Reaction of NO_2 with Palladium(II) and Platinum(II) Aryl Complexes; The Crystal Structure of *trans*-$[Pd(ONO_2)_2(OPPh_3)(PPh_3)]$†

Christopher J. Jones, Jon A. McCleverty,* and Anne S. Rothin
Department of Chemistry, University of Birmingham, P.O. Box 363, Birmingham B15 2TT
Harry Adams and Neil A. Bailey*
Department of Chemistry, University of Sheffield, Sheffield S3 7HF

$[Pd(C_6H_4NO_2\text{-}p)I(PPh_3)_2]$ and $[Pd(Ph)Cl(Ph_2PCH_2PPh_2)]$ do not react with NO but react with NO_2 to give $[Pd(NO_3)_2(OPPh_3)(PPh_3)]$ and $[PdCl(NO_3)(Ph_2PCH_2CH_2PPh_2)]$ respectively. The structure of $[Pd(NO_3)_2(OPPh_3)(PPh_3)]$ has been confirmed by *X*-ray crystallography, the metal co-ordination polyhedron being planar with *trans* monodentate nitrato groups. Reaction of $[Pt(R)I(PPh_3)_2]$ (R = $C_6H_4NO_2\text{-}p$ or Ph) with NO_2 gave $[Pt(R)(NO_3)(PPh_3)_2]$, species shown spectroscopically to contain monodentate nitrate. Treatment of $[Pd(NO_2)_2(PPh_3)_2]$ with NO_2 gave $[Pd(NO_3)_2(PPh_3)_2]$, while NO or CO caused deoxygenation of $[Pd(NO_3)_2L_2]$ (L = PPh_3 or PEt_3) and $[Pt(Ph)(NO_3)(PPh_3)_2]$ to the nitro species $[Pd(NO_2)_2L_2]$ and $[Pt(Ph)(NO_2)(PPh_3)_2]$. Reaction of $[Ni(NO_3)_2(PEt_3)_2]$ with NO or NO_2 afforded $[Ni(NO_3)_2(OPEt_3)_2]$. The possible mechanisms of these oxygen-transfer reactions are briefly discussed.

A number of d^0, d^8, and d^{10} alkyl[1] and aryl[2] complexes react with NO giving compounds containing the *N*-alkyl- or *N*-aryl-*N*-nitrosohydroxylaminato ligand, $[ONN(R)O]^-$. In contrast, however, it has been reported[3,4] that Pt^{II} alkyls afford only nitro or nitrato derivatives. Thus *cis*-$[PtMe_2L_2]$ (L = PMe_2Ph[3] or PEt_3[4]) reacted with NO giving, initially, *cis,cis,cis*-$[PtMe_2(NO_2)_2L_2]$ which subsequently isomerised and reacted with $[PtMe_2L_2]$ to give *trans*-$[PtMe(NO_2)L_2]$ and *fac*-$[PtMe_3(NO_2)L_2]$ (L = PMe_2Ph). *cis*-$[PtMe_2(PMe_2Ph)_2]$ also reacted with NO_2 giving analogous nitrato complexes and, under different conditions, mixtures of $[PtMe(NO_2)(PMe_2Ph)_2]$ and $[PtMe(NO_3)(PMe_2Ph)_2]$ 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*-$[M(R)X(PPh_3)_2]$ (M = Pd or Pt, R = Ph or $C_6H_4NO_2\text{-}p$, X = Cl or I) with NO and NO_2.

Experimental

The starting materials $[Pt(R)I(PPh_3)_2]$ (R = Ph or $C_6H_4NO_2\text{-}p$),[5] $[Pd(Ph)Cl(PPh_3)_2]$,[6] $[Pd(C_6H_4NO_2\text{-}p)I(PPh_3)_2]$,[7] $[Pd(Ph)Cl(Ph_2PCH_2CH_2PPh_2)]$,[7] and $[Ni(NO_3)_2(PEt_3)_2]$[8] were prepared as described in the literature. The complexes $[Pd(NO_x)_2(PR_3)_2]$ (x = 2 or 3, R = Ph or Et) were obtained by reaction of $[PdCl_2(PR_3)_2]$ with $NaNO_2$ or $AgNO_3$ in chloroform. NO gas was prepared as described elsewhere[9] and purified by passage through KOH pellets and a trap containing molecular sieves cooled at −78 °C. NO_2–N_2O_4 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 N_2O_4 was degassed thoroughly with dry N_2 to remove oxygen. All solvents were thoroughly dried and degassed prior to use, and all reactions were carried out under dry N_2 or in the presence of NO or NO_2 with N_2 as a diluant.

