

Reaction of NO₂ with Palladium(II) and Platinum(II) Aryl Complexes; The Crystal Structure of *trans*-[Pd(ONO₂)₂(OPPh₃)(PPh₃)][†]

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[Pd(C₆H₄NO₂-*p*)I(PPh₃)₂] and [Pd(Ph)Cl(Ph₂PCH₂CH₂PPh₂)] do not react with NO but react with NO₂ to give [Pd(NO₃)₂(OPPh₃)(PPh₃)] and [PdCl(NO₃)(Ph₂PCH₂CH₂PPh₂)] respectively. The structure of [Pd(NO₃)₂(OPPh₃)(PPh₃)] has been confirmed by X-ray crystallography, the metal co-ordination polyhedron being planar with *trans* monodentate nitrate groups. Reaction of [Pt(R)I(PPh₃)₂] (R = C₆H₄NO₂-*p* or Ph) with NO₂ gave [Pt(R)(NO₃)(PPh₃)₂], species shown spectroscopically to contain monodentate nitrate. Treatment of [Pd(NO₂)₂(PPh₃)₂] with NO₂ gave [Pd(NO₃)₂(PPh₃)₂], while NO or CO caused deoxygenation of [Pd(NO₃)₂L₂] (L = PPh₃ or PEt₃) and [Pt(Ph)(NO₃)(PPh₃)₂] to the nitro species [Pd(NO₂)₂L₂] and [Pt(Ph)(NO₂)(PPh₃)₂]. Reaction of [Ni(NO₃)₂(PEt₃)₂] with NO or NO₂ afforded [Ni(NO₃)₂(OPEt₃)₂]. The possible mechanisms of these oxygen-transfer reactions are briefly discussed.

A number of *d*⁰, *d*⁸, and *d*¹⁰ alkyl¹ and aryl² complexes react with NO giving compounds containing the *N*-alkyl- or *N*-aryl-*N*-nitrosohydroxylaminate ligand, [ONN(R)O]⁻. In contrast, however, it has been reported^{3,4} that Pt^{II} alkyls afford only nitro or nitrate derivatives. Thus *cis*-[PtMe₂L₂] (L = PMe₂Ph³ or PEt₃⁴) reacted with NO giving, initially, *cis,cis,cis*-[PtMe₂(NO₂)₂L₂] which subsequently isomerised and reacted with [PtMe₂L₂] to give *trans*-[PtMe(NO₂)L₂] and *fac*-[PtMe₃(NO₂)L₂] (L = PMe₂Ph). *cis*-[PtMe₂(PMe₂Ph)₂] also reacted with NO₂ giving analogous nitrate complexes and, under different conditions, mixtures of [PtMe(NO₂)(PMe₂Ph)₂] and [PtMe(NO₃)(PMe₂Ph)₂] could be formed.³

In seeking to extend the scope of reactions of metal-aryl complexes with oxides of nitrogen, particularly NO, with the hope of observing 'insertion' processes, we have studied the behaviour of *trans*-[M(R)X(PPh₃)₂] (M = Pd or Pt, R = Ph or C₆H₄NO₂-*p*, X = Cl or I) with NO and NO₂.

Experimental

The starting materials [Pt(R)I(PPh₃)₂] (R = Ph or C₆H₄NO₂-*p*),⁵ [Pd(Ph)Cl(PPh₃)₂],⁶ [Pd(C₆H₄NO₂-*p*)I(PPh₃)₂],⁷ [Pd(Ph)Cl(Ph₂PCH₂CH₂PPh₂)],⁷ and [Ni(NO₃)₂(PEt₃)₂]⁸ were prepared as described in the literature. The complexes [Pd(NO₂)₂(PR₃)₂] (x = 2 or 3, R = Ph or Et) were obtained by reaction of [PdCl₂(PR₃)₂] with NaNO₂ or AgNO₃ in chloroform. NO gas was prepared as described elsewhere⁹ and purified by passage through KOH pellets and a trap containing molecular sieves cooled at -78 °C. NO₂-N₂O₄ was prepared by the reaction of NO gas with oxygen or by heating lead nitrate,¹⁰ and was trapped at -78 °C. The trap containing white N₂O₄ was degassed thoroughly with dry N₂ to remove oxygen. All solvents were thoroughly dried and degassed prior to use, and all reactions were carried out under dry N₂ or in the presence of NO or NO₂ with N₂ as a diluent.

I.r. spectra were recorded using a PE297 spectrophotometer

and ¹H n.m.r. spectra obtained using Varian HA100 or JEOL JMN-PMX-60 instruments. ³¹P n.m.r. spectra were obtained using a JEOL FX90 instrument at the University of Sheffield. Analyses were performed by the Microanalytical Laboratories of the Chemistry Department, University of Birmingham.

Reaction of [Pd(C₆H₄NO₂-*p*)I(PPh₃)₂] with NO₂: [Pd(NO₃)₂(OPPh₃)(PPh₃)]—NO₂ was bubbled into a solution of [Pd(C₆H₄NO₂-*p*)I(PPh₃)₂] (0.5 g, 0.57 mmol) in dichloromethane (30 cm³) for 10 min. The mixture was then flushed with N₂ and filtered, the filtrate being evaporated *in vacuo*. The residue was crystallised twice from dichloromethane and n-hexane (the filtrate from the first crystallisation being pale purple). The complex was isolated as orange-yellow microcrystals (yield 0.31 g, 70%).

Reaction of [Pd(Ph)Cl(Ph₂PCH₂CH₂PPh₂)] with NO₂: *cis*-[PdCl(NO₃)(Ph₂PCH₂CH₂PPh₂)]—NO₂ was bubbled through a solution of *cis*-[Pd(Ph)Cl(Ph₂PCH₂CH₂PPh₂)] (0.5 g, 0.71 mmol) in dichloromethane (30 cm³) for 10 min. The solution was purged with N₂ and evaporated *in vacuo*. The resulting orange oil was crystallised from dichloromethane and n-hexane, and the complex obtained as pale yellow crystals which were filtered off and dried *in vacuo* (yield 0.3 g, 70%).

