Reactions of Nitrogen Mono-oxide and Nitrogen Dioxide with Methylplatinum and Methylgold Complexes

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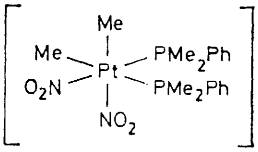
Nitrogen mono-oxide reacts with *cis*-$[PtMe_2(PMe_2Ph)_2]$ to give first *cis-cis-cis*-$[PtMe_2(NO_2)_2(PMe_2Ph)_2]$ which then isomerises to the more stable *cis-cis-trans* isomer. The final products, however, are *trans*-$[PtMe(NO_2)(PMe_2Ph)_2]$ and *fac*-$[PtMe_3(NO_2)(PMe_2Ph)_2]$ formed by reaction of *cis*-$[PtMe_2(PMe_2Ph)_2]$ with $[PtMe_2(NO_2)_2(PMe_2Ph)_2]$. Nitrogen dioxide reacts with *cis*-$[PtMe_2(PMe_2Ph)_2]$ to give *cis-cis-trans*-$[PtMe_2(NO_3)_2(PMe_2Ph)_2]$, while both NO and NO_2 react with $[AuMe_3(PMe_2Ph)]$ to give *cis*-$[AuMe_2(NO_2)(PMe_2Ph)]$. Nitrogen mono-oxide reacts with *trans*-$[PtHI(PMe_2Ph)_2]$ to give *cis*-$[PtI(NO_2)(PMe_2Ph)_2]$, which is also formed in the symmetrisation reaction between *cis*-$[Pt(NO_2)_2(PMe_2Ph)_2]$ and $[PtI_2(PMe_2Ph_2)]$. Possible mechanisms of reaction are discussed.

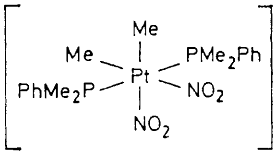
RECENT work has shown that free-radical substitution reactions (S_H2 reactions) take place readily with methyl-platinum(II) or -gold(I) complexes but not with methylgold(III) complexes.[1-3] We hoped to learn more about these reactions by using stable free radicals as reagents, and we have now studied reactions of methyl-platinum(II) -gold(I), and -gold(III) complexes with nitrogen mono-oxide and nitrogen dioxide. There is no evidence for S_H2 reactions in these systems, but other interesting reactions do take place.

Some reactions of NO with transition-metal alkyls have been reported previously. Thus hexamethyltungsten reacts to give $[WMe_4\{N(O)N(O)Me\}_2]$ where each *N*-methyl-*N*-nitrosohydroxylamine group functions as a bidentate ligand co-ordinating through both oxygen atoms,[4] and similar reactions occur with methyltitanium,[5] -zirconium,[5] and -tantalum complexes.[6] Also relevant is the reaction of $[Pt(PPh_3)_4]$ with NO to give the hyponitrite derivative $[Pt(N_2O_2)(PPh_3)_2]$.[7,8]

RESULTS AND DISCUSSION

Reactions of cis-$[PtMe_2(PMe_2Ph)_2]$ *with* NO.—When a solution of *cis*-$[PtMe_2(PMe_2Ph)_2]$ in benzene was treated with excess of nitrogen mono-oxide in a sealed tube at room temperature, white crystals were deposited over a period of 2—3 h. If left for longer periods these crystals slowly redissolved and an almost clear solution was again obtained after several days. The initial white crystals were identified as $[PtMe_2(NO_2)_2(PMe_2Ph)_2]$ of configuration (I) by elemental analysis and by the i.r. and n.m.r. spectra. The complex is sparingly soluble in most organic solvents, but in dichloromethane it dissolves and then isomerises slowly to (II) which could also be prepared from $[PtMe_2I_2(PMe_2Ph)_2]$ and silver nitrite.


