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## Some Reactions of Nitrosyl Complexes of Nickel, Palladium, and Platinum

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The reactions of  $[Ni(NO_2)XL_2]$   $[X = Cl, L = \frac{1}{2}$  dppe (dppe = Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>), PPh<sub>3</sub>, PPr<sup>n</sup><sub>3</sub>, OPPh<sub>3</sub>, or NC<sub>5</sub>H<sub>5</sub>; X = Br, L =  $\frac{1}{2}$  dppe or PPh<sub>3</sub>; X = NO<sub>2</sub>, L =  $\frac{1}{2}$  dppe] and *trans*- $[M(NO_2)_2L_2]$  (M = Pd, L = PEt<sub>2</sub>Ph or PEt<sub>3</sub>; M = Pt, L = PEt<sub>2</sub>Ph, PEt<sub>3</sub>, or PBu<sup>n</sup><sub>3</sub>) with carbon monoxide have been examined. The nickel compounds react to produce the corresponding nitrosyl compounds  $[Ni(NO)XL_2]$  and CO<sub>2</sub>. The palladium and platinum compounds react with CO to form  $[M(CO)_2L_2]$  complexes and subsequently higher clusters, except for  $[Pt(NO_2)_2(PEt_3)_2]$ where evidence for the formation of  $[Pt(NO)(NO_2)(PEt_3)_2]$  and  $[Pt(NCO)(NO_2)(PEt_3)_2]$  has been found. On reaction with dioxygen the compounds  $[Ni(NO)XL_2]$  afford the nitro-complexes  $[Ni(NO_2)XL_2]$  exclusively, the rate of the reaction depending on L. The compound  $[Pt(NO)(NO_3)(PPh_3)_2]$ , prepared from the reaction of N<sub>2</sub>O<sub>4</sub> with  $[Pt(PPh_3)_4]$  in toluene, reacts with O<sub>2</sub> to produce *trans*- $[Pt(NO_3)_2(PPh_3)_2]$ . In solution,  $[Pt(NO)(NO_3)(PPh_3)_2]$ reacts with  $[NO][PF_6]$  to form  $[{Pt(PPh_3)_2}_2N_2O_2][PF_6]_2$ .

THE object of this work was two-fold. First, to attempt to prepare planar complexes  $[M(NO)XL_2]$  (M = Pd or Pt) containing (*formally*) the M<sup>II</sup> and NO<sup>-</sup> ions and to compare their chemistry with the quasi-tetrahedral nickel complexes  $[Ni(NO)XL_2]$ , known to be derivatives of Ni<sup>0</sup> and NO<sup>+</sup>; and secondly, to investigate the reactions (1). Some aspects of this work have been communicated previously.<sup>1</sup>

$$\{M^{-}(NO_{2})\} \xrightarrow[O_{2}]{CO} \{M^{-}NO\} + CO_{2} \qquad (1)$$

RESULTS AND DISCUSSION

Reaction of  $[M(NO_2)XL_2]$  Complexes with CO.—The reaction of  $[Ni(NO_2)_2(PEt_3)_2]$  with carbon monoxide to produce  $[Ni(NO)(NO_2)(PEt_3)_2]$  was first reported by Booth and Chatt.<sup>2</sup> By a similar route (Scheme 1) we have prepared a range of complexes of general formula  $[Ni(NO)XL_2]$  in order to examine their reactions with

$$[NiX_{2}L_{2}] \xrightarrow{Na[NO_{3}]} [Ni(NO)XL_{2}] + NaX + CO_{2}$$
  
Scheme 1 X = Cl, L =  $\frac{1}{2}$  dppe, PPh<sub>3</sub>, PPr<sup>a</sup><sub>3</sub>, OPPh<sub>3</sub>, or NC<sub>5</sub>H<sub>5</sub>  
X = Br L =  $\frac{1}{2}$  dppe, or PPh<sub>2</sub>: X = NO<sub>2</sub> L =  $\frac{1}{2}$  dppe (dppe