***trans*-[Pt(C₆H₄NO₂-*p*)(NO₃)(PPh₃)₂].—Method 1.** To [Pt(C₆H₄NO₂-*p*)I(PPh₃)₂] (0.25 g, 0.26 mmol) dissolved in chloroform (50 cm³), AgNO₃ (0.09 g, 0.53 mmol) was added and the mixture stirred at room temperature (r.t.) for 2 d. The resulting suspension was filtered and the filtrate treated with n-hexane. The volume of the solution was partially reduced *in vacuo* giving a white solid which was filtered off. This compound was recrystallised from dichloromethane and n-hexane, affording the complex as white needles which were filtered off and dried *in vacuo* (yield 0.19 g, 78%). The complex was isolated with 0.5 mol of dichloromethane of crystallisation [¹H n.m.r. (CDCl₃): δ, 7.7–7.1 (m, 30 H, PPh₃), 7.1–6.6 (A₂B₂ pair, 4 H, C₆H₄NO₂), and 5.28 (s, 1 H, CH₂Cl₂)].

Method 2. NO₂ was passed through a solution of [Pt(C₆H₄NO₂-*p*)I(PPh₃)₂] (0.25 g, 0.26 mmol) in dichloromethane (30 cm³) for 10 min. The mixture was then purged with N₂ and evaporated *in vacuo*, giving a pink-white solid. This was crystallised from dichloromethane–n-hexane mixtures to which

[†] Bis(nitrate-*O*)(triphenylphosphine)(triphenylphosphine oxide)-palladium(II).

Supplementary data available (No. SUP 56573, 7 pp.): H-atom coordinates, thermal parameters, least-squares planes data. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii–xx. Structure factors are available from the editorial office.

a small amount of decolourising charcoal was added. The complex was obtained, after filtration and drying *in vacuo*, as white needles (yield 0.15 g, 61%). The reaction could also be carried out in benzene, and the complex was isolated containing 1 mol of benzene of crystallisation.

trans-[Pt(Ph)(NO₂)(PPh₃)₂].—To [Pt(Ph)I(PPh₃)₂] (1 g, 1.08 mmol) dissolved in chloroform (30 cm³), AgNO₂ (0.21 g, 1.4 mmol) was added and the mixture stirred overnight at room temperature. The resulting suspension was filtered and the filtrate evaporated *in vacuo* to give a white solid. This compound was recrystallised from dichloromethane and *n*-hexane, affording the complex as white microcrystals which were filtered off and dried *in vacuo* (yield 0.85 g, 93%).

[Pt(Ph)(NO₃)(PPh₃)₂].—*Method 1*. The complex was prepared in the same way as its C₆H₄NO₂-*p* analogue by Method 2 above, using [Pt(Ph)I(PPh₃)₂] (0.25 g, 0.27 mmol). The resulting red-brown solution was purged with N₂, evaporated *in vacuo*, and the residue crystallised from dichloromethane-ether-*n*-hexane mixtures to which decolourising charcoal had been added. The complex was filtered off, dried *in vacuo*, and obtained as white microcrystals (yield 0.15 g, 65%).

Method 2. The complex was obtained as in Method 1 for the C₆H₄NO₂-*p* analogue above, using [Pt(Ph)I(PPh₃)₂] (0.4 g, 0.43 mmol) and AgNO₃ (0.12 g, 0.71 mmol) in chloroform (30 cm³) overnight. The complex was recrystallised as in Method 1 above, and was isolated as white microcrystals (yield 0.28 g, 76%).

Method 3. NO₂ was passed through a solution of [Pt(Ph)(NO₂)(PPh₃)₂] (0.25 g, 0.3 mmol) in dichloromethane (30 cm³) for 5–10 min. The resulting solution was purged with N₂, evaporated *in vacuo*, and the residue crystallised as in Method 1. The complex was obtained as white microcrystals (yield 0.18 g, 71%).

Reaction of [Pd(NO₂)₂(PPh₃)₂] with NO₂: [Pd(NO₃)₂(PPh₃)₂].—NO₂ was passed through a solution of [Pd(NO₂)₂(PPh₃)₂] (0.25 g, 0.35 mmol) in dichloromethane (30 cm³) for 10–15 min. The solution was then purged with N₂ and evaporated *in vacuo* leaving a yellow solid which was recrystallised from dichloromethane-*n*-hexane mixtures. The complex was filtered off and dried *in vacuo*, being isolated as a yellow powder (yield 0.24 g, 90%).

Reaction of [Pd(NO₃)₂(PPh₃)₂] with NO: [Pd(NO₂)₂(PPh₃)₂].—NO was passed through a dichloromethane solution (30 cm³) of [Pd(NO₃)₂(PPh₃)₂] (0.5 g, 0.66 mmol) for 20–25 min. The solution was then purged with N₂ and filtered giving a pale yellow solid and an orange-yellow filtrate. The solid was recrystallised from dichloromethane-*n*-hexane mixtures, and dried *in vacuo*, giving [Pd(NO₂)₂(PPh₃)₂] as pale yellow microcrystals (yield 0.17 g, 35%). Evaporation of the filtrate gave an orange-yellow solid which was also recrystallised from dichloromethane-*n*-hexane mixtures, but was shown by i.r. spectroscopy to be a mixture of [Pd(NO₂)₂(PPh₃)₂] and [Pd(NO₃)₂(PPh₃)₂] or a mixed nitro-nitrate species. Separation of the components of this mixture could not be achieved by chromatography on alumina using CH₂Cl₂ as eluant.