(I)


(II)

The clear solution obtained from *cis*-$[PtMe_2(PMe_2Ph)_2]$ and NO after longer reaction times contained neither (I) nor (II) but an equimolar mixture of *fac*-$[PtMe_3(NO_2)(PMe_2Ph)_2]$ and *trans*-$[PtMe(NO_2)(PMe_2Ph)_2]$. These products almost certainly arise by reaction of (I) or (II) with unchanged *cis*-$[PtMe_2(PMe_2Ph)_2]$. Thus we were able to show independently that (II) reacts with *cis*-$[PtMe_2(PMe_2Ph)_2]$ according to equation (1). Such exchange reactions between methyl-platinum(II) and -platinum(IV) complexes are quite general.[9,10]

$$[PtMe_2(NO_2)_2(PMe_2Ph)_2] + cis\text{-}[PtMe_2(PMe_2Ph)_2] \longrightarrow fac\text{-}[PtMe_3(NO_2)(PMe_2Ph)_2] + trans\text{-}[PtMe(NO_2)(PMe_2Ph)_2] \quad (1)$$

The mechanism of formation of the initial product is more difficult to establish. The gaseous products contained no N_2O and we assume that dinitrogen is formed according to equation (2). It is possible that NO first

$$cis\text{-}[PtMe_2(PMe_2Ph)_2] + 4NO \longrightarrow [PtMe_2(NO_2)_2(PMe_2Ph)_2] + N_2 \quad (2)$$

co-ordinates to platinum to give $[PtMe_2(NO)_2(PMe_2Ph)_2]$. If the NO is bound to platinum in the bent form (where it acts as a one-electron ligand) this would be an 18-electron complex.[8] Oxidation of co-ordinated NO to co-ordinated NO_2 by free NO presumably takes place next. Such a process has been established previously[8,11] (although N_2O was also formed in that reaction) as well as in the related reaction of $[RhCl(PPh_3)_3]$ with NO which gave $[RhCl(NO)(NO_2)(PPh_3)_2]$.[12] The difference in in this case can be explained if the formation of two

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[1] M. F. Lappert and P. W. Lednor, *J.C.S. Chem. Comm.*, 1973, 948.

[2] A. Johnson and R. J. Puddephatt, *J.C.S. Dalton*, 1975, 115.

[3] R. Kaptein, P. W. N. M. van Leeuwen, and R. Huis, *J.C.S. Chem. Comm.*, 1975, 568.

[4] S. R. Fletcher, A. Shortland, A. C. Skapski, and G. Wilkinson, *J.C.S. Chem. Comm.*, 1972, 922; *J. Organometallic Chem.*, 1973, **59**, 299.

[5] P. C. Wailes, H. Weigold, and A. P. Bell, *J. Organometallic Chem.*, 1972, **34**, 155.

[6] J. D. Wilkins and M. G. B. Drew, *J. Organometallic Chem.*, 1974, **69**, 111.

[7] S. Cenini, R. Ugo, G. La Monica, and S. D. Robinson, *Inorg. Chim. Acta*, 1972, **6**, 182.

[8] K. G. Caulton, *Co-ordination Chem. Rev.*, 1975, **14**, 317; 1974, **13**, 339.

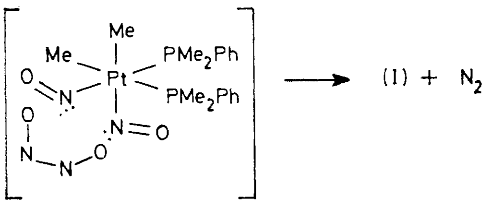
[9] R. J. Puddephatt and P. J. Thompson, *J.C.S. Dalton*, 1975, 1810.

[10] P. J. Thompson and R. J. Puddephatt, *J.C.S. Chem. Comm.*, 1975, 841.

[11] K. G. Caulton, *Inorg. Chem.*, 1974, **13**, 414.

[12] W. B. Hughes, *J.C.S. Chem. Comm.*, 1969, 1126.

mutually *cis* nitro-groups takes place in a concerted manner [equation (3)].