 $X = Br, L = \frac{1}{2} dppe \text{ or } PPh_3; X = NO_2, L = \frac{1}{2} dppe (dppe = Ph_2PCH_2CH_2PPh_2)$ dioxygen. These nitrosyl complexes are intensely

coloured (blue-black) and show a strong NO band in the i.r. spectrum at ca.  $1750 \text{ cm}^{-1}$ . They are air-sensitive but may be stored under dry nitrogen. They are soluble in most common organic solvents. Under the conditions employed (1 atm CO, 25 °C) † no further reaction with CO to produce, for example, NCO derivatives was observed. Preliminary kinetic studies of the reaction of [Ni(NO<sub>2</sub>)<sub>2</sub>(dppe)] with carbon monoxide indicate that the reaction is first order in complex and CO concentrations. A recent report<sup>3</sup> is in agreement with these findings. The rate of reaction of [Ni(NO<sub>2</sub>)ClL<sub>2</sub>] (formed in situ from NiCl<sub>2</sub> and Na[NO<sub>2</sub>]) with CO under constant pressure (1 atm) follows the sequence  $PPr_{3}^{n} >$  $PPh_3 > dppe$ . The CO<sub>2</sub> evolved in the reactions of CO with  $[Ni(NO_2)_2(dppe)]$  was identified by i.r. and mass spectroscopy.

These complexes were found to be more or less reactive to CO depending on M and the  $PR_3$  ligand. Thus,  $[Pd(NO_2)_2(PEt_3)_2]$  in benzene reacted with a CO stream at 1 atm, whereas with  $[Pd(NO_2)_2(PEtPh_2)_2]$  elevated pressure and temperature were required (typically 100—120 atm CO and 70 °C) to obtain reasonable conversion into products and even under these conditions relatively low conversion was observed for the platinum compounds. In general terms, the reactions followed the same course irrespective of the nature of M or L (Scheme 2). As the reaction progressed the

trans-
$$[M(NO_2)_2L_2] \xrightarrow{C_4H_4, 70^\circ C}$$
  
 $[M(CO)_2L_2] + [M_3(CO)_3L_4] + higher clusters$   
SCHEME 2 M = Pd, L = PEt<sub>2</sub>Ph or PEt<sub>3</sub>; M = Pt,  
L = PEt<sub>2</sub>Ph, PBu<sup>n</sup><sub>3</sub>, PEt<sub>3</sub>, or PEtPh<sub>2</sub>

solution became red and eventually a red oil could be separated. The compounds  $[M(CO)_2L_2]$  and  $[M_3(CO)_3 L_4$ ] were identified as components of this red oil on the basis of their i.r. spectra.<sup>4</sup> We could not obtain pure samples of these compounds for analysis. Similarly difficulties have been found previously in attempts to separate these components.<sup>4</sup> The appearance of a strong single band in the region of  $1800 \text{ cm}^{-1} \{v(CO), v(CO)\}$  $[M_3(CO)_3L_4]$  at first misled us into believing that formation of a nitrosyl complex had occurred since the compounds [Ni(NO)XL<sub>2</sub>] show a strong absorption near to this region. In a separate experiment the reaction of [PtCl<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>] with CO was therefore examined. This reaction [equation (2)] followed a similar course and the i.r. spectrum of the resulting solution was very similar to that formed above. In all reactions, over prolonged

$$[\operatorname{PtCl}_{2}(\operatorname{PEt}_{3})_{2}] \xrightarrow[10^{\circ} C]{20^{\circ} C} [\operatorname{Pt}(\operatorname{CO})_{2}(\operatorname{PEt}_{3})_{2}] + [\operatorname{Pt}_{3}(\operatorname{CO})_{3}(\operatorname{PEt}_{3})_{4}] + \operatorname{COCl}_{2}(?) \quad (2)$$

periods of time (>24 h), the formation of larger clusters was observed (see ref. 4).

