

The Reaction of Nitric Oxide with Square-planar d^8 Complexes of Rhodium(I)

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Summary The reaction of nitric oxide with square-planar d^8 complexes of rhodium(I) of the type RhClL_3 yields five-co-ordinate nitrosyl-nitro-derivatives $\text{RhCl}(\text{NO}_2)(\text{NO})\text{L}_2$.

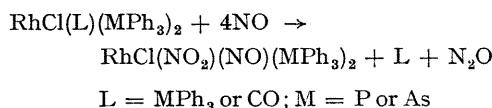
THE action of a number of small molecular species, including H_2 , X_2 , CO , SO_2 , O_2 , and C_2F_4 , on square-planar d^8 complexes of iridium(I) and rhodium(I) have been studied.¹ There has been no report of their reaction with nitric oxide. Two limiting modes of behaviour have been observed: scission of the addend molecule to give octahedral Ir^{III} and Rh^{III} complexes (H_2 , X_2) or adduct formation to give five-co-ordinate Ir^{I} and Rh^{I} derivatives (CO , SO_2). With O_2 and C_2F_4 an intermediate situation results in which the metal is between a five-co-ordinate d^8 and a six-co-ordinate d^6 configuration.

We have found that with NO disproportionation of the addend molecule occurs to give five-co-ordinate $\text{NO}-\text{NO}_2$ complexes. A green solid, decomposing at $154-156^\circ$ and air-stable in the solid state, can be isolated from benzene or chloroform solutions of $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$ after treatment with NO (Matheson, 99.6%) under nitrogen. The i.r. spectrum (KBr) of this material in the $670-4000\text{ cm}^{-1}$ region shows, in addition to triphenylphosphine bands, absorptions at $1666(\text{vs})$, $1640(\text{m, sh})$, $1408(\text{s})$, $1309(\text{s})$, and $816(\text{m})\text{ cm}^{-1}$. The first two bands lie in the range assignable to ν_{NO} in metal- NO complexes.² The three remaining bands lie in the regions associated with the asymmetric and symmetric stretching and the bending vibrations of a metal-bonded NO_2 group.³ The presence of a weak band at 581 cm^{-1} indicates an N -bonded nitro- rather than an O -bonded nitrito-group.³ The complex $\text{Rh}(\text{NO}_2)(\text{CO})(\text{PPh}_3)_2$ [prepared from $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$ and KNO_2 in aqueous acetone] showed nitro-bands at 1355 , 1326 , 812 , and 602 cm^{-1} . On the basis of the i.r. spectrum and analytical data we formulate the product as $\text{RhCl}(\text{NO}_2)(\text{NO})(\text{PPh}_3)_2$, (I).

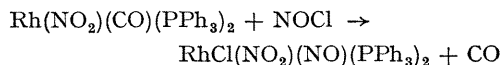
In chlorobenzene, $\text{RhCl}(\text{PPh}_3)_3$ also reacted with NO to give (I). Analogous behaviour was exhibited by the complexes $\text{RhCl}(\text{CO})(\text{AsPh}_3)_2$ and $\text{RhCl}(\text{AsPh}_3)_3$ which gave

olive-brown $\text{RhCl}(\text{NO}_2)(\text{NO})(\text{AsPh}_3)_2$ (II), m.p. $211-213^\circ$ (dec.). The i.r. spectrum of (II) showed ν_{NO} at $1656(\text{s})$ and $1629(\text{s})\text{ cm}^{-1}$ and nitro-group bands at 1406 , 1300 , and 815 cm^{-1} .

Small amounts of NO_2 in the NO can lead to nitro-derivatives; thus, the reaction of NO with $\text{Ni}(\text{CO})_2(\text{PPh}_3)_2$ gives $[\text{Ni}(\text{NO})_2(\text{PPh}_3)_2]_2\text{O}$ in the absence of NO_2 but $\text{Ni}(\text{NO}_2)(\text{NO})(\text{PPh}_3)_2$ in its presence.^{4a} We have purified our NO by a procedure reported to remove all NO_2 ^{4a} and have found that the same products are formed. The i.r. spectrum of the gas phase of a reaction utilizing purified NO indicated the presence of N_2O . These data suggest that the following general reaction is occurring:



Such a metal-catalysed disproportionation of NO to NO_2 and N_2O has been observed in the reaction of NO with $\text{Ni}(\text{CO})_4$ to give $\text{Ni}(\text{NO}_2)\text{NO}$.^{4b} Formally, one may view the reaction as an oxidative-addition of $\text{NO}+\text{NO}_2^-$ to the d^8 Rh^{I} system. Indeed, we have found that (I) can be obtained by the addition of $\text{NO}+\text{Cl}^-$:



Both the triphenylphosphine and triphenylarsine derivatives exhibit two bands in the $\text{N}-\text{O}$ stretching region with a separation of *ca.* 27 cm^{-1} in KBr. Solution (CHCl_3) spectra show the same 27 cm^{-1} splitting which we attribute to the presence of isomers. These complexes are iso-electronic with the iridium complex $[\text{IrCl}(\text{NO})(\text{CO})(\text{PPh}_3)_2]^+$ which has been found by X -ray studies to contain a bent (124°) $\text{Ir}-\text{N}-\text{O}$ bond.⁵ The low values of ν_{NO} in the present Rh complexes are close to that found in the cationic Ir complex (1680 cm^{-1}) and suggest that they may contain nonlinear $\text{Rh}-\text{N}-\text{O}$ linkages.

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⁴ (a) R. D. Feltham, *Inorg. Chem.*, 1964, **3**, 119; (b) *ibid.*, p. 121.

⁵ D. J. Hodgson, N. C. Payne, J. A. McGinnety, R. G. Pearson, and J. A. Ibers, *J. Amer. Chem. Soc.*, 1968, **90**, 4486.