Oxidation of Co-ordinated Ligands *via* Oxygen Adducts of Ruthenium and Osmium: Oxidation of CO to CO_3^{2-} and NO to NO_3

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RECENT reports have described both stoicheiometric and catalytic oxidations involving oxygen complexes; *e.g.* the oxidation of phosphines to phosphine oxides and isocyanides to isocyanates is catalysed by oxygen complexes of palladium and nickel.[1,2] Likewise, compounds containing co-ordinated SO_2 are readily oxidised to sulphate complexes.[3] We now report two examples in which a ligand bound to a metal is oxidised and retained in the co-ordination sphere of the metal in its oxidised state.

The first example involves the oxidation of co-ordinated carbon monoxide to chelated carbonate. The oxygen complex, $Ru(O_2)Cl(NO)(PPh_3)_2$ (V), can be prepared from $RuCl(CO(NO)(PPh_3)_2$ with loss of CO.[4] By contrast, the osmium analogue $OsCl(CO)(NO)(PPh_3)_2$ (I), reacts with oxygen without loss of CO, the CO and O_2

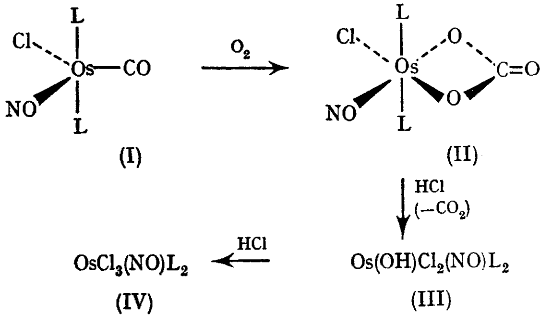
Infrared data for new complexes[a]

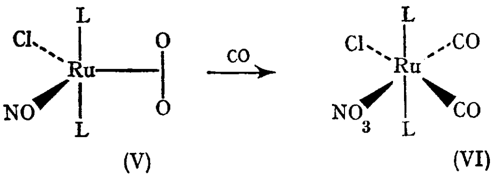
	ν(NO) cm.$^{-1}$	ν(CO) cm.$^{-1}$	ν(M–Cl)[e] cm.$^{-1}$	ν(OH) cm.$^{-1}$
$OsCl(CO)(NO)(PPh_3)_2$ [b]	1565	1910	269	
$OsCl(CO_3)(NO(PPh_3)_2$ [c]	1780		315	
$Os(OH)Cl_2(NO)(PPh_3)_2$	1790		313	3580
$OsCl_3(NO)(PPh_3)_2$	1850		321, 310, 296sh	
$RuCl(NO_3)(CO)_2(PPh_3)_2$ [d]		2050, 1995	289	

[a] All measured as KBr discs (and petroleum jelly mulls below 500 cm.$^{-1}$); [b] All compounds reported give good elemental analyses; [c] I.r. absorption for CO_3^{2-} at 1710, 1030, 760, and 662 cm.$^{-1}$; [d] I.r. absorption for NO_3^- at 1495, 1280, 995, and 790 cm.$^{-1}$; [e] ν(M–Cl) assignments supported by comparison with corresponding bromides in most cases.

being incorporated together as a chelated carbonate group in $Os(CO_3)Cl(NO)(PPh_3)_2$ (II). This oxidation occurs so readily that successful preparation of (I) is possible only when oxygen is rigorously excluded. Compound (II) forms yellow crystals, m.p. 176°; it has been characterised by complete elemental analysis, molecular weight determination (osmometer), i.r. spectrum (see Table), and its further reactions. It is related to the platinum carbonate, $Pt(CO_3)(PPh_3)_2$ which is formed from $Pt(O_2)(PPh_3)_2$ and CO_2 [5,6] or CO.[7] Compound (II) reacts with HCl, with loss of CO_2, to form $Os(OH)Cl_2(NO)(PPh_3)_2$ (III), and with further HCl to form $OsCl_3(NO)(PPh_3)_2$, (IV), which is isomorphous with $RuCl_3(NO)(PPh_3)_2$.[8]

The second example involves the oxidation of a metal nitrosyl group to a covalently bound nitrate. We find that the oxygen complex, (V), reacts smoothly with CO, the co-ordinated oxygen combining with the bound NO to produce a nitrate group. The resulting compound (VI) is mixed chloro-nitrato-derivative of divalent ruthenium. Dichloro- and dinitrato-derivatives of this same type have already been described.[9] Thus the reaction of the ruthenium oxygen complex with CO is quite different from the corresponding reaction involving the platinum oxygen complex, $Pt(O_2)(PPh_3)_2$, which with CO gives $Pt(CO_3)(PPh_3)_2$.[7]





$L=PPh_3$

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