In one case evidence for the formation of NO and NCO compounds was found. The platinum complex *trans*- $[Pt(NO_2)_2(PEt_3)_2]$ , which is appreciably more soluble than its relatives, underwent reaction with carbon

<sup>†</sup> Throughout this paper: 1 atm = 101 325 Pa.

monoxide under relatively mild conditions. In a typical experiment,  $[Pt(NO_2)_2(PEt_3)_2]$  in toluene at 80 °C was treated with 50 atm CO for 4 h. The solution changed from colourless to yellow-orange and, after removal of solvent, an orange solid was obtained. This was dissolved in dichloromethane and after separation on silica five products were obtained but only three could be separated in sufficient yield to permit characterisation. One product, a yellow solid, was soluble in hexane and, in addition to bands which could be assigned to the ligand PEt<sub>3</sub>, exhibited bands at 1634, 1265, 973, and 869 cm<sup>-1</sup>. On the basis of these data and additional analytical data the compound was formulated as  $[Pt(NO)(NO_2)(PEt_3)_2]$ . The band at 1634 cm<sup>-1</sup> is assigned to the NO<sup>-</sup> (nitrosyl) stretch and, significantly, it is similar to that observed for the related compound  $[Pt(NO)(NO_3)(PPh_3)_2]$  (see below). Yields of this compound were very low (<3%).

A second yellow product exhibited a band at 2 230 cm<sup>-1</sup> together with bands arising from co-ordinated  $PEt_{3}$ . This information, together with analytical and mass spectroscopic data, indicated the formula [Pt- $(NCO)Cl(PEt_3)_2$ ]. A third product was identified as  $[PtCl_2(PEt_3)_2]$ , clearly indicating that some reaction with dichloromethane had occurred during work-up. The yields of these two products were in the region of 2%. Attempts to achieve higher yields either by prolonging the reaction time or by using higher pressures of CO and temperatures served to increase the amounts of [Pt- $(CO)_2(PEt_3)_2$  and  $[Pt_3(CO)_3(PEt_3)_4]$ , the other products of the reaction.

The formation of the nitrosyl complex is clearly of interest in view of the reactions observed with nickel but this procedure does not offer a convenient source of such complexes. The formation of the isocyanate complex suggests that, in contrast to the nickel system, further reduction of the nitrosyl ligand may also occur [equation (3)]. The final product  $[Pt(NO)(NO_{2})]$ -

$$[Pt(NO_2)_2(PEt_3)_2] \xrightarrow{+CO} [Pt(NO)(NO_2)(PEt_3)_2] \xrightarrow{+2CO} [Pt(NCO)(NO_2)(PEt_3)_2] \xrightarrow{+2CO} [Pt(NCO)(NO_2)(PEt_3)_2] (3)$$

 $(PEt_3)_2$ ] reacted with  $CH_2Cl_2$  to produce the observed chloro-derivative. Attempts to isolate the nitro-complex using alternative work-up procedures failed.

The formation of this NCO complex is of considerable interest. We have previously noted <sup>1</sup> that the complex  $[Ir(CO)(NO)(PPh_3)_2]$  reacts with PPh<sub>3</sub> on irradiation to produce  $[Ir(NCO)(PPh_3)_3]$  and suggested the formation of an iridium nitrene intermediate (Scheme 3). A similar mechanism (Scheme 4) may operate here.

In a separate experiment the reaction of [Pt(NO)- $(NO_2)(PEt_3)_2$  with CO, under conditions similar to those described above, was observed to produce some  $[Pt(CO)_2(PEt_3)_2]$  and  $[Pt_3(CO)_3(PEt_3)_4]$ , leading us to suggest the overall reaction sequence in Scheme 5.



SCHEME 5 (i) CO; (ii) Coupling; (iii) CH<sub>2</sub>Cl<sub>2</sub>

The further reaction of [Pt(NO)(NO2)(PEt3)2] to produce either [Pt(NCO)Cl(PEt<sub>3</sub>)<sub>2</sub>] or [Pt(CO)<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>] may be correlated with the expectation that the planar 16-electron complex  $[Pt^{II}(NO^{-})(NO_{2})(PEt_{3})_{2}]$  would undergo an associative addition of CO to produce as a reaction intermediate [Pt(NO)(NO<sub>2</sub>)(CO)(PEt<sub>3</sub>)<sub>2</sub>], a fiveco-ordinate 18-electron compound. In contrast, the quasi-tetrahedral 18-electron nickel complex [Ni(NO<sup>+</sup>)-XL<sub>2</sub>] is expected to less readily add further CO. Thus, Schemes 6 or 7 may be written.

