# Conversion of CO and NO into $CO_2$ and $N_2O$ by Dinitrosyl Species

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*Summary* Evidence supporting a mechanism involving the formation of dinitrogen dioxide intermediates in the conversion of CO and NO into $CO_2$ and $N_2O$ by dinitrosyl complexes is given.

In a previous communication[1] we reported the production of $CO_2$ and $N_2O$ from the reaction of CO with $[Ir(NO)_2(PPh_3)_2]PF_6$, forming $[Ir(CO)_3(PPh_3)_2]PF_6$ which in turn reacts with NO to regenerate the dinitrosyl. In a subsequent communication Ibers and Haymore[2] reported that several other dinitrosyl complexes of Ir and Rh catalytically convert NO and CO into $N_2O$ and $CO_2$. In order to account for this phenomenon they suggested that many of the "20-electron" dinitrosyls contemplated as intermediates in these reactions are better formulated as 18-electron, N–N-bonded *cis*-dinitrogen dioxide complexes. Further studies following our initial report have led us to the same conclusion. We have made the following observations:†

(a) In the reaction of equimolar amounts of $Rh(NO)_2L_2^+$ and $Rh(^{15}NO)_2L_2^+$ with CO under ambient conditions $^{14}N_2O$, $^{14}N^{15}NO$, and $^{15}N_2O$ are rapidly produced in the ratio 1:2:1.

(b) $Rh(NO)_2L_2^+$ and $Rh(^{15}NO)_2L_2^+$ do not undergo NO scrambling over a period of 24 h at 25°.

(c) $Rh(NO)_2L_2^+$ reacts with CO in the presence of $^{15}NO$ to give a mixture of $^{14}N_2O$, $^{14}N^{15}NO$, and $^{15}N_2O$.

(d) $Rh(NO)_2L_2^+$ does not undergo appreciable exchange with $^{15}NO$ over a period of 6 h at 25° although over much longer periods some reaction is observed (see below).

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† L = $PPh_3$ or $PPh_2Me$.

(e) $^{31}P$ n.m.r. studies of $Rh(NO)_2L_2^+$ over a temperature range show no evidence of phosphine dissociation.

The previously proposed intramolecular nitrene mechanism[1] is almost certainly ruled out by observations (a) and (c). In reactions where a nitrene intermediate is produced, *e.g.* equation (1), capture of the bonded adjacent group (CO)

$$\mathrm{Ir(NO)(PPh_3)_2CO + 2PPh_3 \xrightarrow{h\nu} Ir(PPh_3)_3NCO + OPPh_3} \qquad (1)$$

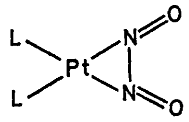
occurs in preference to capture of non-bonded ligand.[3] It is reasonable to suppose that a dissociative step which is essential in order to account for (a) and (c) would not compete effectively with this process. We believe that observations (a)—(e) are best explained in terms of the following scheme:

$$\begin{aligned}
&\mathrm{M(NO)_2L_2^+\ (\mathbf{1}) + CO \rightleftharpoons M(N_2O_2)L_2CO^+\ (\mathbf{2})} && \text{(i)}\\
&\mathrm{M(N_2O_2)L_2CO^+ + CO \rightleftharpoons ML_2(CO)_2^+ + N_2O_2} && \text{(ii)}\\
&\mathrm{M(N_2O_2)L_2CO^+ + 2CO \rightleftharpoons ML_2(CO)_2^+ + N_2O + CO_2} && \text{(iii)}\\
&\mathrm{N_2O_2 \rightleftharpoons 2NO} && \text{(iv)}\\
&\mathrm{ML_2(CO)_2^+ + CO \rightleftharpoons ML_2(CO)_3^+} && \text{(v)}\\
&\mathrm{(M = Rh\ or\ Ir)}
\end{aligned}$$

In agreement with the earlier suggestion[1,2] we believe that the initial step involves the formation of the five-co-ordinate intermediate (**2**). Although we are unable to provide direct experimental evidence for this intermediate some justification for proposing an associative pathway follows from observations (d) and (e) which clearly rule out the possibility of dissociations of the type:

$$\mathrm{M(NO)_2L_2^+ \rightleftharpoons M(NO)L_2^+ + NO}$$
$$\text{and}\quad \mathrm{M(NO)_2L_2^+ \rightleftharpoons M(NO)_2L^+ + L}$$

It would appear that the function of the incoming CO ligand is to induce the coupling of the two NO ligands to give the $N_2O_2$ intermediate (**2**). This is reasonable since the coupling of two NO groups has been observed[4] in the reaction of $L_4Pt$ with NO to produce $L_2Pt(N_2O_2)$ (previously referred to as a hyponitrite derivative[2,4]). The precise nature of this complex has not been established but i.r. studies are compatible with structure (**3**).[4] We find that