(3)

It is also possible that a hyponitrito-complex [PtMe$_2$(N$_2$O$_2$)(PMe$_2$Ph)$_2$] could be formed first {*cf.* the reaction of NO with [Pt(PPh$_3$)$_4$] [7]}, followed by oxidation of the hyponitrite ligand by free NO. This mechanism is particularly attractive in that concerted attack on *cis*-[PtMe$_2$(PMe$_2$Ph)$_2$] by the dimer N$_2$O$_2$ to give a hyponitrite complex with later oxidation to give the dinitro-complex would be expected to give a product of stereochemistry (I) as observed.

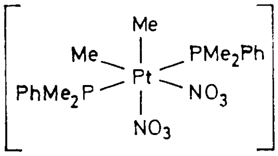
An attempt was made to check this mechanism by preparing the hyponitrite [PtMe$_2$(N$_2$O$_2$)(PMe$_2$Ph)$_2$] independently and studying its reaction with NO. The required hyponitrite complex was prepared by reaction of [PtMe$_2$I$_2$(PMe$_2$Ph)$_2$] with Ag$_2$[N$_2$O$_2$]. It is a colourless, very sparingly soluble, complex, suggesting that it might be polymeric with bridging hyponitrite ligands. The presence of the hyponitrite group was indicated by the characteristic very strong peak in the i.r. spectrum at 1 100 cm^{-1} (*cf.* 1 050 cm^{-1} in Ag$_2$[N$_2$O$_2$]), but no conclussions about the precise bonding [7] can be drawn. A suspension of the hyponitrite complex in benzene reacted slowly with a large excess of NO to give [PtMe$_2$(NO$_3$)$_2$(PMe$_2$Ph)$_2$] in low yield. The gas phase was shown to contain some NO$_2$ and it is possible that disproportionation of NO to NO$_2$ and N$_2$O took place followed by reaction of NO$_2$ with the hyponitrite complex (see later). Thus it seems unlikely that a hyponitrite is involved in the reaction of *cis*-[PtMe$_2$(PMe$_2$Ph)$_2$] with NO, although it is possible that a more reactive complex with chelating rather than bridging hyponitrite groups might be formed as a short-lived intermediate.

Whatever the mechanism it is clear that NO neither inserts into the Pt–Me bond nor displaces a methyl radical from platinum, but simply oxidises Pt$^{\text{II}}$ to Pt$^{\text{IV}}$. The apparent disproportionation to give a trimethylplatinum(IV) and a monomethylplatinum(II) complex is due to a subsequent exchange reaction.

Reaction of cis-[PtMe$_2$(PMe$_2$Ph)$_2$] *with* NO$_2$.—The complex *cis*-[PtMe$_2$(PMe$_2$Ph)$_2$] reacted with a fourfold excess of NO$_2$ according to equation (4). The

$$cis\text{-}[PtMe_2(PMe_2Ph)_2] + 4NO_2 \longrightarrow [PtMe_2(NO_3)_2(PMe_2Ph)_2] + 2NO \quad (4)$$

resulting dinitratoplatinum(IV) complex was shown to have stereochemistry (III) by its n.m.r. spectrum. Complex (III) was prepared independently from [PtMe$_2$I$_2$(PMe$_2$Ph)$_2$] and silver nitrate. The reaction to form (III) is very rapid, and this high rate is necessary for its formation since (III) reacts rapidly with *cis*-[PtMe$_2$(PMe$_2$Ph)$_2$] according to equation (5).[10] The *fac*-[PtMe$_3$(NO$_3$)(PMe$_2$Ph)$_2$] then underwent reductive elimination



(III)

$$[PtMe_2(NO_3)_2(PMe_2Ph)_2] + cis\text{-}[PtMe_2(PMe_2Ph)_2] \longrightarrow cis\text{-}[PtMe(NO_3)(PMe_2Ph)_2] + fac\text{-}[PtMe_3(NO_3)(PMe_2Ph)_2] \quad (5)$$

of ethane to give *trans*-[PtMe(NO$_3$)(PMe$_2$Ph)$_2$]. This subsequent reaction was complete in *ca.* 1 h at 35 °C.[10] The isolation of (III) only in the reaction of *cis*-[PtMe$_2$(PMe$_2$Ph)$_2$] with NO$_2$ is then a result of reaction (4) being faster than (5), in contrast to the analogous reaction of *cis*-[PtMe$_2$(PMe$_2$Ph)$_2$] with NO described above.