We also suggest that after the initial formation of  $[Pt(NO)(NO_2)(PEt_3)_2]$  further reaction with CO to

 $[Ni(NO_2)XL_2] \xrightarrow{CO} Ni(NO_2)X(CO)L_2 \xrightarrow{-CO_2} [Ni(NO)XL_2] \xrightarrow{CO} No$  reaction intermediate planar stable tetrahedral (16-e complex) configuration ' (18-e complex)

SCHEME 6 Proposed reaction pathway for reduction of [Ni(NO<sub>2</sub>)XL<sub>2</sub>] by CO

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A key intermediate in Scheme 7 is  $[M(N_2O_2)L_2]$ . The platinum complex  $[Pt(N_2O_2)(PPh_3)_2]$  was first prepared <sup>5</sup> by the reaction of NO with  $[Pt(PPh_3)_4]$ . We recently reported <sup>6</sup> a single-crystal X-ray analysis of this compound which was found to contain the *cis*hyponitrite ligand. The mechanism by which this compound is formed is not known, although a reasonable route would be as in Scheme 9.



In this work we have established that  $[Pt(N_2O_2)-(PPh_3)_2]$  reacts with CO (1 atm) under mild conditions (25 °C) to produce  $[Pt(CO)_2(PPh_3)_2]$  (then polymers), CO<sub>2</sub>, and N<sub>2</sub>O.

The Preparation of [Pt(NO)(NO<sub>3</sub>)(PPh<sub>3</sub>)<sub>2</sub>].-The nitrosylnitrato-complex [Pt(NO)(NO<sub>3</sub>)(PPh<sub>3</sub>)<sub>2</sub>] has been prepared from the reaction of  $[Pt(PPh_3)_n]$  (n = 3 or 4) in toluene with dinitrogen tetraoxide at 0 °C. This biege coloured compound is obtained in low yields (ca. 10%), the major products of the reaction being [Pt- $(NO_2)_2(PPh_3)_2$  and  $[Pt(NO_3)_2(PPh_3)_2]$ . In the solid state the nitrosyl complex is moderately stable in the absence of air but in solution in a range of organic solvents it rapidly undergoes rearrangement to produce  $[Pt(NO_2)_2(PPh_3)_2]$  which precipitates. This rearrangement has presumably brought about a simple intramolecular oxygen-atom transfer (Scheme 10). This is reminiscent of the reaction in which the labelled nitronitrosyl complex [Fe(<sup>15</sup>NO)(<sup>14</sup>NO<sub>2</sub>)(S<sub>2</sub>CNMe<sub>2</sub>)<sub>2</sub>] was found 7 to undergo oxygen transfer (Scheme 11). We have established that the corresponding nickel compound  $[Ni(NO)(NO_3)(PPh_3)_2]$  does not undergo a similar reaction even over a period of several days, again emphasising the different chemistries of the planar Pt<sup>II</sup>–NO<sup>-</sup> and tetrahedral Ni<sup>0</sup>–NO<sup>+</sup> species.





intermediate

$$-co_2 - N_2 O + co$$

(ii) $[M(CO)_2L_2] \longrightarrow [M_3(CO)_4L_3] \longrightarrow higher clusters$ 

SCHEME 7 Proposed pathway for reaction of  $[M(NO_2)_2L_2]$  complexes with CO.  $M \rightarrow Pd$  or Pt. (i) Rearrangement; (ii) polymerisation



produce ' $Pt(NO)_2(PEt_3)_2$ ' may be considered to occur by one of two routes. First, *via* the same nitrene intermediate discussed above followed by an intramolecular oxygen-atom transfer as in Scheme 8, or secondly *via* direct oxygen-atom transfer from the NO<sub>2</sub> ligand to CO.