Reaction of [Pd(NO₃)₂(PEt₃)₂] with NO: [Pd(NO₂)₂(PEt₃)₂].—NO was passed through a dichloromethane solution (30 cm³) containing [Pd(NO₃)₂(PEt₃)₂] (0.5 g, 1.0 mmol) for 30 min. The solvent was then evaporated *in vacuo* and the residue chromatographed on silica gel using ethyl acetate as eluant. The pale yellow fraction was collected, evaporated *in vacuo* and the

solid recrystallised from dichloromethane-*n*-hexane mixtures. The complex was obtained as a white powder (yield 0.19 g, 41%).

Reaction of [Pt(Ph)(NO₃)(PPh₃)₂] with NO.—NO was passed through a solution of [Pt(Ph)(NO₃)(PPh₃)₂] (0.25 g) in dichloromethane (30 cm³) for 30 min. The solution was then purged with N₂ and evaporated *in vacuo*. The product, which was not purified, was identified by i.r. spectroscopy as a mixture of the starting material and [Pt(Ph)(NO₂)(PPh₃)₂].

Reaction of [Pd(NO₃)₂(PPh₃)₂] with CO: [Pd(NO₂)₂(PPh₃)₂].—CO was passed through a dichloromethane solution (30 cm³) of [Pd(NO₃)₂(PPh₃)₂] (0.75 g) for 1 h at r.t. The solution was then purged with N₂ and filtered to give a pale yellow solid. The [Pd(NO₂)₂(PPh₃)₂] so formed was recrystallised from dichloromethane-*n*-hexane mixtures and dried *in vacuo*. Further product was obtained from the filtrate by its evaporation *in vacuo*, and chromatographing the residue on silica gel using ethyl acetate-*n*-hexane mixtures (70:30 v/v) as eluant. The yellow fraction afforded, on reducing the solution *in vacuo*, the complex as yellow crystals (combined yield 0.35 g, 49%).

Reaction of [Pd(NO₃)₂(PEt₃)₂] with CO: [Pd(NO₂)₂(PEt₃)₂].—The complex was obtained in the same way as its PPh₃ analogue, using [Pd(NO₃)₂(PEt₃)₂] (0.5 g, 1.0 mmol) and was isolated as a white powder (yield 0.26 g, 55%).

Reaction of [Ni(NO₃)₂(PEt₃)₂] with NO: [Ni(NO₃)₂(OPEt₃)₂].—NO was passed through a solution of [Ni(NO₃)₂(PEt₃)₂] (0.5 g, 1.19 mmol) in benzene (30 cm³) for 25 min. During this time the colour of the solution changed from deep green to yellow. On purging the solution with N₂ and adding light petroleum (b.p. 40–60 °C), a yellow solid was precipitated. This was filtered off and recrystallised from benzene-light petroleum giving the complex as yellow prisms (yield 0.25 g, 46%).

Reaction of [Ni(NO₃)₂(PEt₃)₂] with NO₂: [Ni(NO₃)₂(OPEt₃)₂].—The reaction described above was repeated using NO₂ in place of NO. The complex was isolated as described above (yield 0.31 g, 57%).

cis-[Pd(Ph)(NO₂)(Ph₂PCH₂CH₂PPh₂)]·CH₂Cl₂.—[Pd(Ph)Cl(Ph₂PCH₂CH₂PPh₂)]·CH₂Cl₂ (0.5 g, 0.71 mmol) and AgNO₂ (0.14 g, 0.91 mmol) were stirred together in chloroform (30 cm³) for 24 h. The mixture was filtered and the filtrate evaporated *in vacuo*. The residue was crystallised from dichloromethane (*n*-hexane mixtures for the presence of charcoal), affording the complex as pale yellow crystals which were filtered off and dried *in vacuo* (yield 0.43 g, 85%).

Crystal and Molecular Structure Analysis of [Pd(NO₃)₂(OPPh₃)(PPh₃)].—C₃₆H₃₀N₂O₇P₂Pd, *M* = 770.99 (crystallises from dichloromethane and *n*-hexane as irregular, yellow bricks; crystal dimensions 0.39 × 0.23 × 0.24 mm), orthorhombic, *a* = 14.442(6), *b* = 25.618(14), *c* = 18.639(19) Å, *U* = 6 896(8) Å³, *D*_m = 1.47, *D*_c = 1.485 g cm⁻³, *Z* = 8, space group *Pbca* (*D*_{2h}¹⁴, no. 61), Mo-*K*_α radiation (*λ* = 0.710 69 Å), μ(Mo-*K*_α) = 6.70 cm⁻¹, *F*(000) = 3 136.

Three-dimensional *X*-ray diffraction data were collected in the range 3.5 < 2θ < 50° on a Nicolet/Syntex R3 diffractometer by the ω-scan method. 2 608 independent reflections for which *I*/σ(*I*) > 3.0 were corrected for Lorentz and polarisation effects. The structure was solved by standard Patterson and Fourier methods and refined by block-diagonal least squares. Hydrogen atoms were placed in calculated positions (C–H 0.98 Å); their contributions were included in structure factor

Table 1. Atomic positional parameters with estimated standard deviations in parentheses for $[\text{Pd}(\text{NO}_3)_2(\text{PPh}_3)(\text{OPPh}_3)]$