It is probable that (III) is formed by the reactions of equation (6). The evidence is as follows. (1) We have

$$\begin{array}{l} cis\text{-}[PtMe_2(PMe_2Ph)_2] + 2NO_2 \longrightarrow [PtMe_2(NO_2)_2(PMe_2Ph)_2] \\ \qquad\qquad \big\downarrow 2NO_2 \\ \qquad\qquad [PtMe_2(NO_3)_2(PMe_2Ph)_2] + 2NO \quad (6) \end{array}$$

shown independently that (II) reacts with NO$_2$ to give (III) and NO. Oxidation of nitro- to nitrato-ligands by NO$_2$ has been observed once previously.[13] (2) The reaction of *cis*-[PtMe$_2$(PMe$_2$Ph)$_2$] with less than 4 mol equivalents of NO$_2$ gives mixtures of nitro- and nitrato-platinum complexes. Thus in one case a reaction of stoicheiometry (7) was shown to take place. These

$$2\ cis\text{-}[PtMe_2(PMe_2Ph)_2] + 3NO_2 \longrightarrow trans\text{-}[PtMe(NO_2)(PMe_2Ph)_2] + trans\text{-}[PtMe(NO_3)(PMe_2Ph)_2] + C_2H_6 + NO \quad (7)$$

products are presumably formed by exchange reactions of (II) and (III) with excess of *cis*-[PtMe$_2$(PMe$_2$Ph)$_2$] as described earlier, followed by reductive elimination of ethane from the resulting *fac*-[PtMe$_3$X(PMe$_2$Ph)$_2$] (X = NO$_2$ or NO$_3$). The formation of the nitroplatinum complex in this reaction is too fast to be explained in terms of reaction of NO (formed during the reaction) with *cis*-[PtMe$_2$(PMe$_2$Ph)$_2$].

Reactions with [AuMe$_3$(PMe$_2$Ph)] *and* [AuMe(PMe$_2$Ph)].—Nitrogen dioxide reacted rapidly with [AuMe$_3$(PMe$_2$Ph)] according to equation (8). The gold com-

$$[AuMe_3(PMe_2Ph)] + 2NO_2 \longrightarrow cis\text{-}[AuMe_2(NO_2)(PMe_2Ph)] \ (+ MeNO_2 + CH_4) \quad (8)$$

plex was an oil which we were unable to crystallise, but it was positively characterised by elemental analysis, i.r. and n.m.r. spectra, and by an independent synthesis from *cis*-[AuMe$_2$Cl(PMe$_2$Ph)] and silver(I) nitrite.

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[13] C. C. Addison, R. Davis, and N. Logan, *J. Chem. Soc.* (*A*), 1970, 3333.

We have been unable to account in a quantitative way for the fate of the methyl group which was cleaved from gold, but both nitromethane and methane were detected in approximately equal amounts by n.m.r. and g.l.c. analysis. The mechanism of this reaction is uncertain, but the products are consistent with homolytic displacement of a methyl radical by NO_2, the methyl radical then reacting with more NO_2 to give nitromethane or abstracting hydrogen from the solvent to give methane. Such a mechanism may be enforced in this case because Au^{III} cannot undergo oxidation as observed for the platinum(II) complex, although previous work has indicated that gold(III) complexes do not undergo S_H2 reactions readily.[2]