SCHEME 10



Reaction of  $[M(NO)XL_2]$  Complexes with Dioxygen. From a study of the oxygenation of  $[Co(NO)L_4]$  complexes (see below) in the presence of Lewis bases (B), Clarkson and Basolo<sup>8</sup> observed the formation of the corresponding nitro-compound  $[Co(NO_2)L_4]$  exclusively. In contrast, Trogler and Marzilli<sup>9</sup> observed the formation of both nitro- and nitrato-compounds during the reaction of [Co(NO)(dmg)B] (dmg = dimethylglyoximate) with O<sub>2</sub>, and exclusive oxidation of  $[Ir(NO)Cl(X)(CO)-(PPh_3)_2]$  (X = Cl, Br, I, NCS, or N<sub>3</sub>) to  $[Ir(NO_3)Cl(X)-(CO)(PPh_3)_2]$  has been reported by Kubota and Phillips.<sup>10</sup>

In this work we have examined the reaction of dioxygen with the formally NO<sup>+</sup> derivatives [Ni(NO)- $XL_2$ ] and the formally NO<sup>-</sup> derivative [Pt(NO)(NO<sub>3</sub>)-(PPh<sub>3</sub>)<sub>2</sub>] and note two different reaction pathways. (i) The quasi-tetrahedral nickel complexes react to produce the corresponding nitro-compounds with no evidence for the formation of nitrato-species. The reaction is sluggish at room temperature but rapid on irradiation. (ii) The planar platinum complex [Pt-(NO)(NO<sub>3</sub>)(PPh<sub>3</sub>)<sub>2</sub>] reacts rapidly with dioxygen to produce the dinitrato-complex [Pt(NO<sub>3</sub>)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>]. Small but varying amounts of [Pt(NO<sub>2</sub>)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] are also formed during this reaction by the oxygen-atom transfer mechanism outlined above.

It has been argued <sup>8</sup> <sup>10</sup> that the reaction of dioxygen with metal nitrosyl complexes occurs initially by the electrophilic attack of  $O_2$  on co-ordinated NO<sup>-</sup> ligands to produce a peroxynitrite intermediate. The peroxynitrite may then either attack a second molecule of NO<sup>-</sup> complex to produce a peroxy-bridged species (which undergoes homolytic fission to produce a nitrocompound) or undergo rearrangement to a nitratoderivative (Scheme 12). A key step in these reactions is the generation of the NO<sup>-</sup> complex. Thus, the function of base in the reaction of  $[Co(NO)L_4]$ , [Co(NO)-(dmg)], or  $[Ir(NO)Cl(CO)(PPh_3)_2]^+$  with dioxygen is to produce the reactive NO<sup>-</sup> species, *e.g.* as in equation (4).

$$[Co(NO^+)(dmg)] \xrightarrow{B} [Co(NO^-)(dmg)B]$$
(4)

The factors which influence the subsequent reaction of the peroxynitrite have not been defined. Clarkson and Basolo<sup>8</sup> argue that reaction to produce nitro-compounds proceeds via electrophilic attack of M-N(O)O<sub>2</sub> on M-NO<sup>-</sup> to produce M-N(O)O<sub>2</sub>(O)N-M. We recently provided evidence <sup>11</sup> that for the nickel compound [Ni-(NO)Cl(dppe)] a nickel(1) peroxy-bridged species similar to that proposed by Clarkson and Basolo<sup>8</sup> was produced in the reaction with O<sub>2</sub> and that this decayed to produce exclusively [Ni(NO<sub>2</sub>)Cl(dppe)]. With these nickel systems, reaction occurs in the absence of base although it is photoinitiated. In the absence of Ni(NO<sup>-</sup>) complex, therefore, we concluded that the reaction followed a sequence in which  $Ni-N(O)O_2$  was produced by a radical mechanism and then, more importantly to these arguments, the Ni-N(O)O<sub>2</sub>(O)N-Ni dimer was produced by nucleophilic addition of -N(O)O<sub>2</sub> ligand to coordinated NO<sup>+</sup>. The consequence of this view is that nitro-derivatives will be formed only when the reaction with O<sub>2</sub> is carried out in the presence of both co-ordinated NO<sup>+</sup> and NO<sup>-</sup>, and nitrato-derivatives will be formed only in the absence of an NO<sup>+</sup> species.