Atom	X/a	Y/b	Z/c	Atom	X/a	Y/b	Z/c
Pd(1)	0.190 08(6)	0.094 31(3)	0.012 52(4)	C(13)	0.189 3(9)	0.259 5(4)	0.098 6(5)
P(1)	0.240 05(23)	0.219 66(11)	0.030 29(14)	C(14)	0.098 9(10)	0.249 8(6)	0.115 6(6)
P(2)	0.213 70(19)	0.008 43(10)	0.010 03(14)	C(15)	0.053 1(12)	0.280 1(7)	0.169 1(8)
O(1)	0.174 9(5)	0.176 2(2)	0.011 3(4)	C(16)	0.104 2(15)	0.320 0(7)	0.200 6(8)
O(2)	0.296 3(5)	0.099 3(3)	-0.058 6(3)	C(17)	0.192 4(15)	0.328 9(5)	0.185 0(7)
O(3)	0.337 7(8)	0.119 5(4)	-0.164 8(5)	C(18)	0.236 4(13)	0.299 9(5)	0.133 6(6)
O(4)	0.191 4(7)	0.116 0(3)	-0.139 8(4)	C(19)	0.208 6(7)	-0.013 6(4)	-0.082 5(5)
O(5)	0.085 3(6)	0.090 1(3)	0.084 9(4)	C(20)	0.284 8(8)	-0.036 3(5)	-0.114 7(6)
O(6)	0.043 4(7)	0.111 3(4)	0.191 0(5)	C(21)	0.279 1(9)	-0.050 7(5)	-0.186 8(6)
O(7)	0.187 7(7)	0.117 4(4)	0.162 3(4)	C(22)	0.198 6(10)	-0.042 5(5)	-0.224 1(5)
N(1)	0.273 5(7)	0.112 0(3)	-0.124 4(4)	C(23)	0.124 1(10)	-0.019 6(5)	-0.193 0(5)
N(2)	0.106 3(8)	0.107 6(4)	0.148 9(4)	C(24)	0.128 8(9)	-0.004 3(5)	-0.121 1(6)
C(1)	0.351 1(9)	0.200 1(4)	0.063 4(6)	C(25)	0.137 3(8)	-0.034 5(4)	0.061 7(5)
C(2)	0.425 1(9)	0.191 6(5)	0.020 0(7)	C(26)	0.143 0(10)	-0.030 3(5)	0.135 7(5)
C(3)	0.509 4(11)	0.176 2(6)	0.044 8(9)	C(27)	0.094 1(11)	-0.067 3(6)	0.177 6(6)
C(4)	0.519 1(12)	0.165 4(6)	0.117 9(10)	C(28)	0.038 7(10)	-0.103 1(6)	0.144 7(7)
C(5)	0.447 8(12)	0.173 1(7)	0.161 9(8)	C(29)	0.029 9(9)	-0.105 0(5)	0.073 0(7)
C(6)	0.362 3(10)	0.189 3(6)	0.136 6(7)	C(30)	0.081 4(8)	-0.071 3(4)	0.029 2(6)
C(7)	0.262 8(9)	0.260 6(4)	-0.048 3(5)	C(31)	0.326 6(7)	-0.005 6(4)	0.047 6(5)
C(8)	0.322 4(12)	0.301 6(5)	-0.046 4(6)	C(32)	0.354 7(9)	-0.057 6(5)	0.055 2(7)
C(9)	0.337 2(13)	0.329 8(5)	-0.109 5(7)	C(33)	0.441 3(10)	-0.067 8(5)	0.086 9(7)
C(10)	0.291 6(13)	0.317 9(5)	-0.170 8(6)	C(34)	0.496 0(10)	-0.027 2(5)	0.112 1(7)
C(11)	0.233 4(11)	0.276 0(5)	-0.171 9(6)	C(35)	0.465 6(9)	0.023 4(5)	0.106 2(7)
C(12)	0.218 1(10)	0.246 6(5)	-0.112 0(6)	C(36)	0.381 1(8)	0.033 7(4)	0.074 1(6)

calculations ($B = 7.0 \text{ \AA}^2$) but no refinement of positional parameters was permitted. Refinement converged at R 0.0541 with allowance for anisotropic thermal motion of all non-hydrogen atoms and for the anomalous scattering of palladium and phosphorus. Table 1 lists the atomic positional parameters with estimated standard deviations. Scattering factors were taken from ref. 11; unit weights were used throughout the refinement; computer programs formed part of the Sheffield X -ray system.

Results and Discussion

(i) *Reactions with NO*.—There was no reaction between pure NO and $[\text{M}(\text{R})\text{I}(\text{PPh}_3)_2]$ ($\text{M} = \text{Pd}$ or Pt , $\text{R} = \text{Ph}$ or $\text{C}_6\text{H}_4\text{NO}_2$ - p) or $[\text{Pd}(\text{Ph})\text{Cl}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)]$ in either dichloromethane or benzene under ambient conditions. Various reaction times were used but even after several hours no new products were identified. This is in marked contrast to the work described by Puddephatt and Thompson³ and Wilkinson and co-workers⁴ who were able to obtain, from Pt^{II} methyls under mild conditions, dinitroplatinum(IV) derivatives.

The reason for this apparent lack of reactivity is not obvious. It could be related to steric factors, since the previous work had used complexes of PMe_2Ph and PEt_3 , but this seems unlikely in view of the ability of $[\text{M}(\text{R})\text{X}(\text{PPh}_3)_2]$ to react with CO *via* an associative process to give metal-acyl derivatives.⁵ It is possible that the metal-aryl-triphenylphosphine complexes are less 'electron rich' than $[\text{PtMe}_2\text{L}_2]$ ($\text{L} = \text{PMe}_2\text{Ph}$ or PEt_3), and this could contribute to reduced reactivity. It is perhaps less surprising that Pd does not react to give Pd^{IV} dinitro derivatives, since Pd^{IV} complexes are significantly less stable than their Pt^{IV} analogues. Indeed, there are very few stable Pd^{IV} complexes containing Pd-C σ bonds, and these involve the electronegative C_6F_5^- group.¹²

(ii) *Reactions with NO₂*.—In studying the reactions of $[\text{M}(\text{R})\text{X}(\text{PPh}_3)_2]$ with NO, it was observed that low yields of new products were formed when small amounts of NO₂ were present in the NO gas [see section (iii)]. Ultimately, it was established that the yield of these products could be significantly increased by carrying out the reaction with NO₂ alone.

