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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 known¹ there are no nitrido-analogues, and no arsine or stibine nitrido-complexes of any metal. We find that the salts $Bun_4N[OsNX_4]$, made by addition of Bun_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 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 $Os\equiv N$ stretching i.r. bands near 1060 cm^{-1} the frequencies of which decrease by *ca*. 30 cm^{-1} on ^{15}N substitution.

Addition of an equimolar quantity of $Ph_4As[H_5O_2]Cl_2$, to Ph₄As[OsNCl₄] with triphenylphosphine in acetone yields a second paramagnetic product of empirical formula [Os-NHCl₄(PPh₃)₂],Me₂CO (II) (μ_{eff} 1.6 B.M.); this may also be made directly from (I) and Ph₄As[H₅O₂]Cl₂ in acetone. If

						Colour	$\nu(M \equiv 14N)/cm^{-1}$	$\nu(M \equiv 15 N) / cm^{-1}$	M.p. $(t/^{\circ}C)$
OsNCl ₃ (PPh ₃) ₂		• •		••	••	Brown	1058	1027	145 (decomp.)
OsNCl ₃ (AsPh ₃) ₂		• •	••	• •	••	Brown	1059		257
OsNBr ₂ (AsPh ₂) ₂		• •	••	••	••	Brown	1068	1035	221
OsNCl _a (SbPh _a) ₂				••	••	Orange	1065	1032	170
Os(NPPha)Cla(PP	h,),,M	le,CO ((I)			Orange	1127a	1104 ^a	136
Os(NPPh ₃)Br ₃ (PI	Ph_), N	le,CO	• • •	••		Brown	1123ª		122
Os(NHPPh ₃)Čl ₄ (H	PPh ₃),	Me ₂ CO	(II)	• •	••	\mathbf{Red}	924 ^a	906a	163 (decomp.)

TABLE

^a P-N stretching frequency.

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

or triphenylstibine to give $[OsNX_3(AsPh_3)_2]$ or $[OsNCl_3(SbPh_3)_2]$. With triphenylphosphine, however, a suspension of Ph₄As $[OsNCl_4]$ 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

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

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(NPPh₃)Cl₃(PPh₃)₂],Me₂CO (I) and [Os(NHPPh₃)Cl₄(PPh₃)],-Me_sCO (II) for the following reasons. Prolonged treatment of (II) with an equimolar quantity of Ph₄As[H₅O₂]Cl₂ gives [Ph₃PNH₂]Cl and Ph₄As[OsCl₅(PPh₃)] in high yields. Triphenylphosphineimine is known to react quantitatively with hydrogen chloride to give [Ph3PNH2]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 ¹⁵N substitution, and we assign these to P-N stretching modes (similar bands and shifts have been observed in Ph₃PNH and its complexes and in Ph₃PNR⁴). 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 $\tau - 2.5$ which we assign to the ortho-protons on the Ph₃P group directly

temperature-independent paramagnetism.5† Since (I) and (II) are obtained from [OsNCl₄]⁻, 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 $Re \equiv N$ in $[ReNCl_2(PEt_2Ph)_3]$,⁶ although nitrene-like behaviour has been observed for rhenium7 and iridium⁸ imido-complexes.

Shifts of this magnitude, together with sharp resonances,

are characteristic of osmium(IV) complexes which exhibit

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