Thus, the compounds  $[Pt(NO)(NO_3)(PPh_3)_2]$  and  $[Ir(NO)Cl(X)(CO)(PPh_3)_2]$ , which contain the NO<sup>-</sup> ligand, react to produce exclusively nitrato-complexes, whereas the compounds [Co(NO)(dmg)] and  $[Ir(NO)Cl(CO)-(PPh_3)_2]^+$ , which are NO<sup>+</sup> derivatives, react only in the presence of base (to provide some NO<sup>-</sup> complex) to produce a mixture of nitro- and nitrato-derivatives. The relative amounts of nitro- and nitrato-derivatives will depend upon the standing concentration of NO<sup>+</sup> species. For  $[Co(NO)L_4]$ , for example, the large excess of base presumably removes all the NO<sup>+</sup> compound and thereby leads to the exclusive formation of the nitro-derivative. These conclusions are summarised in Scheme 13.

As we have indicated previously,<sup>1</sup> the continuous conversion of CO into  $CO_2$  by atmospheric oxygen occurs in the presence of  $[Ni(NO_2)_2(dppe)]$  or  $[Ni(NO)(NO_2)-(dppe)]$  under ambient conditions. The same observ-



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ation has been reported more recently by Feltham and Kriege.<sup>3</sup>



SCHEME 13 (i) No base required; (ii) rearrangement, since no NO<sup>+</sup> complex present; (iii) base required, py = pyridine; (iv) mixture of nitro- and nitrato-complexes depending on [py]; (v) nature of products depends on [B]

Some Reactions of  $[Pt(N_2O_2)(PPh_3)_2]$ .—The cis-hyponitrite complex  $[Pt(N_2O_2)(PPh_3)_2]$  reacts with [NO]- $[PF_6]$  in dichloromethane to produce a yellow salt of formula  $[{Pt(PPh_3)_2}_2N_2O_2][PF_6]_2$ . The reaction was monitored by following the change of i.r. spectrum of the reacting solution with time. As the  $[NO][PF_6]$  was added to a suspension of [Pt(N<sub>2</sub>O<sub>2</sub>)(PPh<sub>3</sub>)<sub>2</sub>] in CH<sub>2</sub>Cl<sub>2</sub> a clear yellow solution was produced which exhibited two bands at 1 631 and 1 587 cm<sup>-1</sup> and of relative intensity ca. 1:2. The bands soon disappear and a white microcrystalline solid precipitates. Analytically pure samples of this solid are best obtained from the reaction in MeOH-C<sub>6</sub>H<sub>6</sub>. In solution  $[Pt(N_2O_2)(PPh_3)_2]$  is very reactive towards CO2 and care must be exercised to carry out the reaction in a dry inert atmosphere. Contamination of the product with  $[Pt(PPh_3)_2(CO_3)]$  is revealed by the presence of a v(CO) band at 1 680 cm<sup>-1</sup>.

The i.r. spectrum of  $[{Pt(PPh_3)_2}_2N_2O_2][PF_6]_2$  shows strong bands at 1 137 and 1 045 cm<sup>-1</sup> which, by comparison with  $[{Co(NH_3)_5}_2N_2O_2]^{4+}$ , are assigned to a bridging  $N_2O_2$  group. Isotopically labelled examples (<sup>15</sup>NO) show shifts similar to that observed for the cobalt compound:

$[{Co(NH_3)_5}_2N_2O_2]^{4+}$		$[{Pt(PPh_3)_2}_2N_2O_2]^{2+}$	
14N	$^{15}N$	<sup>14</sup> N	$^{15}N$
1 136s	1 112s	1.137s	1 105s
1 046s	1 027s	1 045s	1 028s
932s	918s	obscured	

The appearance of the two bands at 1 631 and 1 586 cm<sup>-1</sup> during the course of this reaction leads us to suppose that an oxidative elimination of the  $N_2O_2$  ligand occurs [equation (5)]. Certainly the profile of this spectrum

$$\frac{[Pt(N_2O_2)(PPh_3)_2] + 2[NO][PF_6]}{[Pt(NO)_2(PPh_3)_2]^{2+} + 2NO}$$
(5)

resembles that observed for other related dinitrosyl species such as  $[Ir(NO)_2(PPh_3)_2]^+$ . Dimerisation could then occur with the elimination of NO<sup>+</sup> [equation (6)].

