i.r. bands near 1060 cm^{-1} the frequencies of which decrease by *ca.* 30 cm^{-1} on ^{15}N substitution.

TABLE

	Colour	$\nu(M\equiv{}^{14}N)/cm^{-1}$	$\nu(M\equiv{}^{15}N)/cm^{-1}$	M.p. (t/°C)
$OsNCl_3(PPh_3)_2$	Brown	1058	1027	145 (decomp.)
$OsNCl_3(AsPh_3)_2$	Brown	1059		257
$OsNBr_3(AsPh_3)_2$	Brown	1068	1035	221
$OsNCl_3(SbPh_3)_2$	Orange	1065	1032	170
$Os(NPPh_3)Cl_3(PPh_3)_2,Me_2CO$ (I)	Orange	1127[a]	1104[a]	136
$Os(NPPh_3)Br_3(PPh_3)_2,Me_2CO$	Brown	1123[a]		122
$Os(NHPPh_3)Cl_4(PPh_3),Me_2CO$ (II)	Red	924[a]	906[a]	163 (decomp.)

[a] P–N stretching frequency.

Elemental analyses for all complexes (C, H, N, O, halogen) are in satisfactory agreement with the quoted formulae.

Addition of an equimolar quantity of $Ph_4As[H_5O_2]Cl_2$, to $Ph_4As[OsNCl_4]$ with triphenylphosphine in acetone yields a second paramagnetic product of empirical formula $[OsNHCl_4(PPh_3)_2],Me_2CO$ (II) (μ_{eff} 1·6 B.M.); this may also be made directly from (I) and $Ph_4As[H_5O_2]Cl_2$ in acetone. If aqueous HCl is used for these two reactions, $[OsCl_4(PPh_3)_2]$ is formed. Deprotonation of (II) to give (I) may be accomplished with strong bases, *e.g.* triethylamine, in the presence of triphenylphosphine. We formulate (I) and (II) as Os^{IV} derivatives of triphenylphosphine imine, ***i.e.*** [Os

$(NPPh_3)Cl_3(PPh_3)_2]$,Me_2CO (I) and $[Os(NHPPh_3)Cl_4(PPh_3)]$,Me_2CO (II) for the following reasons. Prolonged treatment of (II) with an equimolar quantity of $Ph_4As[H_5O_2]Cl_2$ gives $[Ph_3PNH_2]Cl$ and $Ph_4As[OsCl_5(PPh_3)]$ in high yields. Triphenylphosphineimine is known to react quantitatively with hydrogen chloride to give $[Ph_3PNH_2]Cl$.[3] The i.r. spectra of (I) and (II) have strong bands at 1127 and 924 cm^{-1} respectively, which shift downwards some 20 cm^{-1} on ^{15}N substitution, and we assign these to P–N stretching modes (similar bands and shifts have been observed in Ph_3PNH and its complexes and in Ph_3PNR [4]). Complex (II) has additional strong bands at 3299 and 1243 cm^{-1} which we assign to the N–H stretching and deformation modes respectively. There is no evidence from the i.r. data that the acetone molecule is co-ordinated in either complex. The ^1H n.m.r. spectrum of (I) could not be measured owing to the low solubility of the compound, but that of (II) gave a sharp resonance centred at τ — 2·5 which we assign to the *ortho*-protons on the Ph_3P group directly co-ordinated to osmium; its intensity relative to the remaining phenyl protons is consistent with this assignment. Shifts of this magnitude, together with sharp resonances, are characteristic of osmium(IV) complexes which exhibit temperature-independent paramagnetism.[5]†

Since (I) and (II) are obtained from $[OsNCl_4]^-$, and (I) can also be made by reaction of triphenylphosphine with $[OsNCl_3(LPh_3)_2]$ (L = P or As), we propose that their formation proceeds by nucleophilic attack of the phosphine on the co-ordinated nitrogen, which is here behaving as an electrophilic nitrene. This is in contrast to the nucleophilic behaviour of Re≡N in $[ReNCl_2(PEt_2Ph)_3]$,[6] although nitrene-like behaviour has been observed for rhenium[7] and iridium[8] imido-complexes.

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[1] B. Bell, J. Chatt, J. R. Dilworth, and G. J. Leigh, *Inorg. Chim. Acta,* 1972, **6**, 635.
[2] W. P. Griffith and D. Pawson, *J.C.S. Dalton*, 1973, in the press.
[3] R. Appel and A. Hauss, *Ber.*, 1960, **93**, 405.
[4] W. Wiegrabe, H. Bock, and W. Luttke, *Ber.*, 1966, **99**, 3737; H. Bock and H. Dieck, *Z. Naturforsch.*, 1966, **21**B, 739.
[5] J. Chatt, G. J. Leigh, and D. M. P. Mingos, *J. Chem. Soc.* (*A*), 1969, 1674.
[6] J. Chatt and B. T. Heaton, *J. Chem. Soc.* (*A*), 1971, 705.
[7] J. Chatt, R. J. Dosser, and G. J. Leigh, *J.C.S. Chem. Comm.*, 1972, 1243.
[8] B. C. Lane, J. W. McDonald, F. Basolo, and R. G. Pearson, *J. Amer. Chem. Soc.*, 1972, **94**, 3786.