Hydrogen Transfer from HCl to the Nitrosyl Ligand. Examples of Co-ordinated HNO, $NHOH^-$, and NH_2OH

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Summary The nitrosyl complexes, $OsCl(CO)(NO)(PPh_3)_2$, $Os(NO)_2(PPh_3)_2$, and $Ir(NO)(PPh_3)_3$ react reversibly with one, two, and three moles of HCl, respectively, forming $OsCl_2(CO)(HNO)(PPh_3)_2$, $OsCl_2(NHOH)(NO)(PPh_3)_2$, and $IrCl_3(NH_2OH)(PPh_3)_2$.

PROTONATION by strong acids to form metal hydrides is a characteristic reaction of many low-valent complexes.[1] When an acetylene is one of the ligands in the complex, *e.g.*, in $Pt(RC{\equiv}CR)(PPh_3)_2$ it has been reported that reaction with HCl gives $PtCl_2(PPh_3)_2$ and hydrogen transfers to $RC{\equiv}CR$ giving $RCH{=}CHR$.[2] We now describe the reaction of HCl with low-valent complexes of osmium and iridium containing the nitrosyl ligand, in which hydrogen transfer to NO occurs and the successive reduction products, HNO, $NHOH^-$, and NH_2OH are found co-ordinated to the metal.

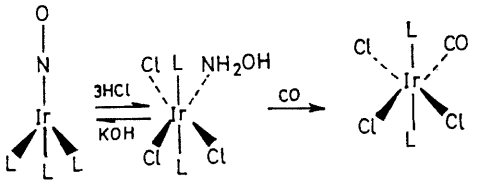
$Ir(NO)(PPh_3)_3$ is protonated by non-complexing acids, *e.g.*, HPF_6, forming $[IrH(NO)(PPh_3)_3]PF_6$.[3] However, when an excess of HCl (either gaseous or concentrated aqueous solution) is added to a dichloromethane solution of $Ir(NO)(PPh_3)_3$ a yellow crystalline material of composition $Ir(NO)(PPh_3)_3,3HCl$ is formed. We formulate this as an iridium(III) hydroxylamine complex, $IrCl_3(NH_2OH)(PPh_3)_2$, since the i.r. spectrum shows no absorption attributable to ν_{NO} or ν_{Ir-H} but instead has bands appropriate for ν_{NH}, ν_{OH}, and ν_{Ir-Cl} (see Table), and also because reaction with CO gives the known compound, $IrCl_3(CO)(PPh_3)_2$ by displacement of NH_2OH. The original nitrosyl complex is re-formed by the action of KOH.

I.r. data[a] for new complexes[b]

	ν_{NO} cm^{-1}	ν_{CO} cm^{-1}	ν_{M-Cl} cm^{-1}	$\nu_{NH,OH}$ cm^{-1}
$Ir(NO)(PPh_3)_3$	1600vs			
$IrCl_3(NH_2OH)(PPh_3)_2$			330sh, 320s, br	3300w, 3240w, 3160w
$Os(NO)_2(PPh_3)_2$	1665vs, 1615s			
$OsCl_2(NHOH)(NO)(PPh_3)_2$ ..	1860vs		310, 291	3310w, 3200w, 2600m, br
$OsCl(CO)(NO)(PPh_3)_2$	1560s	1905s	296	
$OsCl_2(HNO)(CO)(PPh_3)_2$ ..	1410s	1975s	293, 280	

[a] As Nujol mulls. [b] Satisfactory elemental analyses have been obtained.

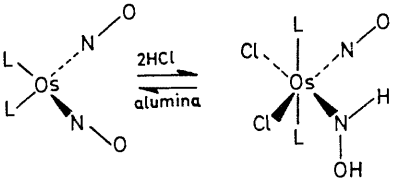
It is possible that intermediates in this reaction are first an iridium(I) complex, $IrCl(HNO)(PPh_3)_3$, (from $[IrH(NO)(PPh_3)_3]^+$ by hydride migration on to NO induced by



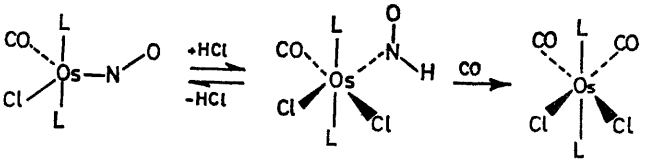
L = PPh_3

co-ordination of chloride ion) which reacts further with HCl to give $IrCl_2(NHOH)(PPh_3)_3$ and finally $IrCl_3(NH_2OH)(PPh_3)_2$. We have encountered stable examples of these intermediates in the reaction of osmium nitrosyls with HCl. $Os(NO)_2(PPh_3)_2$[4] forms an adduct with two moles of HCl formulated as $OsCl_2(NHOH)(NO)(PPh_3)_2$ since the product has a single strong ν_{NO} at 1860 cm^{-1}, a position characteristic of other $OsX_3(NO)(PPh_3)_2$ compounds (X = anionic ligand);[5] and i.r. bands due to ν_{NH}, ν_{OH}, and ν_{Os-Cl} (see Table). The reaction is reversed upon attempted chromatography on alumina, and $Os(NO)_2(PPh_3)_2$ is recovered quantitatively.

To form a stable adduct with one mole of HCl, a five-co-ordinate nitrosyl complex would be required, and accordingly we investigated the reaction of $OsCl(CO)(NO)(PPh_3)_2$[5] with HCl. A crystalline 1 : 1 adduct is formed, the physical properties of which (see Table) are consistent with an octahedral osmium(II) complex containing co-ordinated HNO, $OsCl_2(HNO)(CO)(PPh_3)_2$, the first such example to be



reported. The stabilisation through co-ordination of otherwise reactive species *e.g.*, HNC,[6] carbenes[7] *etc.*, is well recognised. The HNO ligand is displaced by CO giving $OsCl_2(CO)_2(PPh_3)_2$[8] and in solution HCl is easily lost to re-form $OsCl(CO)(NO)(PPh_3)_2$.



L = PPh_3

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