Table 2. Analytical data^a (%)

Complex	C	H	N
$[\text{Pd}(\text{NO}_3)_2(\text{OPPh}_3)(\text{PPh}_3)]$	56.0 (56.1)	4.3 (3.9)	3.6 (3.6)
$[\text{PdCl}(\text{NO}_3)(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)]$	52.3 (51.9)	4.1 (4.0)	1.9 (2.3)
$[\text{Pt}(\text{C}_6\text{H}_4\text{NO}_2\text{-}p)(\text{NO}_3)(\text{PPh}_3)_2] \cdot 0.5\text{CH}_2\text{Cl}_2$	54.0 (54.0)	3.5 (3.7)	2.7 (3.0)
$[\text{Pt}(\text{C}_6\text{H}_4\text{NO}_2\text{-}p)(\text{NO}_3)(\text{PPh}_3)_2] \cdot \text{C}_6\text{H}_6$	58.5 (58.7)	4.3 (4.1)	2.7 (2.9)
$[\text{Pt}(\text{Ph})(\text{NO}_3)(\text{PPh}_3)_2]$	^b 58.2 (58.7)	4.3 (4.1)	1.6 (1.6)
	^c 58.6 (58.7)	4.4 (4.1)	1.7 (1.6)
	^d 59.0 (58.7)	3.8 (4.1)	1.9 (1.6)
$[\text{Pt}(\text{Ph})(\text{NO}_2)(\text{PPh}_3)_2]$	59.8 (59.9)	4.1 (4.2)	1.6 (1.7)
$[\text{Pd}(\text{NO}_3)_2(\text{PPh}_3)_2]$	57.3 (57.3)	3.9 (4.0)	3.3 (3.7)
$[\text{Pd}(\text{NO}_3)_2(\text{PEt}_3)_2]$	30.7 (30.9)	6.8 (6.5)	5.9 (6.0)
$[\text{Pd}(\text{Ph})(\text{NO}_3)(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2) \cdot \text{CH}_2\text{Cl}_2]$	55.4 (55.6)	4.4 (4.4)	2.3 (2.0)
$[\text{Pd}(\text{NO}_2)_2(\text{PPh}_3)_2]$	^e 59.7 (59.8)	4.7 (4.2)	2.8 (3.9)
	^f 59.2 (59.8)	4.5 (4.2)	3.0 (3.9)
$[\text{Pd}(\text{NO}_2)_2(\text{PEt}_3)_2]$	^g 32.8 (33.2)	7.1 (7.0)	6.4 (6.4)
	^f 32.9 (33.2)	6.9 (7.0)	6.5 (6.4)
$[\text{Ni}(\text{NO}_3)_2(\text{PEt}_3)_2]$	34.3 (34.4)	7.4 (7.2)	6.6 (6.7)
$[\text{Ni}(\text{NO}_3)_2(\text{OPEt}_3)_2]$	^g 31.8 (32.0)	6.4 (6.7)	6.0 (6.2)
	^h 32.1 (32.0)	6.7 (6.7)	5.9 (6.2)

^a Calculated values in parentheses. ^b By Method 1. ^c By Method 2.

^d By Method 3. ^e From $[\text{Pd}(\text{NO}_3)_2\text{L}_2] + \text{CO}$. ^f From $[\text{Pd}(\text{NO}_3)_2\text{L}_2] + \text{NO}$. ^g From $[\text{Ni}(\text{NO}_3)_2(\text{PEt}_3)_2] + \text{NO}$. ^h From $[\text{Ni}(\text{NO}_3)_2(\text{PEt}_3)_2] + \text{NO}_2$.

Reaction of $[\text{Pd}(\text{C}_6\text{H}_4\text{NO}_2\text{-}p)\text{I}(\text{PPh}_3)_2]$ with NO₂ in dichloromethane afforded orange-yellow crystalline $[\text{Pd}(\text{NO}_3)_2(\text{OPPh}_3)(\text{PPh}_3)]$. After removal of the solid, the filtrate was pale purple, suggesting that I₂ might have been formed in the reaction. The complex was characterised by elemental analysis (Table 2), i.r. (Table 3), and ³¹P n.m.r. spectroscopy (Table 4), and by an X -ray crystallographic examination.

The i.r. spectra of the product established that the $\text{C}_6\text{H}_4\text{-NO}_2$ - p ligand was absent, there being no absorptions in the range 1 560–1 575 cm^{-1} (out-of-plane C–H bending modes) or at 1 500s, 1 340s, 850m, and 825m cm^{-1} , characteristic of the p -NO₂ group. However, new absorptions were present in the regions 1 515s–1 475s, 1 285s–1 260s, 1 020m–965m, and