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. ^{31}P 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 $[Pd(C_6H_4NO_2\text{-}p)I(PPh_3)_2]$ *with* NO_2: $[Pd(NO_3)_2(OPPh_3)(PPh_3)]$.—$NO_2$ was bubbled into a solution of $[Pd(C_6H_4NO_2\text{-}p)I(PPh_3)_2]$ (0.5 g, 0.57 mmol) in dichloromethane (30 cm^3) for 10 min. The mixture was then flushed with N_2 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 $[Pd(Ph)Cl(Ph_2PCH_2CH_2PPh_2)]$ *with* NO_2: *cis*-$[PdCl(NO_3)(Ph_2PCH_2CH_2PPh_2)]$.—$NO_2$ was bubbled through a solution of *cis*-$[Pd(Ph)Cl(Ph_2PCH_2CH_2PPh_2)]$ (0.5 g, 0.71 mmol) in dichloromethane (30 cm^3) for 10 min. The solution was purged with N_2 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-$[Pt(C_6H_4NO_2\text{-}p)(NO_3)(PPh_3)_2]$.—*Method 1*. To $[Pt(C_6H_4NO_2\text{-}p)I(PPh_3)_2]$ (0.25 g, 0.26 mmol) dissolved in chloroform (50 cm^3), $AgNO_3$ (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. ($CDCl_3$): δ, 7.7—7.1 (m, 30 H, PPh_3), 7.1—6.6 (A_2B_2 pair, 4 H, $C_6H_4NO_2$), and 5.28 (s, 1 H, CH_2Cl_2)].

Method 2. NO_2 was passed through a solution of $[Pt(C_6H_4NO_2\text{-}p)I(PPh_3)_2]$ (0.25 g, 0.26 mmol) in dichloromethane (30 cm^3) for 10 min. The mixture was then purged with N_2 and evaporated *in vacuo*, giving a pink-white solid. This was crystallised from dichloromethane–n-hexane mixtures to which

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† Bis(nitrato-*O*)(triphenylphosphine)(triphenylphosphine oxide)-palladium(II).

Supplementary data available (No. SUP 56573, 7 pp.): H-atom co-ordinates, 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)(NO_2)(PPh_3)$_2$].—To [Pt(Ph)I(PPh_3)$_2$] (1 g, 1.08 mmol) dissolved in chloroform (30 cm^3), $AgNO_2$ (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)(NO_3)(PPh_3)$_2$].—*Method 1.* The complex was prepared in the same way as its $C_6H_4NO_2$-*p* analogue by Method 2 above, using [Pt(Ph)I(PPh_3)$_2$] (0.25 g, 0.27 mmol). The resulting red-brown solution was purged with N_2, 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 $C_6H_4NO_2$-*p* analogue above, using [Pt(Ph)I(PPh_3)$_2$] (0.4 g 0.43 mmol) and $AgNO_3$ (0.12 g, 0.71 mmol) in chloroform (30 cm^3) overnight. The *complex* was recrystallised as in Method 1 above, and was isolated as white microcrystals (yield 0.28 g, 76%).

Method 3. NO_2 was passed through a solution of [Pt(Ph)(NO_2)(PPh_3)$_2$] (0.25 g, 0.3 mmol) in dichloromethane (30 cm^3) for 5—10 min. The resulting solution was purged with N_2, 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(NO_2)$_2$(PPh_3)$_2$] *with* NO_2: [Pd(NO_3)$_2$(PPh_3)$_2$].—NO_2 was passed through a solution of [Pd(NO_2)$_2$(PPh_3)$_2$] (0.25 g, 0.35 mmol) in dichloromethane (30 cm^3) for 10—15 min. The solution was then purged with N_2 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(NO_3)$_2$(PPh_3)$_2$] *with* NO: [Pd(NO_2)$_2$(PPh_3)$_2$].—NO was passed through a dichloromethane solution (30 cm^3) of [Pd(NO_3)$_2$(PPh_3)$_2$] (0.5 g, 0.66 mmol) for 20—25 min. The solution was then purged with N_2 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(NO_2)$_2$(PPh_3)$_2$] 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(NO_2)$_2$(PPh_3)$_2$] and [Pd(NO_3)$_2$(PPh_3)$_2$] or a mixed nitro–nitrato species. Separation of the components of this mixture could not be achieved by chromatography on alumina using CH_2Cl_2 as eluant.

Reaction of [Pd(NO_3)$_2$(PEt_3)$_2$] *with* NO: [Pd(NO_2)$_2$(PEt_3)$_2$].—NO was passed through a dichloromethane solution (30 cm^3) containing [Pd(NO_3)$_2$(PEt_3)$_2$] (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)(NO_3)(PPh_3)$_2$] *with* NO.—NO was passed through a solution of [Pt(Ph)(NO_3)(PPh_3)$_2$] (0.25 g) in dichloromethane (30 cm^3) for 30 min. The solution was then purged with N_2 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)(NO_2)(PPh_3)$_2$].