$$2[Pt(NO)_{2}(PPh_{3})_{2}]^{2^{+}} \longrightarrow \\ [\{Pt(PPh_{3})_{2}\}_{2}N_{2}O_{2}]^{2^{+}} + 2NO^{+}$$
(6)

EXPERIMENTAL

*Materials.*—The various  $[M(NO_2)_2L_2]$  complexes were prepared by the literature method.<sup>2</sup> All preparations had the correct C, H, and N analyses. Carbon monoxide was used directly from a cylinder without further purification. Solvents were AnalaR grade and unless otherwise stated were used as supplied.

Reactions of Complexes with CO.-(i) [NiX<sub>2</sub>L<sub>2</sub>]. The literature method <sup>2</sup> was employed. The products were identified on the basis of their i.r. spectroscopic data and C, H, and N analyses. All had previously been reported.

(ii) trans- $[M(NO_2)_2L_2]$ . These reactions were carried out in a stainless-steel rocking autoclave (100 cm<sup>3</sup>). In a typical experiment,  $[P(NO_2)_2(PEtPh_2)_2]$  (0.4 g) in degassed benzene (40 cm<sup>3</sup>) was treated with CO at 120 atm and 70 °C for 12 h. The resulting red solution was reduced in volume in vacuo to ca. 15 cm<sup>3</sup>. After filtering the solution to remove unreacted  $[P(NO_2)_2(PEtPh_2)_2]$ , the solution was further reduced in volume to yield a red oil. The latter was dissolved in dichloromethane and, on addition of nhexane, dark red crystals were obtained. These were very air-sensitive and were not characterised further.

In all cases the i.r. spectra of the red oils corresponded closely to those reported by Chatt and Chini<sup>4</sup> for the polynuclear clusters of Pd and Pt prepared by a different route. In a separate experiment we repeated the Chatt and Chini preparation from  $[PtCl_2(PEtPh_2)_2]$  with K[OH] and CO and obtained a red oil which showed an identical i.r. spectrum to that observed in the above experiment.

(*iii*)  $[Pt(NO_2)_2(PEt_3)_2]$ . The complex  $[Pt(NO_2)_2(PEt_3)_2]$ (1.4 g) was dissolved in hot toluene  $(40 \text{ cm}^3)$  and treated with carbon monoxide (50 atm) at 80 °C for 4 h. After cooling the solvent was removed under vacuum to leave an orange solid. This solid was dissolved in dichloromethane and separated into components by t.l.c. on silica plates using a mixture of hexane-ethyl acetate (1:1) as eluant. Two components were identified as cis- and trans- $[Pt(NO_2)_2]$ -(PEt<sub>3</sub>)<sub>2</sub>]. A third component, a yellow solid, was soluble in hexane and exhibited bands at 1 634s, 1 265s, 973m, and 869m cm<sup>-1</sup> in addition to bands which may be attributed to co-ordinated PEt<sub>a</sub>. The molecular weight was established from the mass spectrum (m/e = 507) (Found: C, 28.3; H, 5.5; N, 5.4. Calc. for  $C_{12}H_{30}N_2O_3P_2Pt$ : C, 28.4; H, 5.6; N, 5.5%). A fourth component, also a yellow solid, exhibited a band in the i.r. at 2 230m, br cm<sup>-1</sup> in addition to bands due to PEt<sub>3</sub>. The mass spectrum exhibited a parent ion {Found: m/e = 508. Calc. for [Pt(NCO)Cl-(PEt<sub>3</sub>)<sub>2</sub>]: m/e 508} (Found: C, 30.1; H, 5.9; N, 2.9. Calc. for  $C_{13}H_{30}CINOP_2Pt$ : C, 30.7; H, 5.2; N, 2.8%). The other products of the reaction,  $[Pt(CO)_2(PEt_3)_2]$ ,  $[Pt_3(CO)_3(PEt_3)_4]$ , and other higher clusters, were identified on the basis of their i.r. spectra.

