Oxygenation of the Nitrosyl Ligand in Complexes of Nickel and Platinum

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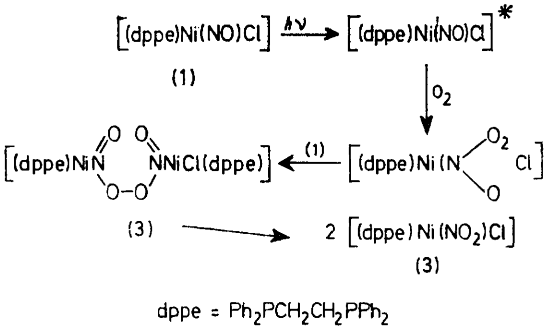
Summary On irradiation [Ni(NO)Cl(dppe)] (dppe = $Ph_2PCH_2CH_2PPh_2$) reacts with molecular oxygen to give [$Ni(NO_2)Cl$(dppe)]; a nickel(I) (d^9) intermediate has been characterised by e.s.r. studies.

THE oxygenation of co-ordinated nitric oxide by molecular oxygen to form nitro or nitrato complexes has recently attracted considerable attention.[1,2] Basolo and Clarkson[1] have shown from kinetic studies that the oxygenation of five-co-ordinate cobalt nitrosyl complexes in the presence of bases is best explained in terms of an intermediate involving an O–N–O–O–N–O unit acting as a bridge between two cobalt ions. Here we report the reaction of the four-co-ordinate nitrosyl complex [Ni(NO)Cl(dppe)] (**1**) with O_2 to give [$Ni(NO_2)Cl$(dppe)] (**2**) and present evidence to support the formation of peroxy-bridged dinitrogen tetroxide intermediate containing Ni^I.

An orange-yellow solution of (**2**) is slowly formed when oxygen is bubbled through a deep blue solution of (**1**) in boiling dimethylformamide. However, quantitative yields of the same complex are rapidly produced when a solution of (**1**) in CH_2Cl_2 is irradiated with Pyrex-filtered sunlight or the light from a low-pressure mercury lamp in the presence of oxygen.† No observable reaction takes place when a solution of (**1**) in CH_2Cl_2 is left in the dark for 12 h in the presence of O_2. No e.s.r. signal is observed for a solution of complex (**1**) in thoroughly degassed pure CH_2Cl_2 before and after u.v. irradiation. However, after short (*ca.* 1 min) irradiation of (**1**) in the presence of oxygen a symmetric e.s.r. signal with $g = 2{\cdot}035$ is observed at room temperature.‡ On freezing the sample and recording the spectrum at 77 K, an axially symmetric signal appeared with $g_\perp$ 2·042 and $g_\parallel$ 2·017 (diphenylpicrylhydrazyl as a standard).

The room-temperature value is indicative of an electron hole attributable to a d^9 Ni^+ complex. It is reasonable to assume that oxygenation proceeds by attack of dioxygen on the nitrosyl ligand to produce a peroxy-nitrate intermediate as has been proposed for reaction of certain cobalt and iridium nitrosyls, followed by reaction with another molecule of (**1**) to give complex (**3**) (Scheme). Homolytic dissociation of the peroxy-bridge and simultaneous electron transfer from the metal atoms then leads to the formation of (**2**). The fact that $g_\perp > g_\parallel > g_e$ in the frozen solution is indicative of a tetragonally distorted tetrahedral geometry around the atoms in (**3**).[3] It is worth noting that no hyperfine coupling is observed at either room or liquid-nitrogen temperature.



The fact that oxygenation§ takes place only under photoirradiation or thermal excitation implies a formal change either of type (i) or of type (ii). Importantly, $[Ni(NO_2)X(dppe)]$ reacts with CO under ambient conditions to regenerate complex (**1**) and the catalytic oxidation of CO by O_2 is achieved.

$$\mathrm{Ni^0\text{–}\overset{+}{N}O \longrightarrow Ni^{2+}\text{–}\bar{N}O} \qquad \text{(i)}$$

$$\mathrm{Ni^0\text{–}\overset{+}{N}O \longrightarrow Ni^{+}\text{–}\dot{N}O} \qquad \text{(ii)}$$

Some related platinum complexes† have also been prepared [reactions (1)—(3)]. All exhibit an NO stretching vibration in the region of 1600 cm^{-1} and on this basis are probably best formulated as NO^- derivatives of square-planar Pt^{II}; as such, they may be related to the O_2-sensitive nickel(II) species postulated in reaction (i).

$$\mathrm{[(Ph_3P)_nPt] + N_2O_4 \xrightarrow[PhMe]{0\,^\circ C} [(Ph_3P)_2Pt(NO)(NO_3)]} \qquad (1)$$

$$\mathrm{[(PhMe_2P)_2Pt(NO_2)_2] \xrightarrow[80\,^\circ C;\ 190\ atm]{CO} [(PhMe_2P)_2Pt(NO)(NO_2)] + CO_2} \qquad (2)$$

$$\mathrm{[(Ph_3P)_2Pt(NO)(NO_3)] \xrightarrow{I^-} [(Ph_3P)_2Pt(NO)I]} \qquad (3)$$

We have observed that in solution the planar $[(Ph_3P)_2Pt(NO)(NO_3)]$ undergoes an interesting *O*-transfer reaction to produce $[(Ph_3P)_2Pt(NO_2)_2]$. However, we find that the pseudo tetrahedral $[(Ph_3P)_2Ni(NO)(NO_3)]$ does not undergo this transfer under the same conditions again emphasising the difference in reactivity between $M^0\text{–}NO^+$ and $M\text{–}NO^-$ systems.

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† Satisfactory analytical data has been obtained for both the nitrosyl and the nitro complexes. The nitrosyl complex exhibits ν(NO) at 1735 cm^{-1} (CH_2Cl_2). The nitro complex has i.r. bands at 1380, 1230, and 820 cm^{-1}

‡ This reaction has also been monitored by following the change in i.r. spectrum. On irradiation the band at 1735 cm^{-1} decreases in intensity and is replaced by a new band at *ca.* 1710 cm^{-1}. As the reaction proceeds this band also decays.

§ The reaction is not restricted to complex (**1**) and a number of other $[Ni(NO)XL_2]$ complexes have also been found to undergo reaction with O_2 to produce the corresponding $[Ni(NO_2)XL_2]$ derivatives.

[1] S. G. Clarkson and F. Basolo, *Inorg. Chem.*, 1973, **12**, 1528.
[2] M. Kubota and D. A. Phillips, *J. Amer. Chem. Soc.*, 1975, **97**, 5638.
[3] J. E. Wertz and J. R. Bolton, 'Electron Spin Resonance,' McGraw-Hill, New York, 1972, p. 324.