Reaction of [Pd(NO_3)$_2$(PPh_3)$_2$] *with* CO: [Pd(NO_2)$_2$(PPh_3)$_2$].—CO was passed through a dichloromethane solution (30 cm^3) of [Pd(NO_3)$_2$(PPh_3)$_2$] (0.75 g) for 1 h at r.t. The solution was then purged with N_2 and filtered to give a pale yellow solid. The [Pd(NO_2)$_2$(PPh_3)$_2$] 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(NO_3)$_2$(PEt_3)$_2$] *with* CO: [Pd(NO_2)$_2$(PEt_3)$_2$].—The *complex* was obtained in the same way as its PPh_3 analogue, using [Pd(NO_3)$_2$(PEt_3)$_2$] (0.5 g, 1.0 mmol) and was isolated as a white powder (yield 0.26 g, 55%).

Reaction of [Ni(NO_3)$_2$(PEt_3)$_2$] *with* NO: [Ni(NO_3)$_2$($OPEt_3$)$_2$].—NO was passed through a solution of [Ni(NO_3)$_2$(PEt_3)$_2$] (0.5 g, 1.19 mmol) in benzene (30 cm^3) for 25 min. During this time the colour of the solution changed from deep green to yellow. On purging the solution with N_2 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(NO_3)$_2$(PEt_3)$_2$] *with* NO_2: [Ni(NO_3)$_2$($OPEt_3$)$_2$].—The reaction described above was repeated using NO_2 in place of NO. The *complex* was isolated as described above (yield 0.31 g, 57%).

cis-[Pd(Ph)(NO_2)($Ph_2PCH_2CH_2PPh_2$)]·CH_2Cl_2.—[Pd(Ph)Cl($Ph_2PCH_2CH_2PPh_2$)]·CH_2Cl_2 (0.5 g, 0.71 mmol) and $AgNO_2$ (0.14 g, 0.91 mmol) were stirred together in chloroform (30 cm^3) 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(NO_3)$_2$($OPPh_3$)(PPh_3)].—$C_{36}H_{30}N_2O_7P_2Pd$, 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) Å^3, D_m = 1.47, D_c = 1.485 g cm^{-3}, Z = 8, space group *Pbca* (D_{2h}^{15}, no. 61), Mo-K_α radiation ($\bar{\lambda}$ = 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 $3.5 < 2\theta < 50°$ on a Nicolet/Syntex R3 diffractometer by the ω-scan method. 2 608 Independent reflections for which $I/\sigma(I) > 3.0$ 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 $[Pd(NO_3)_2(PPh_3)(OPPh_3)]$

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

calculations (B = 7.0 Å^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 $[M(R)I(PPh_3)_2]$ (M = Pd or Pt, R = Ph or $C_6H_4NO_2$-*p*) or $[Pd(Ph)Cl(Ph_2PCH_2CH_2PPh_2)]$ 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 Thompson[3] and Wilkinson and co-workers[4] 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 $[M(R)X(PPh_3)_2]$ 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 $[PtMe_2L_2]$ (L = PMe_2Ph 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* NO_2.—In studying the reactions of $[M(R)X(PPh_3)_2]$ with NO, it was observed that low yields of new products were formed when small amounts of NO_2 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 NO_2 alone.

Table 2. Analytical data[a] (%)

Complex	C	H	N
$[Pd(NO_3)_2(OPPh_3)(PPh_3)]$	56.0 (56.1)	4.3 (3.9)	3.6 (3.6)
$[PdCl(NO_3)(Ph_2PCH_2CH_2PPh_2)]$	52.3 (51.9)	4.1 (4.0)	1.9 (2.3)
$[Pt(C_6H_4NO_2\text{-}p)(NO_3)(PPh_3)_2]\cdot 0.5CH_2Cl_2$	54.0 (54.0)	3.5 (3.7)	2.7 (3.0)
$[Pt(C_6H_4NO_2\text{-}p)(NO_3)(PPh_3)_2]\cdot C_6H_6$	58.5 (58.7)	4.3 (4.1)	2.7 (2.9)
$[Pt(Ph)(NO_3)(PPh_3)_2]$	[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)
$[Pt(Ph)(NO_2)(PPh_3)_2]$	59.8 (59.9)	4.1 (4.2)	1.6 (1.7)
$[Pd(NO_3)_2(PPh_3)_2]$	57.3 (57.3)	3.9 (4.0)	3.3 (3.7)
$[Pd(NO_3)_2(PEt_3)_2]$	30.7 (30.9)	6.8 (6.5)	5.9 (6.0)
$[Pd(Ph)(NO_2)(Ph_2PCH_2CH_2PPh_2)]\cdot CH_2Cl_2$	55.4 (55.6)	4.4 (4.4)	2.3 (2.0)
$[Pd(NO_2)_2(PPh_3)_2]$	[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)
$[Pd(NO_2)_2(PEt_3)_2]$	[e]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)
$[Ni(NO_3)_2(PEt_3)_2]$	34.3 (34.4)	7.4 (7.2)	6.6 (6.7)
$[Ni(NO_3)_2(OPEt_3)_2]$	[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 $[Pd(NO_3)_2L_2]$ + CO. [f] From $[Pd(NO_3)_2L_2]$ + NO. [g] From $[Ni(NO_3)_2(PEt_3)_2]$ + NO. [h] From $[Ni(NO_3)_2(PEt_3)_2]$ + NO_2.

