Oxygen Adducts from Nitrosyl Derivatives of Zerovalent Ruthenium

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RUTHENIUM is reported to form more nitrosyl complexes than any other element, but in most of these the metal is formally in the divalent state. We have been seeking zerovalent ruthenium nitrosyl complexes since these compounds may undergo oxidative addition reactions in a manner similar to $Ru(CO)_3(PPh_3)_2$,[1] and complexes of Rh^I, Ir^I, and Pt^0 generally.[2]

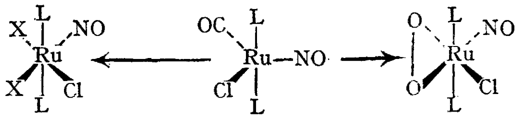
I.r. data on ruthenium nitrosyl complexes[a]

	ν(NO) cm.$^{-1}$	ν(CO) cm.$^{-1}$	ν(Ru–Cl) cm.$^{-1}$	ν(Ru–Br) cm.$^{-1}$	ν(O–O) cm.$^{-1}$
$RuCl(CO)(NO)(PPh_3)_2$[b]	1595	1925	266		
$RuBr(CO)(NO)(PPh_3)_2$	1595	1925		<200	
$RuOH(CO)(NO)(PPh_3)_2$	1555	1923			
$RuCl_3(NO)(PPh_3)_2$	1877		329,321		
$RuClBr_2(NO)(PPh_3)_2$	1875		313	264,253	
$Ru(O_2)Cl(NO)(PPh_3)_2$	1765		313		875

[a] Measured as KBr discs (or petroleum jelly mulls below 500 cm.$^{-1}$). [b] All compounds reported give good elemental analyses.

Nitrosyl derivatives have been prepared by the reaction of *N*-methyl-*N*-nitrosotoluene-*p*-sulphonamide (I) with metal hydrides.[3] The major product from the reaction of (I) with $RuHCl(CO)(PPh_3)_3$ [4] is $RuCl(CO)(NO)(PPh_3)_2$ (II). Compound (II) is remarkable for the ease with which the chloride ligand is displaced, *e.g.* chromatography on alumina converts (II) to the hydroxy-derivative $RuOH(CO)(NO)(PPh_3)_2$ (III). The very low value of 266 cm.$^{-1}$ for ν (Ru–Cl) in (II) (see Table for i.r. data) is in keeping with the lability of the chloride group. Compounds (II), (III), and the corresponding bromide are all monomeric in benzene solution (molecular weight measurement by osmometer).

Compound (II) reacts with halogens, hydrogen halides, carbon tetrachloride, and chloroform to form divalent ruthenium nitrosyl compounds (IV) of the type described previously.[5] Solutions of (II) react readily with air or oxygen to give the oxygen adduct $Ru(O_2)Cl(NO)(PPh_3)_2$ (V). This adduct can be isolated as a crystalline solid, m.p. 166°, which shows strong absorption in the i.r. spectrum at 875 cm.$^{-1}$. The oxygen addition appears to be irreversible. The geometry of the adduct is depicted as octahedral by analogy with the electronically similar complex $Ir(O_2)Cl(CO)(PPh_3)_2$ for which the crystal structure has been determined.[6] Compound (II) is depicted as a trigonal bipyramid but it is possible that the geometry is more nearly a tetragonal pyramid with a bent nitrosyl group at the apex. Such a structure has been reported for the closely related complex $[IrCl(CO)(NO)(PPh_3)_2]^+$.[7]



(IV) (II) (V)

$L = PPh_3$, $X = Cl, Br$

An analogous osmium comples, $OsCl(CO)(NO)(PPh_3)_2$ has been prepared from $OsHCl(CO)(PPh_3)_3$ but its reaction with oxygen is quite different.

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