A Series of Nitrogen Complexes of Osmium(II)

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ALTHOUGH nitrogen complexes have been known for 3½ years, only about ten are sufficiently stable for reasonably complete characterisation,[1] and even close analogues of these are difficult or impossible to obtain. Only one short series of very close analogues, those of [$CoH(N_2)(PPh_3)_3$] derived from tri-*p*-tolyl-, tri-*p*-chlorophenyl-, and tri-*p*-fluorophenyl-phosphines, has been reported,[2] although we and others[3] have attempted the preparations of other series. Now we report a new series of nitrogen complexes which accommodates a variety of tertiary phosphines.

Recently we reported that the hydrazine reduction of [$OsCl_3(PBu_2Ph)_3$] produces a nitrogen complex, probably [$OsCl_2(N_2)(PBu_2Ph)_3$], (I), which we were unable to obtain pure by this reaction.[4] The lower dialkylphenylphosphines gave lower yields or none at all. However, by an adaptation of the method of Shilov and his co-workers,[5] we have now succeeded in preparing a surprisingly extensive series of stable analogues of (I). They are obtained by the reaction of amalgamated zinc with *mer*-$[OsX_3(PR_3)_3]$ ($X = Cl$ or Br, PR_3 = tertiary phosphine) in dry tetrahydrofuran under nitrogen at atmospheric pressure. Except when $PR_3 = PMe_2Ph$, a green solution, possibly of $[OsX_2(THF)(PR_3)_3]$, is initially produced. This takes up nitrogen gas to form the complexes (see Table). We have prepared a $^{15}N_2$ analogue to show conclusively that these are nitrogen complexes (see Table).

Nitrogen complexes of the type $[OsX_2(N_2)(PR_3)_3]$
($X = Cl$ or Br, PR_3 = tertiary phosphine)

		$\nu(N{\equiv}N)$ cm.$^{-1}$	
Complex	M.p. °	Benzene	Nujol[a]
$[OsCl_2(N_2)(PMe_2Ph)_3]$	142—144[b]	2082	2078 2060sh
$[OsBr_2(N_2)(PMe_2Ph)]$	132—134[b]	2090	2100 2070sh
$[OsCl_2(N_2)(PEt_2Ph)_3]$	159—160	2063	2080 2050sh
$[OsCl_2(^{15}N_2)(PEt_2Ph)_3]$	159—160	1998[c]	2010[c] 1990sh[c]
$[OsCl_2(N_2)(PPr^n{}_2Ph)]_3$	137—139[b]	2062	2061 2071
$[OsCl_2(N_2)(PBu^n{}_2Ph)_3]$[d]		2060	2080w 2064 2050w
$[OsCl_2(N_2)(PEtPh_2)_3]$[d]		2090	2090
$[OsCl_2(N_2)(PEt_3)_3]$[d]		2064	2064
$[OsBr_2(N_2)(PEt_2Ph)_3]$[d]		2070	2087 2053sh

[a] The $\nu(N{\equiv}N)$ band is often split in the solid state. We commonly find this; evidently the $(N{\equiv}N)$ stretching vibration is very sensitive to environment.

[b] With decomposition.

[c] $\nu(^{15}N{\equiv}^{15}N)$.

[d] Not yet obtained analytically pure.

The solid complexes are stable in air but in solution, in the presence of halide ion, the dialkylphenylphosphine complexes readily oxidize and revert to the red *mer*-$[OsCl_3(PR_2Ph)_3]$. They must be handled in absence of air throughout their preparation and purification. All of the tertiary phosphines we have tried have given analogous nitrogen complexes, but they are difficult to purify and so far only five have been obtained analytically pure. These are faintly pink, probably owing to traces of the trichloro-complex. They are diamagnetic and, by ^1H n.m.r. spectral study, the dimethylphenylphosphine complexes were shown to have a *mer*-configuration of the phosphine ligands, with X apparently *trans* to nitrogen.

This reaction can also be used to prepare corresponding complexes containing analogue of the nitrogen molecule. Thus, the use of carbon monoxide in place of nitrogen gives carbonyl complexes of the type $[OsCl_2(CO)(PR_3)_3]$ which, as expected, have $\nu(C{\equiv}O)$ in the lower range of known terminal carbonyl stretching frequencies, *e.g.* $[OsCl_2(CO)(PEt_2Ph)_3]$ has $\nu(C{\equiv}O)$ 1941 cm.$^{-1}$ (benzene solution). Nitrous oxide forms the nitrogen complexes, and hydrogen gives hydride complexes.

In the nitrogen complexes the $N{\equiv}N$ stretching band is very sharp and intense. The transition moment must thus be high, and so we might expect the bond moment itself to be high and the dipolar nitrogen ligand more open to attack by reagents. Nevertheless its attempted reduction to ammonia has been unsuccessful, but is continuing.

The nitrogen has been displaced quantitatively from the nitrogen complexes by reactions 1 and 2, using an excess of the reagents.

$$[OsCl_2(N_2)(PR_2Ph)_3] + 2Ph_2PCH_2{\cdot}CH_2PPh_2 \xrightarrow[48\text{ hr.}]{120^\circ} [OsCl_2(Ph_2PCH_2{\cdot}CH_2PPh_2)_2] + N_2(R = \text{Et, or Pr}^n) \tag{1}$$

$$2[OsCl_2(N_2)(PEt_2Ph)_3] + Cl_2 \xrightarrow{25^\circ} 2[OsCl_3(PEt_2Ph)_3] + 2N_2\ \{+ \text{ a little } [OsCl_4(PEt_2Ph)_2]\} \tag{2}$$

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