TABLE 1

Analytical and infrared data for the complexes

Complex	Analysis (%) [a] C	H	N	I.r. bands (cm^{-1}), $\nu(NO_2)$ or $\nu(NO_3)$ [b]
trans-$[PtMe(NO_2)(PMe_2Ph)_2]$	38.7 (38.3)	4.8 (4.7)	3.0 (2.6)	1 350vs, 815s
$[PtMe_2(NO_2)_2(PMe_2Ph)_2]$, (I)	36.7 (36.4)	4.8 (4.7)	5.1 (4.7)	1 370vs, 820m, 335w
$[PtMe_2(NO_2)_2(PMe_2Ph)_2]$, (II)	36.0 (36.4)	5.0 (4.7)	5.0 (4.7)	1 398vs, 824s, 818m, 345w
fac-$[PtMe_3(NO_2)(PMe_2Ph)_2]$	40.4 (40.6)	5.9 (5.5)	2.6 (2.5)	1 375vs, 827m (sh)
$[PtMe_2(NO_3)_2(PMe_2Ph)_2]$, (III)	35.1 (34.6)	4.8 (4.5)	5.4 (4.5)	1 465vs, 1 270vs, 1 010vs, 815m, 808m
$[PtMe_2(N_2O_2)(PMe_2Ph)_2]$	38.7 (38.5)	4.9 (5.0)	4.7 (5.0)	1 100vs [c]
cis-$[PtI(NO_2)(PMe_2Ph)_2]$	29.9 (29.8)	3.7 (3.4)	2.1 (2.2)	1 387vs, 1 333vs, 820vs
cis-$[AuMe_2(NO_2)(PMe_2Ph)]$	31.7 (29.2)	4.5 (4.13)	3.5 (3.41)	1 380s, 834m, 826m

[a] Calculated values are given in parentheses. [b] Only clearly distinguished bands are given. In some cases bands were obscured by other ligand bands; vs = very strong, s = strong, m = medium, w = weak, sh = shoulder. [c] $\nu(N_2O_2)$.

TABLE 2

N.m.r. data for the complexes [a]

Complex	δ(MeP) p.p.m.	^2J(PH) Hz	^3J(PtH) Hz	δ(MePt) or δ(MeAu) p.p.m.	^3J(PH) Hz	^2J(PtH) Hz
trans-$[PtMe(NO_2)(PMe_2Ph)_2]$	1.66 (t)	7.0	32.5	−0.02 (t)	7.5	70.9
trans-$[PtMe(NO_3)(PMe_2Ph)_2]$	1.54 (t)	6.8	30.0	0.26 (t)	7.1	85.8
$[PtMe_2(NO_2)_2(PMe_2Ph)_2]$, (I)	1.75 (d)	10.0	*b*	0.84 (dd)	8.1, 3.0	60
	1.77 (d)	10.0	*b*	1.23 (dd)	7.2, 4.0	*b*
	1.60 (d)	11.5	*b*			
	1.55 (d)	11.5	*b*			
$[PtMe_2(NO_2)_2(PMe_2Ph)_2]$, (II)	1.94 (t)	7.7	17.5	0.30 (t)	6.2	59.5
$[PtMe_2(NO_3)_2(PMe_2Ph)_2]$, (III)	1.92 (t)	7.7	17.3	0.83 (t)	5.9	71.5
cis-$[PtI(NO_2)(PMe_2Ph)_2]$	1.80 (d)	11.1	31.0			
	1.47 (d)	11.3	41.0			
cis-$[AuMe_2Cl(PMe_2Ph)]$	1.26 (d)	10.4		0.75 (d), 1.28(d)	8.9, 8.8	
cis-$[AuMe_2(NO_2)(PMe_2Ph)]$	1.74 (d)	10.6		0.89 (d) [c]	9.3	
cis-$[AuMe_2(NO_2)(PMe_2Ph)]$ [d]	1.21 (d)	10.2		0.86 (d)	9.3	
				1.30 (d)	9.3	

[a] In CH_2Cl_2 unless otherwise specified. d = Doublet, t = triplet. [b] Platinum-195 satellites were not resolved. [c] Chemical shifts of the two methylgold groups were accidentally degenerate in CH_2Cl_2. [d] Solvent benzene.

The complex *cis*-$[AuMe_2(NO_2)(PMe_2Ph)]$ was also isolated from the reaction of $[AuMe_3(PMe_2Ph)]$ with a large excess of NO, but this reaction took several days to reach completion.

