

ELECTROPHILIC BEHAVIOUR OF THE NITRIDE LIGAND IN
OSMIUM AND RUTHENIUM COMPLEXES

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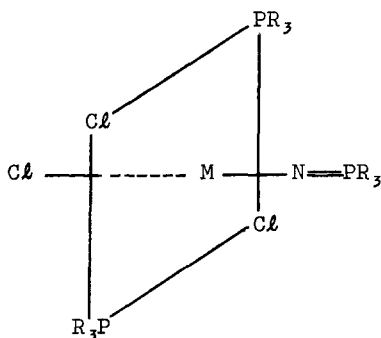
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In a previous communication (1) we reported the preparation of $[\text{Os}(\text{NPPh}_3)\text{Cl}_3(\text{PPh}_3)_2]$ (A) from triphenylphosphine and the nitrido complexes $\text{Bu}_4^{\text{n}}\text{N}[\text{OsNCl}_4]$. On the basis of its chemical reactions and spectroscopic properties we proposed that (A) contained a coordinated $(\text{Ph}_3\text{P}=\text{N})^-$ group which had been generated by nucleophilic attack of the phosphine on the nitride ligand. We now extend this work by reporting the isolation and characterisation of a number of new osmium and ruthenium complexes similar to (A), $[\text{M}(\text{NPR}_3)\text{Cl}_3(\text{PR}_3)_2]$ ($\text{M} = \text{Os}, \text{Ru}$; $\text{PR}_3 = \text{PPhEt}_2, \text{PPh}_2\text{Et}, \text{PPh}_2\text{Me}, \text{PEt}_3$), and the oxidation by chlorine of the osmium complexes to the nitrido species $[\text{OsNCl}_3(\text{PR}_3)_2]$.

Reaction of $\text{Bu}_4^{\text{n}}\text{N}[\text{OsNCl}_4]$ (2) in boiling methanol with a six-fold excess of triphenylarsine yields nitrido complexes $[\text{MNCl}_3(\text{AsPh}_3)_2]$. Suspensions of these complexes in dry acetone under nitrogen react with an excess of tertiary phosphine PR_3 to give $[\text{M}(\text{NPR}_3)\text{Cl}_3(\text{PR}_3)_2]$ in good yield. The new complexes were fully characterised by elemental analyses. The osmium complexes have magnetic moments at room temperature of 1.9 B.M., and those of ruthenium 2.9 B.M., which are typical values for M^{IV} species. The complexes are somewhat unstable in solution but appear to be monomeric in benzene. Their infra-red spectra show strong broad bands in the $1050 - 1200 \text{ cm}^{-1}$ region in addition to the normal phosphine modes. We assign these bands to $\text{P}=\text{N}$ stretching modes of the coordinated $(\text{R}_3\text{P}=\text{N})^-$ ligand.

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An X-ray crystal structure determination of $[\text{Ru}(\text{NPPhEt}_2)\text{Cl}_3(\text{PPhEt}_2)_2]$ shows this to have the configuration indicated in the figure; the Ru-N-P angle is close to 180° (3). We propose that, as suggested for the triphenylphosphine- $[\text{OsNCl}_4]^-$ reaction (1), nucleophilic attack by PR_3 on the nitrido ligand in $[\text{MNC}_3(\text{AsPh}_3)_2]$ has occurred (with dimethylphenylphosphine, the intermediate species $[\text{M}(\text{NPPhMe}_2)\text{Cl}_3(\text{AsPh}_3)_2]$ can be isolated). Such behaviour may be due to the high oxidation state of the metal and the strength of the resulting phosphorus-nitrogen bond.



Treatment of suspensions in methanol of $[\text{Os}(\text{NPR}_3)\text{Cl}_3(\text{PR}_3)_2]$ with chlorine yields the diamagnetic nitrido complexes $[\text{OsNCl}_3(\text{PR}_3)_2]$; these have strong $\text{Os} \equiv \text{N}$ stretching vibrations in the infrared near 1060 cm^{-1} . We propose that these complexes have structures similar to $[\text{M}(\text{NPR}_3)\text{X}_3(\text{PR}_3)_2]$, a terminal nitrido ligand replacing the coordinated $(\text{NPR}_3)^-$ ligand.

Further studies on these and on related species are in progress.

ACKNOWLEDGEMENTS

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Table

		$\nu_{\text{P=N}}^*$ (cm^{-1})	M.P. ($^{\circ}\text{C}$)
$[\text{Os}(\text{NPPh}_2\text{Et})\text{Cl}_3(\text{PPh}_2\text{Et})_2] \cdot \text{Me}_2\text{CO}$	Orange	1085	132
$[\text{Ru}(\text{NPPh}_2\text{Et})\text{Cl}_3(\text{PPh}_2\text{Et})_2] \cdot \text{Me}_2\text{CO}$	Brown	1063	114
$[\text{Os}(\text{NPPhEt}_2)\text{Cl}_3(\text{PPhEt}_2)_2]$	Orange	1204	134
$[\text{Ru}(\text{NPPhEt}_2)\text{Cl}_3(\text{PPhEt}_2)_2]$	Brown	1165	134
$[\text{Os}(\text{NPPh}_2\text{Me})\text{Cl}_3(\text{PPh}_2\text{Me})_2]$	Orange	1128	165(d)
$[\text{Ru}(\text{NPPh}_2\text{Me})\text{Cl}_3(\text{PPh}_2\text{Me})_2]$	Brown	1114	145
$[\text{Os}(\text{NPPhMe}_2)\text{Cl}_3(\text{AsPh}_3)_2]$	Pink	1081	156
$[\text{Ru}(\text{NPPhMe}_2)\text{Cl}_3(\text{AsPh}_3)_2]$	Green	1055	
$[\text{Os}(\text{NPET}_3)\text{Cl}_3(\text{PET}_3)_2]$	Orange	1125	
$[\text{Ru}(\text{NPET}_3)\text{Cl}_3(\text{PET}_3)_2]$	Brown	1099	
$[\text{OsNCl}_3(\text{AsPh}_3)_2]$	Pink	1059*	257
$[\text{RuNCl}_3(\text{AsPh}_3)_2]$	Brown-yellow	1023*	169
$[\text{OsNCl}_3(\text{PPh}_2\text{Et})_2]$	Light brown	1062*	176
$[\text{OsNCl}_3(\text{PPhEt}_2)_2]$	Yellow-brown	1070*	129
$[\text{OsNCl}_3(\text{PPh}_2\text{Me})_2]$	Light brown	1067*	160
$[\text{OsNCl}_3(\text{PET}_3)_2]$	Brown	1070*	

* $\nu_{\text{M} \equiv \text{N}}$

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