Table 3. Selected i.r. spectral data for the palladium and platinum complexes

Complex	Frequencies (cm ⁻¹) ^a
[Pd(C ₆ H ₄ NO ₂ - <i>p</i>)I(PPh ₃) ₂]	1 560m (δ C-H; Pd-C ₆ H ₄ NO ₂); 1 500s (ν _{asym} NO ₂); 1 340s (ν _{sym} NO ₂); 850m, 825m (δ ONO)
[Pd(NO ₃) ₂ (PPh ₃) ₂]	1 495—1 480vs (ν _{asym} NO ₂); 1 272s (ν _{sym} NO ₂); 1 000s (ν N-O); 802w (δ ONO)
[Pd(NO ₃) ₂ (OPPh ₃)(PPh ₃)]	1 500—1 480vs (ν _{asym} NO ₂); 1 280s, 1 265m (ν _{sym} NO ₂); 1 145 (ν PO, OPPh ₃); 965m (ν N-O); 795w (δ ONO)
[Pd(Ph)Cl(Ph ₂ PCH ₂ CH ₂ - PPh ₂)]·CH ₂ Cl ₂	1 565m (δ C-H; Pd-C ₆ H ₅)
[PdCl(NO ₃)(Ph ₂ PCH ₂ CH ₂ - PPh ₂)]	1 480—1 470s (ν _{asym} NO ₂); 1 282vs (ν _{sym} NO ₂); 1 000m (ν N-O); 805w (δ ONO)
[Pd(Ph)(NO ₂)(Ph ₂ PCH ₂ CH ₂ - PPh ₂)]·CH ₂ Cl ₂	1 565m (δ C-H; Pd-C ₆ H ₅); 1 385vs (ν _{asym} NO ₂); 1 330s (ν _{sym} NO ₂); 815m (δ ONO)
[Pt(C ₆ H ₄ NO ₂ - <i>p</i>)I(PPh ₃) ₂]	1 560m (δ C-H; Pt-C ₆ H ₄ NO ₂); 1 505s (ν _{asym} NO ₂); 1 340s (ν _{sym} NO ₂); 850m, 825m (δ ONO)
[Pt(C ₆ H ₄ NO ₂ - <i>p</i>)(NO ₃)- (PPh ₃) ₂]	1 560m (δ C-H; Pt-C ₆ H ₄ NO ₂); 1 500s (ν _{asym} NO ₂); ^b 1 475s (ν _{asym} NO ₂); 1 340s (ν _{sym} NO ₂); ^b 1 280s (ν _{sym} NO ₂); 1 000m (ν N-O); 850m, 825m (ν ONO); ^b 798w (δ ONO)
[Pt(Ph)I(PPh ₃) ₂]	1 565m (δ C-H; Pt-C ₆ H ₅)
[Pt(Ph)(NO ₃)(PPh ₃) ₂]	1 572m (δ C-H; Pt-C ₆ H ₅); 1 475s (ν _{asym} NO ₂); 1 280vs (ν _{sym} NO ₂); 1 000m (ν N-O); 798w (δ ONO)
[Pt(Ph)(NO ₂)(PPh ₃) ₂]	1 575m (δ C-H; Pt-C ₆ H ₅); 1 370s (ν _{asym} NO ₂); 1 325s (ν _{sym} NO ₂); 815m (δ ONO)

^a In KBr discs. ^b Assigned to C₆H₄NO₂-*p* group.**Table 4.** ³¹P N.m.r. data

Complex	δ/p.p.m.*	J(Pt-P)/Hz
[Pd(C ₆ H ₄ NO ₂ - <i>p</i>)I(PPh ₃) ₂]	22.6 (s)	—
[Pd(NO ₃) ₂ (PPh ₃) ₂]	32.0 (s)	—
[Pd(NO ₃) ₂ (OPPh ₃)(PPh ₃)]	41.2 (s), 18.9 (s)	—
[Pt(C ₆ H ₄ NO ₂ - <i>p</i>)I(PPh ₃) ₂]	20.2 (t)	2 952
[Pt(Ph)I(PPh ₃) ₂]	21.8 (t)	3 088
[Pt(Ph)(NO ₂)(PPh ₃) ₂]	18.3 (t)	3 177
[Pt(Ph)(NO ₃)(PPh ₃) ₂]	22.3 (t)	3 245

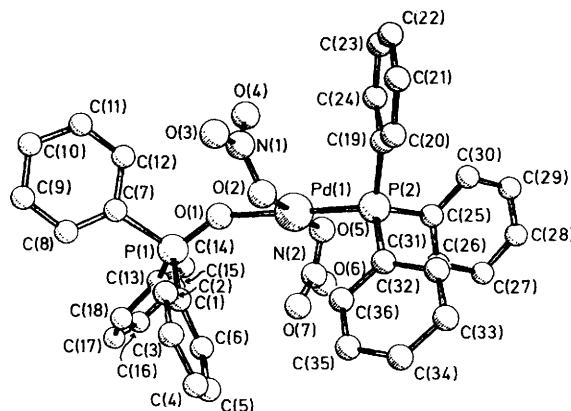
* Measured in CDCl₃ w.r.t. H₃PO₄; s = singlet, t = triplet.

810w—795w cm⁻¹ which are consistent with the presence of monodentate nitrate.¹³ In addition, a band at 1 145 cm⁻¹ was assigned to ν(PO) of co-ordinated Ph₃PO, consistent with data from other triphenylphosphine oxide complexes.¹⁴ The ³¹P n.m.r. spectrum of [Pd(C₆H₄NO₂-*p*)I(PPh₃)₂] revealed a single resonance at δ 22.6 p.p.m. in CDCl₃ [with respect to (w.r.t.) external H₃PO₄] due to two equivalent mutually *trans* PPh₃ ligands. [Pd(NO₃)₂(PPh₃)₂] also exhibited a singlet at δ 32.0 p.p.m., whereas the new compound showed two signals, at δ 41.2 and 18.9 p.p.m., clearly establishing the presence of P nuclei in two different environments. If this species had contained two mutually *cis* PPh₃ ligands, then ²J(P-P) coupling of ca. 15 Hz might have been expected. The ³¹P n.m.r. spectrum could therefore be consistent with the presence of Ph₃PO as one of the ligands.

The nature of the new compound, [Pd(NO₃)₂(OPPh₃)-

Table 5. Selected bond lengths (Å) and angles (°) with estimated standard deviations in parentheses for [Pd(NO₃)₂(OPPh₃)(PPh₃)]