Both NO and NO_2 reacted rapidly with $[AuMe(PMe_2Ph]$ but the gold-containing products were unstable and rapidly decomposed to metallic gold and dimethylphenylphosphine oxide. In the reaction with NO_2, nitromethane was also identified as a product. Attempts to prepare $[Au(NO_2)(PMe_2Ph)]$ and $[Au(NO_3)(PMe_2Ph)]$ from $[AuBr(PMe_2Ph)]$ and the corresponding silver salt also led to complete decomposition to metallic gold. It is possible that one of these complexes is the initial product of reaction of $[AuMe(PMe_2Ph)]$ with NO and NO_2.

Reaction of trans-$[PtHI(PMe_2Ph)_2]$ *with* NO.—Nitrogen mono-oxide reacted with *trans*-$[PtHI(PMe_2Ph)_2]$ to give *cis*-$[PtI(NO_2)(PMe_2Ph)_2]$ together with a small amount of $[PtI_2(PMe_2Ph)_2]$. We were unable to determine the fate of the hydride group in this reaction. The platinum-containing product could also be obtained in quantitative yield by reaction of *cis*-$[Pt(NO_2)_2(PMe_2Ph)_2]$ with a *cis–trans* mixture of $[PtI_2(PMe_2Ph)_2]$.

Characterisation of the Products.—Elemental analyses of the products are given in Table 1, together with the i.r. bands due to the nitro- or nitrato-groups. The nature of binding of the nitro-groups can easily be determined from the i.r. data.[14-16] The complexes prepared are all *N*-nitro-derivatives as expected for the soft platinum and gold centres. *O*-Nitroplatinum(IV) complexes are known [16] but there is no evidence for their formation as intermediates in the system studied here.

The stereochemistries of the complexes were deduced from the n.m.r. spectra. This is a well established method for complexes of this type.[9,17] The data are given in Table 2, and the general method of analysis is illustrated for the isomers of $[PtMe_2(NO_2)_2(PMe_2Ph)_2]$. In isomer (II) the phosphine ligands are mutually *trans*

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[14] K. Nakamoto, 'Infrared Spectra of Inorganic and Coordination Compounds,' 2nd edn., Wiley–Interscience, New York, 1970, pp. 160—166.

[15] K. R. Dixon, K. C. Moss, and M. A. R. Smith, *J.C.S. Dalton*, 1975, 990.

[16] J. R. Hall and G. A. Swile, *J. Organometallic Chem.*, 1975, **96**, C61.

[17] J. D. Ruddick and B. L. Shaw, *J. Chem. Soc.* (*A*), 1969, 2801.

so that the methylphosphorus peak in the n.m.r. spectrum appeared as a triplet [due to the large value of ^2J(PP)] with satellites due to coupling with ^{195}Pt.[17] The methylplatinum groups are equivalent and also gave a triplet due to coupling with two equivalent ^{31}P atoms. In isomer (I), all the four methylphosphorus groups are in different environments due to the chemical inequivalence of the two phosphine ligands and the lack of a plane of symmetry in the molecule. Since the phosphines are mutually *cis* [and hence ^2J(PP) is small], four doublets were observed for the methylphosphorus groups.[17] The methylplatinum groups are also non-equivalent and each gave a doublet of doublets in the n.m.r. spectrum due to coupling with the non-equivalent phosphorus atoms. The magnitude of the coupling ^2J($PtCH_3$) in these complexes can also be useful since the *N*-nitro-group is expected to have higher *trans* influence than the *O*-nitro-group.[17,18]

EXPERIMENTAL

General methods and the preparation of *cis*-[$PtMe_2(PMe_2Ph)_2$],[17] [$AuMe(PMe_2Ph)$],[2] and [$AuMe_3(PMe_2Ph)$] [9] have been described previously.

Nitrogen mono-oxide was purified by passing it through a column of potassium hydroxide pellets. Nitrogen dioxide was a commercial sample and was used without further purification. Both reagents were admitted to reaction mixtures in measured quantities using standard vacuum-line techniques.