In a separate experiment the use of  $CH_2Cl_2$  in the separating procedure was excluded. Instead, ethyl acetate and methanol were employed. However, although small amounts of materials were obtained which exhibited bands in the region of 2 200 cm<sup>-1</sup>, insufficient material was obtained to enable full characterisation.

Reaction of  $[Pt(N_2O_2)(PPh_3)_2]$  with  $[NO][PF_6]$ .—The complex  $[\operatorname{Pt}(N_2O_2)(\operatorname{PPh}_3)_2]$  was prepared according to the literature method.<sup>5</sup> To [NO][PF<sub>6</sub>] (180 mg, 1 mmol) in MeOH-C<sub>6</sub>H<sub>6</sub> (1:1, 60 cm<sup>3</sup>) was added  $[Pt(N_2O_2)(PPh_3)_2]$ (200 mg, 0.25 mmol). A pale yellow colour was produced immediately and a white solid separated. This solid was filtered off, washed with diethyl ether, and dried under vacuum. Yield 120 mg, m.p. 195-200 °C (decomp.) (Found: C, 48.0; H, 3.4; N, 1.7; P, 9.7. Calc. for [{Pt- $(PPh_3)_2\}_2N_2O_2][PF_6]_2$ : C, 48.2; H, 3.3; N, 1.6; P, 10.5%). In acetonitrile (attempt to determine conductivity) N<sub>2</sub>O was slowly evolved.

Reaction of  $[Pt(PPh_3)_4]$  with  $N_2O_4$ .—To an orange solution of  $[Pt(PPh_3)_n]$  (n = 3 or 4) (200 mg) in toluene (30 cm<sup>3</sup>) at 0 °C was slowly added  $N_2O_4$  (ca. 2 cm<sup>3</sup>) in toluene (10 cm<sup>3</sup>). A pale yellow solution was formed and a white solid separated. The solution was flushed vigorously by a fast stream of nitrogen and the solution then filtered. The filtrate was taken to dryness under vacuum when a beige solid remained. This was washed with warm hexane and dried under vacuum. On the basis of i.r. spectroscopic examination, the white solid was identified as a mixture of  $[Pt(NO_2)_2(PPh_3)_2]$  and  $[Pt(NO_3)_2(PPh_3)_2]$ . The beige solid was identified as [Pt(NO)(NO<sub>3</sub>)(PPh<sub>3</sub>)<sub>2</sub>] (Found: C, 52.8; H, 3.8; N, 3.5. Calc. for C<sub>36</sub>H<sub>30</sub>N<sub>2</sub>O<sub>4</sub>P<sub>2</sub>Pt: C, 53.3; H, 3.7; N,  $3.5^{0/}_{0}$ ).

Reaction of [Pt(NO)(NO<sub>3</sub>)(PPh<sub>3</sub>)<sub>2</sub>] with Dioxygen.-Oxygen was bubbled slowly through a stirred solution of  $[Pt(NO)(NO_3)(PPh_3)_2]$  in  $CH_2Cl_2$ . After removal of solvent a white crystalline solid remained. This was identified on the basis of analytical and i.r. spectroscopic data as [Pt- $(NO_3)_2(PPh_3)_2$ ]. The i.r. spectrum also revealed the

presence of small amounts of the dinitro-complex  $[Pt(NO_2)_2 (PPh_3)_2$ ]

Conversion of  $[Pt(NO)(NO_3)(PPh_3)_2]$  into  $[Pt(NO_2)_2$ -(PPh<sub>3</sub>)<sub>2</sub>].-A solution of [Pt(NO)(NO<sub>3</sub>)(PPh<sub>3</sub>)<sub>2</sub>] in CH<sub>2</sub>Cl<sub>2</sub> was stirred for ca. 1 h. After removal of solvent a white crystalline material remained. This was identified on the basis of the i.r. spectra and analytical data as  $[Pt(NO_2)_2]$ -(PPh<sub>3</sub>)<sub>2</sub>].

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