A New Disproportionation of Nitric Oxide in its Reaction with $Co(PPh_3)_3(NO)$

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Summary Nitric oxide reacts with $Co(PPh_3)_3(NO)$ under mild conditions to give a nitrosylnitrito-complex of cobalt, $Co(NO_2)(PPh_3)(NO)_2$ and N_2.

FEW examples of metal-catalysed disproportionation of NO to NO_2 and N_2O have been observed in the reactions of gaseous NO with transition-metal complexes. Thus, the reaction of nitric oxide with $Ni(CO)_4$[1] and with $Co_2(CO)_8$[2] gives nitrosylnitrito-complexes, and with square planar complexes of Rh^I gives nitrosylnitro-complexes.

For the latter reaction the stoicheiometry shown in equation (1) has been observed.[3]

$$RhCl(L)(MPh_3)_2 + 4NO \rightarrow RhCl(NO_2)(NO)(MPh_3)_2 + L + N_2O \quad (1)$$

(L = MPh_3 or CO; M = P or As)

In our study on nitrosyl complexes of cobalt[4] we have found that $Co(PPh_3)_3(NO)$ reacts with purified NO in aromatic hydrocarbons at room temperature and atmospheric pressure according to equation (2).

$$Co(PPh_3)_3(NO) + 7NO \rightarrow Co(NO_2)(PPh_3)(NO)_2 + 2\ OPPh_3 + 2N_2O + 0{\cdot}5N_2 \quad (2)$$

The stoicheiometry of equation (2) has been determined by quantitative gas-absorption determinations and i.r. and g.c. analyses of the gaseous products.

The already known[5] oxidation of the phosphine to the corresponding oxide and the consequent reduction of NO to N_2O is observed together with metal-catalysed disproportionation of NO to co-ordinated nitrite and nitrogen.

Formally reaction (2) can be considered the result of a disproportionation of NO to $NO^+NO_2^-$ and N_2, according to equation (3), followed by an oxidative addition of

$$3NO \rightarrow NO^+NO_2^- + 0{\cdot}5N_2 \quad (3)$$

$NO^+NO_2^-$ to the cobalt [equation (4)] whereas the excess of

$$Co(PPh_3)(NO) + NO^+NO_2^- \rightarrow Co(NO_2)(PPh_3)(NO)_2 \quad (4)$$

ligand is oxidised by NO [equation (5)].

$$2PPh_3 + 4NO \rightarrow 2\ OPPh_3 + 2N_2O \quad (5)$$

$Co(NO_2)(PPh_3)(NO)_2$ is a black crystalline compound moderately stable in the air. It can also be conveniently obtained according to the alternative reaction [equation (6)].

$$[Co(PPh_3)_2(NO)_2]ClO_4 + KNO_2 \rightarrow Co(NO_2)(PPh_3)(NO)_2 + PPh_3 + KClO_4 \quad (6)$$

The formulation of the complex is based on correct elemental analysis and on molecular weight determination.

The presence of the co-ordinated nitrosyl groups is shown by the absorption bands at 1830 and 1760 cm^{-1} in the i.r. spectrum of the complex, whereas the presence of the O-bonded nitrito-group is supported by the asymmetric and symmetric NO_2 stretching frequencies observed at 1404 and 1095 cm^{-1}.[6]

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