Bis(dimethylphenylphosphine)dimethyldinitroplatinum(IV), *Configuration*(II).—This was prepared from *cis-trans-cis*-[$PtMe_2I_2(PMe_2Ph)_2$] (0.53 g) and silver(I) nitrite (0.5 g) in acetone (15 cm^3). The solution was stirred overnight, filtered to remove silver salts, and the solvent evaporated to give the product as white crystals (0.37 g, 89%), m.p. 160 °C (decomp. with effervescence). *Bis(dimethylphenylphosphine)dimethyldinitratoplatinum*(IV) was prepared similarly from *cis-trans-cis*-[$PtMe_2I_2(PMe_2Ph)_2$] (0.2 g) and silver(I) nitrate (0.3 g), yield 0.15 g, m.p. 142—144 °C.

cis-*Chloro(dimethylphenylphosphine)dimethylgold*(III).—This was prepared from [$AuMe_3(PMe_2Ph)$] and anhydrous hydrogen chloride in equimolar quantities in diethyl ether. Evaporation of the solvent gave the *product*, 87%, m.p. 91—92 °C.

cis-*(Dimethylphenylphosphine)dimethylnitrogold*(III).—This was prepared from *cis*-[$AuMe_2Cl(PMe_2Ph)$] with Ag[NO_2] in acetone (10 cm^3). After 1.5 h the solution was filtered and the solvent evaporated to give the product. This was crystallised from dichloromethane–diethyl ether at low temperature but was an oil at room temperature. Attempts to prepare *cis*-[$AuMe_2(NO_3)(PMe_2Ph)$], [$Au(NO_2)(PMe_2Ph)$], and [$Au(NO_3)(PMe_2Ph)$] by analogous methods were unsuccessful, in each case leading to decomposition to metallic gold.

Bis(dimethylphenylphosphine)hyponitritodimethylplatinum(IV).—This was prepared from *cis-trans-cis*-[$PtMe_2I_2(PMe_2Ph)_2$] (0.65 g, 0.86 mmol) with excess of $Ag_2[N_2O_2]$ (0.85 g, 3.1 mmol) in acetone (30 cm^3). The mixture was stirred overnight, filtered, and the solvent was evaporated *in vacuo*. The product was crystallised from dichloromethane, and washed thoroughly with diethyl ether to remove impurities of unchanged [$PtMe_2I_2(PMe_2Ph)_2$], m.p. 128—130 °C.

Reactions of Nitrogen Mono-oxide.—With cis-[$PtMe_2(PMe_2Ph)$]. A solution of *cis*-[$PtMe_2(PMe_2Ph)_2$] (0.45 g, 0.90 mmol) in benzene (4 cm^3) in a Pyrex tube was carefully degassed by several freeze–pump–thaw cycles. Excess of NO (*ca.* 5 mmol) was condensed into the tube, which was then sealed *in vacuo* and allowed to warm to room temperature. After 2.5 h a significant quantity of white needle-like crystals had formed in the tube, but these slowly redissolved. After 7 d the tube was opened and the white crystals were filtered off (0.02 g, m.p. 174—175 °C), and examination of the filtrate by t.l.c. showed it to contain two complexes (R_F, silica-coated plates with diethyl ether as eluant: 0.1 and 0.5). The mixture was separated by chromatography through a silica column. Elution with diethyl ether gave *fac*-[$PtMe_3(NO_2)(PMe_2Ph)_2$] (0.14 g) and subsequent elution with acetone gave *trans*-[$PtMe(NO_2)(PMe_2Ph)_2$] (0.15 g).

