The Nitrosyl Ligand as an Oxidant

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Summary Carbon monoxide reacts with the cationic nitrosyl $[Ir(NO)_2(Ph_3P)_2]^+$ to produce CO_2 and N_2O; tertiary phosphines (R_3P) react similarly to yield R_3PO and N_2O.

THE nitrosyl group is a versatile ligand exhibiting diverse chemical and structural properties.[1] However, little is known of its ability to function as an oxidant. Here we report reactions of the complex cation $[Ir(NO)_2(Ph_3P)_2]^+$ (**1**)

in which the coupling of two NO groups may be induced by reaction with donor ligands (CO or R_3P) leading to oxidation of the ligand (CO to CO_2 or R_3P to R_3PO) and the production of nitrous oxide.

The complex $[Ir(NO)_2(Ph_3P)_2]PF_6$ is unusual in that it readily reacts with carbon monoxide to produce the tricarbonyl cation $[Ir(CO)_3(Ph_3P)_2]^+$ (**2**). The reaction is moderately fast (*ca.* 1 h) in the dark and very rapid in the presence of light but in either case quantitative yields of the salt $[Ir(CO)_3(Ph_3P)_2]PF_6$ are obtained. Such behaviour is unexpected first since nitrosyl groups are notoriously resistant to substitution by CO and secondly displacement of the NO^+ ion by the isoelectronic CO would be expected to lead to the very stable $Ir(NO)(CO)(Ph_3P)_2$ in a manner related to that observed[2] in the reaction of (**1**) with Ph_3As.

$$[Ir(NO)_2(Ph_3P)_2]^+ + 3Ph_3As \longrightarrow Ir(NO)(Ph_3As)_3 + 2Ph_3P + NO^+$$
(**1**) (excess)

Total product analysis revealed that in addition to the salt $[Ir(CO)_3(Ph_3P)_2]PF_6$ the only other products of the reaction are CO_2 and N_2O. The reaction may therefore be represented as in equation (1).

$$Ir(NO)_2(Ph_3P)_2]PF_6 + 4CO \longrightarrow [Ir(CO)_3(Ph_3P)_2]PF_6 + CO_2 + N_2O \quad (1)$$

A plausible mechanism involves the prior formation of the five-co-ordinate adduct $[Ir(NO)_2CO(Ph_3P)_2]^+$ (**3**) which rapidly undergoes oxygen transfer from a co-ordinated NO group to the combined CO followed by an intramolecular attack of the second co-ordinated NO group on the Ir–N system so produced. The "metal nitrene" intermediate (IrN) involved in this scheme is of the type previously described by Knox *et al.*[3] and the overall reaction may be envisaged as leading to the displacement of the two NO groups to give the co-ordinatively unsaturated species $[Ir(Ph_3P)_2]^+$ which then reacts with CO to give (**2**). Other possible mechanisms will be discussed in a full report of this work. Significantly we find that the complex cation (**2**) reacts with NO at 80° in acetone to regenerate cation (**1**) in quantitative amounts, thereby allowing a continuous oxidation–reduction process to take place (see Scheme).

$$[Ir(NO)_2(Ph_3P)_2]^+ \underset{(ii)}{\overset{(i)}{\rightleftharpoons}} [Ir(CO)_3(Ph_3P)_2]^+ + N_2O + CO_2$$
(**1**) (**2**)

SCHEME. (i) Reaction with CO in either Me_2CO or CH_2Cl_2. (ii) Reaction with NO in Me_2CO under reflux.

We have also observed the formation of N_2O in the reaction of (**1**) with certain tertiary phosphines. In these reactions formation of N_2O is accompanied by the production of tertiary phosphine oxide. Thus the reaction of (**1**) with diphos leads to $Ir(diphos)_2^+$ and Ph_3PO.

The pseudotetrahedral ion (**1**) also reacts with other small molecules, *e.g.* O_2, but only in the presence of light. The product of this reaction exhibits a ν_{NO} at 1890 cm^{-1} and is considered to be $[Ir(NO)(ONO_2)(Ph_3P)_2]^+$ (**4**). Presumably the reaction sequence is similar to that suggested by Roper *et al.*[4] for the reaction of $Ru(NO)_2(Ph_3P)_2$ with oxygen except that in this case the reaction must be photoinitiated. As observed with the corresponding chloro-derivative, $[Ir(NO)Cl(Ph_3P)_2]^+$, cation (**4**) is readily hydrolysed to $[Ir(NO)(OH)(Ph_3P_2]^+$. We find that (**1**) is not susceptible to hydrolysis unless both O_2 and light are available.

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[1] See *e.g.* N. Connelly, *Inorg. Chim. Acta, Rev.*, 1972, **6**, 47.
[2] C. A. Reed and W. R. Roper, *J.C.S. Dalton*, 1972, 1243.
[3] A. T. McPhail, G. R. Knox, C. G. Robertson, and G. A. Sim, *J.C.S. Dalton*, 1972, 205.
[4] K. R. Grundy, K. R. Laing, and W. Roper, *Chem. Comm.*, 1970, 1500.