

A New Disproportionation of Nitric Oxide in its Reaction with $\text{Co}(\text{PPh}_3)_3(\text{NO})$

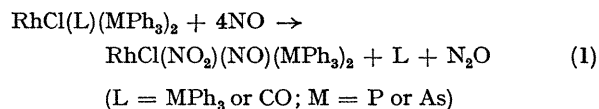
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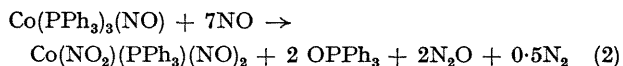
Summary Nitric oxide reacts with $\text{Co}(\text{PPh}_3)_3(\text{NO})$ under mild conditions to give a nitrosylnitrito-complex of cobalt, $\text{Co}(\text{NO}_2)(\text{PPh}_3)(\text{NO})_2$ and N_2 .

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 $\text{Ni}(\text{CO})_4$ ¹ and with $\text{Co}_2(\text{CO})_8$ ² gives nitrosylnitrito-complexes, and with square planar complexes of Rh^I gives nitrosylnitro-complexes.

For the latter reaction the stoichiometry shown in equation (1) has been observed.³



In our study on nitrosyl complexes of cobalt⁴ we have found that $\text{Co}(\text{PPh}_3)_3(\text{NO})$ reacts with purified NO in aromatic hydrocarbons at room temperature and atmospheric pressure according to equation (2).

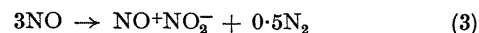


The stoichiometry of equation (2) has been determined by quantitative gas-absorption determinations and i.r. and g.c. analyses of the gaseous products.

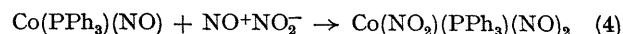
The already known⁵ oxidation of the phosphine to the corresponding oxide and the consequent reduction of NO

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 $\text{NO} + \text{NO}_2^-$ and N_2 , according to equation (3), followed by an oxidative addition of



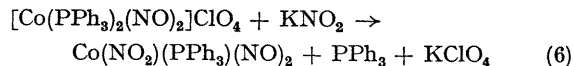
$\text{NO} + \text{NO}_2^-$ to the cobalt [equation (4)] whereas the excess of



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



$\text{Co}(\text{NO}_2)(\text{PPh}_3)(\text{NO})_2$ is a black crystalline compound moderately stable in the air. It can also be conveniently obtained according to the alternative reaction [equation (6)].



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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