In a similar experiment the tube was opened after 1 d. The yield of [$PtMe_2(NO_2)_2(PMe_2Ph)_2$], configuration (I), was 0.09 g. The complex dissolved with difficulty in dichloromethane and isomerised slowly to configuration (II). This was complete in 1 d and (II) was crystallised from the solution, m.p. 162—167 °C. In another experiment uisng a 2 : 1 mol ratio of NO : *cis*-[$PtMe_2(PMe_2Ph)_2$] the reaction was driven to completion by warming overnight to 60 °C. The tube was opened to the vacuum line and a gas-phase i.r. spectrum was recorded for the volatile products. Only trace amounts of unchanged NO were identified, with N_2O positively absent.

With [$AuMe(PMe_2Ph)$]. The complex (0.21 g) in benzene (4 cm^3) was treated with NO (5 mmol) in a sealed tube. Immediately on warming to room temperature a precipitate of gold formed. The only products identified were PMe_2PhO and $MeNO_2$.

With [$AuMe_3(PMe_2Ph)$]. The complex (0.35 g, 0.92 mmol) in benzene (4 cm^3) was treated with NO (5 mmol) in a sealed tube. After 1 d the tube was opened and the solvent evaporated giving *cis*-[$AuMe_2(NO_2)(PMe_2Ph)$] as a colourless oil which could not be crystallised. It was identical with an authentic sample (n.m.r., i.r.).

With [$PtMe_2(N_2O_2)(PMe_2Ph)_2$]. Nitrogen mono-oxide was condensed into a Carius tube (50 cm^3 capacity) containing a suspension of [$PtMe_2(N_2O_2)(PMe_2Ph)_2$] (0.2 g) in benzene (5 cm^3). The tube was sealed and allowed to stand at room temperature for 4 d. The tube was opened and the soluble product was identified as [$PtMe_2(NO_3)_2(PMe_2Ph)_2$], (III), by comparison with an authentic sample.

With trans-[$PtHI(PMe_2Ph)_2$]. The complex (0.36 g) in toluene (10 cm^3) was treated with NO (5 mmol) in a sealed tube. After 12 d the tube was opened and the solution cooled to −23 °C when *cis*-[$PtI(NO_2)(PMe_2Ph)_2$], m.p. 190—191 °C, crystallised. The fraction insoluble in toluene was identified by its n.m.r. spectrum as [$PtI_2(PMe_2Ph)_2$].

Reactions of NO_2.—*With* cis-[$PtMe_2(PMe_2Ph)_2$]. A solution of *cis*-[$PtMe_2(PMe_2Ph)_2$] (0.23 g, 0.46 mmol) in benzene (2 cm^3) in a Pyrex tube was degassed, then NO_2 (2.02 mmol) was condensed into the tube and the tube was sealed. Immediately on warming to room temperature white crystals were deposited. After 1 d the tube was opened to the vacuum line and the gaseous product was identified as NO by its gas-phase i.r. spectrum. The crystals were filtered off and identified as *cis-cis-trans*-[$PtMe_2(NO_3)_2(PMe_2Ph)_2$] (0.2 g), m.p. 143—145 °C.

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[18] T. G. Appleton, H. C. Clark, and L. E. Manzer, *Co-ordination Chem. Rev.*, 1973, **10**, 335.

Treatment of *cis*-[PtMe$_2$(PMe$_2$Ph)$_2$] with excess of NO$_2$ gave the same product together with some [Pt(NO$_3$)$_4$-(PMe$_2$Ph)$_2$], while treatment with an equimolar quantity of NO$_2$ gave a mixture of *trans*-[PtMe(NO$_3$)(PMe$_2$Ph)$_2$] and *trans*-[PtMe(NO$_2$)(PMe$_2$Ph)$_2$] identified by their characteristic n.m.r. spectra.

With [AuMe$_3$(PMe$_2$Ph)]. A similar reaction with [AuMe$_3$-(PMe$_2$Ph)] (0.26 g, 0.68 mmol) and NO$_2$ (0.75 mmol) gave *cis*-[AuMe$_2$(NO$_2$)(PMe$_2$Ph)], identical (n.m.r.) with an authentic sample, and some unchanged starting material. Nitromethane and methane in approximately equimolar amounts were also formed and identified by n.m.r. and g.l.c.

[6/855 *Received, 5th May,* 1976]