Pd(1)-P(2)	2.227(3)	P(1)-O(1)	1.501(8)
Pd(1)-O(1)	2.109(7)	P(1)-C(1)	1.790(12)
Pd(1)-O(2)	2.031(7)	P(1)-C(7)	1.832(11)
Pd(1)-O(5)	2.031(8)	P(1)-C(13)	1.789(12)
O(2)-N(1)	1.311(12)	P(2)-C(19)	1.816(10)
O(3)-N(1)	1.210(14)	P(2)-C(25)	1.832(11)
O(4)-N(1)	1.224(13)	P(2)-C(31)	1.810(11)
O(5)-N(2)	1.310(12)		
O(6)-N(2)	1.204(14)		
O(7)-N(2)	1.228(13)		
P(2)-Pd(1)-O(1)	176.2(2)	O(1)-P(1)-C(1)	115.8(5)
P(2)-Pd(1)-O(2)	86.2(2)	O(1)-P(1)-C(7)	110.4(5)
P(2)-Pd(1)-O(5)	94.3(2)	O(1)-P(1)-C(13)	109.6(5)
O(1)-Pd(1)-O(2)	90.5(2)	C(1)-P(1)-C(7)	106.0(5)
O(1)-Pd(1)-O(5)	89.0(3)	C(1)-P(1)-C(13)	106.4(5)
O(2)-Pd(1)-O(5)	179.0(3)	C(7)-P(1)-C(13)	108.4(5)
Pd(1)-O(1)-P(1)	132.1(4)	Pd(1)-P(2)-C(19)	108.7(3)
Pd(1)-O(2)-N(1)	115.9(6)	Pd(1)-P(2)-C(25)	119.4(4)
Pd(1)-O(5)-N(2)	114.4(6)	Pd(1)-P(2)-C(31)	109.1(4)
O(2)-N(1)-O(3)	115.5(9)	C(19)-P(2)-C(25)	106.7(5)
O(2)-N(1)-O(4)	118.9(9)	C(19)-P(2)-C(31)	110.0(5)
O(3)-N(1)-O(4)	125.7(10)	C(25)-P(2)-C(31)	102.7(5)
O(5)-N(2)-O(6)	116.5(9)		
O(5)-N(2)-O(7)	118.6(9)		
O(6)-N(2)-O(7)	124.9(10)		
Non-bonded contacts			
Pd(1) ... O(4)	2.893(9)	Pd(1) ... H(36)	2.74
Pd(1) ... O(7)	2.855(9)	Pd(1) ... H(29) (-x, -y, -z)	3.00
Angles associated with non-bonded contacts			
O(4) ... Pd(1) ... O(7)	157.0(2)	O(1)-Pd(1) ... O(4)	78.4(3)
P(2)-Pd(1) ... O(4)	99.7(2)	O(1)-Pd(1) ... O(7)	78.7(3)
P(2)-Pd(1) ... O(7)	103.1(2)	H(36) ... Pd(1)	
		... H(29')	175

**Figure.** Molecular structure of [Pd(NO₃)₂(OPPh₃)(PPh₃)] with atom labelling

(PPh₃), was unambiguously established by a single-crystal X-ray study. The structure of the molecule is illustrated in the Figure with the atom labelling used in corresponding Tables. Selected bond lengths and angles (together with estimated standard deviations) are given in Table 5.

The molecule comprises square-planar co-ordinated palladium(II) with two mutually *trans* O-bonded, unidentate nitrate ligands; the remaining sites are occupied by triphenylphosphine and triphenylphosphine oxide ligands; the bond

angle at the oxygen atom of this latter ligand is 132.1° . The pattern of nitrogen–oxygen bond lengths clearly reflects the donor or terminal natures of the oxygen atoms. The nitrate groups are each closely planar, with small in-plane angular deviations from perfect trigonality; the ligands are orientated in such a way that one of the formally terminal oxygen atoms of each group lies rather close to the palladium (2.89 and 2.85 Å), one above and one below the mean co-ordination plane, but, necessarily, well displaced from the axial sites. The angles at the donor oxygen atoms of these nitrate ligands are rather small and the palladium is displaced (0.19 and 0.29 Å) from the nitrate planes. The phenyl rings are each planar and other geometric features of the ligands are unexceptional. There are two close contacts between the palladium atom and hydrogen atoms on phenyl rings; an intramolecular contact (2.74 Å) to H(36) on the *ortho* carbon atom of a phenyl ring of the triphenylphosphine ligand, this contact being on the same side of the co-ordination plane as that to O(7). The other contact is intermolecular and more distant (3.00 Å) to H(29) ($-x, -y, -z$) on a *meta* carbon atom of a different phenyl ring of the same ligand; this contact being on the same side of the co-ordination plane as O(4). These contacts may be simply regarded as the occupancy of sites in the van der Waals envelope of the complex, but such contacts have long been recognised¹⁵ as of importance in the catalysis of homogeneous hydrogenation.

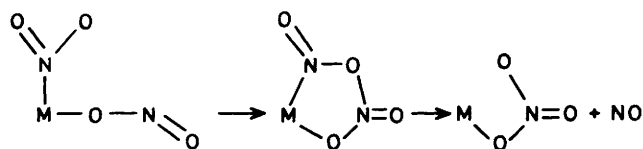
The reaction of *cis*-[Pd(Ph)Cl(PH₂PCH₂CH₂PPh₂)] with NO₂ in dichloromethane similarly resulted in cleavage of the Pd–C bond and formation of *cis*-[PdCl(NO₃)(PH₂PCH₂CH₂PPh₂)]. The i.r. spectrum of this complex showed that the phenyl group was absent but that monodentate NO₃[−] had been formed.

Reaction of *trans*-[Pt(R)I(PPh₃)₂] (R = Ph or C₆H₄NO₂-*p*) with NO₂ afforded the nitrate species [Pt(R)(NO₃)(PPh₃)₂] without cleavage of the Pt–C bond. These complexes could be prepared alternatively by metathetical displacement of I[−] by NO₃[−] using AgNO₃ in chloroform. The i.r. spectra of the nitrate species were consistent with the presence of the aryl ligands and with monodentate NO₃[−]. The ³¹P n.m.r. spectra of [Pt(Ph)I(PPh₃)₂] and [Pt(Ph)(NO₃)(PPh₃)₂] each revealed triplets [¹J(¹⁹⁵Pt–P) *ca.* 3 000 Hz], consistent with two equivalent P nuclei in *trans* configurations.

Thus there is a significant difference between the reactions of related *d*⁸ Pd and Pt aryl complexes with NO₂. The cleavage of Pd–C bonds is not exceptional, since they are generally more reactive than Pt–C bonds, and are known to be readily cleaved by oxidising agents, notably halogens.¹⁶ NO₂ is a fairly strong oxidising agent being comparable, in aqueous solution at least, to bromine.