**(3)**

(**3**) reacts with CO under ambient conditions to produce $N_2O$, $CO_2$, and *cis*-$Pt(CO)_2L_2$ which undergoes subsequent polymerization to $Pt_3(CO)_3L_4$ in accordance with the observations of Chatt and Chini.[5] Thus, we regard complex (**3**) as the first example of an $N_2O_2$ complex of the type postulated by Ibers and Haymore.[2] It is significant that a dinitrosyl of formulation $Pt(NO)_2(PPh_3)_2$ would correspond to a 20-electron system and the addition of CO is not therefore a prerequisite of NO coupling. The important conversion $CO \rightarrow CO_2$ occurs in step (iii). It is probable that reaction occurs at the metal since NO and CO do not undergo rapid reaction in the absence of complex. The compounds $Ru(NO)_2L_2$ and $Os(NO)_2L_2$ react similarly but only under more forcing conditions, *e.g.* equation (2).

$$\mathrm{Ru(NO)_2L_2 \xrightarrow[\text{or CO, } h\nu]{\text{CO, 100 atm., 24h}} Ru(CO)_4L} \qquad (2)$$

In contrast, reaction of $Fe(NO)_2L_2$ with CO proceeds to give $Fe(NO)_2L(CO)$ and $Fe(NO)_2(CO)_2$ but no $CO_2$ or $N_2O$. This change in reactivity may be attributed to the case of phosphine dissociation which effectively prevents the formation of the active 20-electron system. The coupling of the two NO groups is also dependent on the nature of the incoming ligand. Detailed mechanistic studies of these reactions will be described in a full report of this work.

As mentioned above, $[Rh(NO)_2(PPh_2Me)_2]^+$ undergoes slow reaction with NO under ambient conditions to produce the green cation $[Rh(NO)(NO_2)(PPh_2Me)_2]^+$ which in return reacts with CO to regenerate $[Rh(NO)_2(PPh_2Me)_2]^+$. Thus the reaction sequence (3) has been established. The Pt derivative *cis*-$Pt(NO_2)_2L_2$ also reacts with CO to produce

$$\mathrm{M(NO)(NO_2)L_2^+ \underset{CO}{\overset{NO}{\rightleftharpoons}} M(NO)_2L_2^+ \underset{NO}{\overset{CO}{\rightleftharpoons}} ML_2(CO)_3^+} \qquad (3)$$
$$\mathrm{(M = Ir)}$$

$Pt_3(CO)_3L_4$ and $CO_2$ *via* the reaction sequence shown although intermediate (**5**) has not been isolated. The corresponding Pd complexes behave similarly.

$$\begin{tikzcd}
\underset{(\mathbf{4})}{\mathrm{Pt(NO_2)_2L_2}} \arrow[r, "+\mathrm{CO}"] & \underset{(\mathbf{5})}{\text{“}\mathrm{Pt(NO)(NO_2)L_2}\text{”}} \arrow[r, "+\mathrm{CO}"] & \underset{(\mathbf{3})}{\mathrm{Pt(N_2O_2)L_2}} \arrow[d, "+\mathrm{CO}"] \\
 & \underset{(\mathbf{7})}{\mathrm{Pt_3(CO)_3L_4}} & \underset{(\mathbf{6})}{\mathrm{Pt(CO)_2L_2}} \arrow[l]
\end{tikzcd}$$

In contrast, for Ni the reaction stops after the first step:[6]

$$\mathrm{Ni(NO_2)_2L_2 \xrightarrow{CO} Ni(NO)(NO_2)L_2 \nrightarrow}$$

It would appear that in the case of $Pt(NO)(NO_2)L_2$ and in contrast to $Ni(NO)(NO_2)L_2$ an intramolecular redox process ($\mathrm{M^0\text{–}\overset{+}{N}O \rightleftharpoons M^{II}\text{–}\overset{-}{N}O}$) is energetically accessible and reaction occurs *via* CO association.

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[1] B. F. G. Johnson and S. Bhaduri, *J.C.S. Chem. Comm.*, 1973, 650.

[2] B. L. Haymore and J. A. Ibers, *J. Amer. Chem. Soc.*, 1974, **96**, 3325.

[3] B. F. G. Johnson and C. Savory, unpublished observations.

[4] S. Cenini, R. Ugo, G. LaMonica, and S. D. Robinson, *Inorg. Chim. Acta*, 1972, **6**, 182.

[5] J. Chatt and P. Chini, *J. Chem. Soc. A*, 1970, 1538.

[6] G. Booth and J. Chatt, *J. Chem. Soc.*, 1962, 2099.