Dinitrosyl Complexes of Rutheninm and Osmium and their Reaction with Oxygen

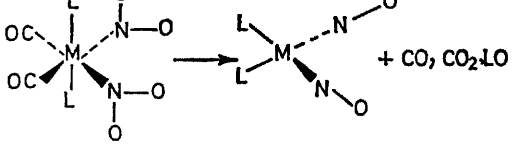
By K. R. GRUNDY, K. R. LAING, and W. R. ROPER*

(*Department of Chemistry, University of Auckland, Auckland, New Zealand*)

Summary The preparation of $M(NO)_2L_2$ ($M = Ru$, Os; $L = PPh_3$) and their oxidation to an oxygen complex $Ru(O_2)(NO_3)(NO)L_2$, and to hydroxy-dinitrosyl cations, $[M(OH)(NO)_2L_2]^+$, having both linear and bent M–N–O groups is described.

IN continuation of our studies[1] on the reactivity of the four-co-ordinate, d^{10}, nitrosyl species, $M'(NO)L_3$ and $M''(NO)_2L_2$ ($M' = Rh$, Ir; $M'' = Ru$, Os; $L = PPh_3$) which are related to PtL_4, we report syntheses of $Ru(NO)_2L_2$ and $Os(NO)_2L_2$ and their reaction with oxygen and with acids.

The dinitrosyls are best prepared *via* an inter-ligand reaction involving co-ordinated nitrite, carbon monoxide, and triphenylphosphine. Oxygen atom transfer from nitrite to carbon monoxide or triphenylphosphine generates the nitrosyl group and carbon dioxide or triphenylphosphine oxide are liberated. The nitrite group is introduced into the easily accessible compounds $RuCl_2(CO)_2L_2$[2] and $OsCl_2(CO)_2L_2$,[3] by reaction with sodium nitrite in dimethylformamide. The dinitrito-compound, $M(ONO)_2(CO)_2L_2$, is formed initially but this isomerises to the dinitro-compound, $M(NO_2)_2(CO)_2L_2$ which undergoes oxygen transfer to give $M(NO)_2L_2$. Carbon monoxide, carbon dioxide, and triphenylphosphine oxide have all been identified as products indicating that the oxygen transfer takes place to both carbon monoxide and triphenylphosphine. Highest yields are obtained when the reaction is carried out with



M = Ru,Os L = PPh3

an excess of triphenylphosphine present (95% for Ru, 75% for Os). An alternative preparation of $Ru(NO)_2L_2$, from RuH_2L_4, is also available.[4]

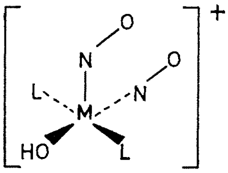
Like $Ir(NO)L_3$[1] and other d^{10} systems,[5] $Os(NO)_2L_2$ is reversibly protonated by strong acids to produce the hydrido-cation, $[OsH(NO)_2L_2]^+$ but we have not yet isolated salts of this cation in a pure state. In the presence of oxygen, further reaction takes place to give hydroxydinitrosyl cations, $[M(OH)(NO)_2L_2]^+$, (M = Ru, Os). Two nitrosyl stretching frequencies (see Table) are observed for these species but with an unusually large separation of around 200 cm^{-1}. We believe this indicates that the two nitrosyl groups are bonded in different ways and that these compounds are of the same structural type as that recently reported for $[RuCl(NO)_2L_2]PF_6$,[6] containing both linear and bent nitrosyl groupings.

I.r. data for nitrosyl complexes[a]

	ν_{NO}[b] (cm^{-1})	Other i.r. bands (cm^{-1})
$Ru(NO)_2L_2$	1665s, 1615vs	
$Os(NO)_2L_2$	1665s, 1615vs	
$[Ru(OH)(NO)_2L_2]BF_4$	1870vs, 1665vs	540 (ν_{Ru-OH})
$[Os(OH)(NO)_2L_2]BF_4$	1842vs, 1632vs	570 (ν_{Os-OH})

[a] Satisfactory elemental analyses have been obtained for the new compounds. [b] As Nujol mulls.

This appears to be the first example of the conversion of a platinum-metal hydride into a platinum-metal hydroxide through reaction with oxygen. The reaction may be proceeding *via* a hydroperoxy-species, $[M(OOH)(NO)_2L_2]^+$, analogous to $[Co(OOH)(CN)_5]^{3-}$ derived from $CoH(CN)_5^{3-}$ (ref. 7). Oxygen reacts similarly with $[IrH(NO)L_3]^+$ to form $[Ir(OH)(NO)L_2]^+$ but here it seems unnecessary to postulate an intermediate hydroperoxide because the other product of the reaction is triphenylphosphine oxide.[8]



$Ru(NO)_2L_2$ reacts with two molecules of oxygen to produce the oxygen complex, $Ru(O_2)(NO_3)(NO)L_2$.[9] A first step must be oxidation of one nitrosyl ligand to nitrate giving the co-ordinatively unsaturated $Ru(NO_3)(NO)L_2$, which reacts rapidly with further oxygen to give $Ru(O_2)(NO_3)(NO)L_2$. Further oxygen transfer to the remaining nitrosyl group is induced by carbon monoxide[10] giving $Ru(NO_3)_2(CO)_2L_2$.[2]

Halogens oxidise $Ru(NO)_2L_2$ eventually to $RuX_3(NO)L_2$, but controlled halogen addition produces $RuX(NO)L_2$ which is not easily isolated as such because of the extraordinary affinity it has for oxygen, forming $Ru(O_2)X(NO)L_2$.[9] $RuCl(NO)L_2$ has recently been described as resulting from the zinc reduction of $RuCl_3(NO)L_2$.[11]

We thank the New Zealand Universities' Grants Committee for support of this work.

(*Received, September* 14*th*, 1970; *Com.* 1550.)

[1] C. A. Reed and W. R. Roper, *Chem. Comm.*, 1969, 155.
[2] J. P. Collman and W. R. Roper, *J. Amer. Chem. Soc.*, 1965, **87**, 4008.
[3] J. P. Collman and W. R. Roper, *J. Amer. Chem. Soc.*, 1966, **88**, 3504.
[4] J. J. Levison and S. D. Robinson, *Chem. and Ind.*, 1969, 1514.
[5] J. P. Collman, *Accounts Chem. Res.*, 1968, **1**, 136.
[6] C. G. Pierpont, D. G. Van Derveer, W. Durland, and R. Eisenberg, *J. Amer. Chem. Soc.*, 1970, **92**, 4760.
[7] J. H. Bayston and M. E. Winfield, *J. Catalysis*, 1964, **3**, 123.
[8] C. A. Reed and W. R. Roper, unpublished data.
[9] K. R. Laing and W. R. Roper, *Chem. Comm.*, 1968, 1556.
[10] K. R. Laing and W. R. Roper, *Chem. Comm.*, 1968, 1568.
[11] M. H. B. Stiddard and R. E. Townsend, *Chem. Comm.*, 1969, 1372.