In the reactions described above, NO₂ was always present in excess, conditions generally comparable to the generation of [PtMe₂(NO₃)₂(PMe₂Ph)₂] from [PtMe₂(PMe₂Ph)₂].³ If insufficient NO₂ was used in the work described here, then a mixture of nitro and nitrate complexes was formed, as indicated by i.r. spectral studies.

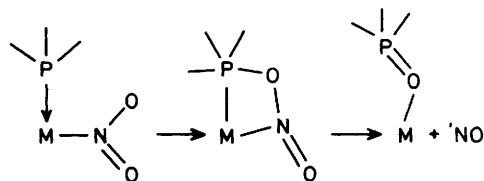
The formation of nitrate products in these reactions could occur *via* an intramolecular oxygen-transfer process involving a cyclic intermediate incorporating co-ordinated nitro and nitrito groups, as depicted in Scheme 1, or *via* a direct O transfer from 'free' NO₂ to a co-ordinated NO₂[−] or ONO[−] ligand. The



Scheme 1.

intramolecular process is analogous to that proposed for the conversion of [Pt(NO)(NO₃)(PPh₃)₂] into [Pt(NO₂)₂(PPh₃)₂].¹⁷ That NO₂ can act as a source of O atoms for the oxygenation of co-ordinated nitrite was demonstrated by the treatment of [Pd(NO₂)₂(PPh₃)₂] and [Pt(Ph)(NO₂)(PPh₃)₂] with NO₂, when [Pd(NO₃)₂(PPh₃)₂] and [Pt(Ph)(NO₃)(PPh₃)₂] were formed. The nature of these complexes was established by elemental analyses and i.r. spectral measurements (which clearly established the presence of NO₃[−] and absence of NO₂[−]) and, indirectly, by ³¹P n.m.r. spectroscopy. The ³¹P n.m.r. spectrum of authentic [Pd(NO₃)₂(PPh₃)₂] was compared with that of the bis-nitrate made as described above, and shown to be identical. It was noted that δ(P) and ¹J(PtP) for [Pt(Ph)(NO₃)(PPh₃)₂] were significantly different to those of its nitro analogue.

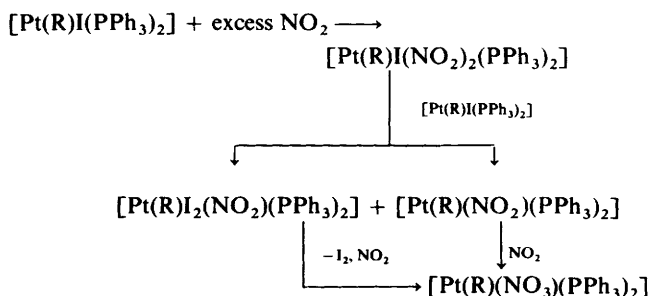
Possible mechanisms for the formation of [Pd(NO₃)₂(OPPh₃)(PPh₃)] from [Pd(C₆H₄NO₂-*p*)(PPh₃)₂] might involve initial addition of NO₂ giving [Pd(C₆H₄NO₂-*p*)(NO₂)₂(PPh₃)₂], analogous to [PtMe₂(NO₂)₂L₂] (L = PMe₂Ph or PEt₃).^{3,4} Reductive elimination of *p*-IC₆H₄NO₂ would then give [Pd(NO₂)₂(PPh₃)₂] which could be further oxygenated by NO₂, as shown, to give [Pd(NO₃)₂(PPh₃)₂]. Such a mechanism does not account for the formation of Ph₃PO, however. The phosphine oxide could arise *via* dissociation of PPh₃ from an intermediate, oxidation of the free ligand by NO₂, and recombination to give co-ordinated Ph₃PO. The oxygenation could also occur in an intramolecular process, *via* a co-ordinated P^V intermediate, as shown in Scheme 2. Such a process is similar to that involving deoxygenation of



Scheme 2.

[Ni(NO₂)₂(PEt₃)₂] by CO, giving [Ni(NO)(NO₂)(PEt₃)₂] and CO₂.¹⁸

The formation of [Pt(R)(NO₃)(PPh₃)₂] might also be expected to proceed *via* the intermediate [Pt(R)I(NO₂)₂(PPh₃)₂]. However, convincing pathways for the degradation of this species to the observed product are difficult to envisage. Scheme 3 would parallel that of the reaction between



Scheme 3.

[PtMe₂(NO₂)₂(PMe₂Ph)₂] and [PtMe₂(PMe₂Ph)₂], which gave [PtMe(NO₂)(PMe₂Ph)₂] and [PtMe₃(NO₂)(PMe₂Ph)₂].³ It is conceivable that [Pt(R)I₂(NO₂)(PPh₃)₂] could

* Reaction of $[\text{Pt}(\text{Ph})(\text{NO}_2)(\text{PPh}_3)_2]$ with I_2 in dichloromethane at r.t. gave uncharacterisable products.

some planar Pd and Pt complexes can be oxygenated by NO_2 to co-ordinated NO_3^- , and that O-transfer to PPh_3 , giving co-ordinated OPPh_3 , can also occur at Pd. Conversely, we have found that, like CO, NO can deoxygenate co-ordinated NO_3^- to NO_2^- . There may therefore be a subtle equilibrium in the reaction system: $\text{M}(\text{NO}_2) + \text{NO}_2 \rightleftharpoons \text{M}(\text{NO}_3) + \text{NO}$. It is also conceivable that certain reactions of NO with low-oxidation state species which give nitro and/or nitrito species¹ may in fact be reactions involving NO_2 present in the NO reagent gas. An example of this behaviour could be the formation of $[\{\text{Co}(\text{NO})_2(\text{NO}_2)\}_n]$ and $[\text{Co}_4(\text{NO})_8(\text{NO}_2)_3(\text{N}_2\text{O}_2)]$ from $[\text{Co}_2(\text{CO})_8]$ or $[\text{Co}(\text{NO})(\text{CO})_3]$ and NO.²²

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