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

By WILLIAM B. HUGHES

(*Research and Development Division, Phillips Petroleum Company, Bartlesville, Oklahoma* 74003)

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 $RhCl(NO_2)(NO)L_2$.

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 NO–NO_2 complexes. A green solid, decomposing at 154—156° and air-stable in the solid state, can be isolated from benzene or chloroform solutions of $RhCl(CO)(PPh_3)_2$ after treatment with NO (Matheson, 99·6%) under nitrogen. The i.r. spectrum (KBr) of this material in the 670—4000 cm.$^{-1}$ region shows, in addition to triphenylphosphine bands, absorptions at 1666(vs), 1640(m, sh), 1408(s), 1309(s), and 816(m) 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 $Rh(NO_2)(CO)(PPh_3)_2$ [prepared from $RhCl(CO)(PPh_3)_2$ 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 $RhCl(NO_2)(NO)(PPh_3)_2$, (I).

In chlorobenzene, $RhCl(PPh_3)_3$ also reacted with NO to give (I). Analogous behaviour was exhibited by the complexes $RhCl(CO)(AsPh_3)_2$ and $RhCl(AsPh_3)_3$ which gave olive-brown $RhCl(NO_2)(NO)(AsPh_3)_2$ (II), m.p. 211—213° (dec.). The i.r. spectrum of (II) showed ν_{NO} at 1656(s) and 1629(s) 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 $Ni(CO)_2(PPh_3)_2$ gives $[Ni(NO)_2(PPh_3)_2]_2O$ in the absence of NO_2 but $Ni(NO_2)(NO)(PPh_3)_2$ 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:

$$RhCl(L)(MPh_3)_2 + 4NO \rightarrow RhCl(NO_2)(NO)(MPh_3)_2 + L + N_2O$$

$$L = MPh_3 \text{ or } CO;\ M = P \text{ or } As$$

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

$$Rh(NO_2)(CO)(PPh_3)_2 + NOCl \rightarrow RhCl(NO_2)(NO)(PPh_3)_2 + CO$$

Both the triphenylphosphine and triphenylarsine derivatives exhibit two bands in the N–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 $[IrCl(NO)(CO)(PPh_3)_2]^+$ which has been found by *X*-ray studies to contain a bent (124°) Ir–N–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 Rh–N–O linkages.

(*Received, July* 14*th*, 1969; *Com.* 1054.)

---

[1] L. Vaska, *Accounts Chem. Res.*, 1968, **1**, 335.

[2] J. Lewis, R. J. Irving, and G. Wilkinson, *J. Inorg. Nuclear Chem.*, 1958, **7**, 32; W. P. Griffith, J. Lewis, and G. Wilkinson, *ibid.*, p. 38.

[3] K. Nakamoto, J. Fujita, and H. Murato, *J. Amer. Chem. Soc.*, 1958, **80**, 4817.

[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.