Reaction of $[Pd(C_6H_4NO_2\text{-}p)I(PPh_3)_2]$ with NO_2 in dichloromethane afforded orange-yellow crystalline $[Pd(NO_3)_2(OPPh_3)(PPh_3)]$. After removal of the solid, the filtrate was pale purple, suggesting that I_2 might have been formed in the reaction. The complex was characterised by elemental analysis (Table 2), i.r. (Table 3), and ^{31}P n.m.r. spectroscopy (Table 4), and by an *X*-ray crystallographic examination.

The i.r. spectra of the product established that the $C_6H_4NO_2$-*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*-NO_2 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]
$[Pd(C_6H_4NO_2\text{-}p)I(PPh_3)_2]$	1 560m (δ C–H; Pd–$C_6H_4NO_2$); 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)
$[Pd(Ph)Cl(Ph_2PCH_2CH_2\text{-}PPh_2)]\cdot CH_2Cl_2$	1 565m (δ C–H; Pd–C_6H_5)
$[PdCl(NO_3)(Ph_2PCH_2CH_2\text{-}PPh_2)]$	1 480—1 470s (ν_{asym} NO_2); 1 282vs (ν_{sym} NO_2); 1 000m (ν N–O); 805w (δ ONO)
$[Pd(Ph)(NO_2)(Ph_2PCH_2CH_2\text{-}PPh_2)]\cdot CH_2Cl_2$	1 565m (δ C–H; Pd–C_6H_5); 1 385vs (ν_{asym} NO_2); 1 330s (ν_{sym} NO_2); 815m (δ ONO)
$[Pt(C_6H_4NO_2\text{-}p)I(PPh_3)_2]$	1 560m (δ C–H, Pt–$C_6H_4NO_2$); 1 505s (ν_{asym} NO_2); 1 340s (ν_{sym} NO_2); 850m, 825m (δ ONO)
$[Pt(C_6H_4NO_2\text{-}p)(NO_3)\text{-}(PPh_3)_2]$	1 560m (δ C–H, Pt–$C_6H_4NO_2$); 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_6H_5)
$[Pt(Ph)(NO_3)(PPh_3)_2]$	1 572m (δ C–H, Pt–C_6H_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_6H_5); 1 370s (ν_{asym} NO_2); 1 325s (ν_{sym} NO_2); 815m (δ ONO)

[a] In KBr discs. [b] Assigned to $C_6H_4NO_2\text{-}p$ group.

Table 4. ^{31}P N.m.r. data

Complex	δ/p.p.m.*	J(Pt–P)/Hz
$[Pd(C_6H_4NO_2\text{-}p)I(PPh_3)_2]$	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)	—
$[Pt(C_6H_4NO_2\text{-}p)I(PPh_3)_2]$	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 $CDCl_3$ w.r.t. H_3PO_4; s = singlet, t = triplet.

Table 5. Selected bond lengths (Å) and angles (°) with estimated standard deviations in parentheses for $[Pd(NO_3)_2(OPPh_3)(PPh_3)]$

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

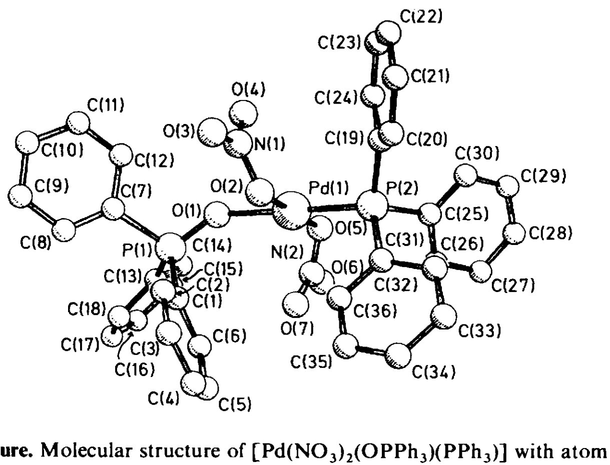


Figure. Molecular structure of $[Pd(NO_3)_2(OPPh_3)(PPh_3)]$ with atom labelling

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 Ph_3PO, consistent with data from other triphenylphosphine oxide complexes.[14] The ^{31}P n.m.r. spectrum of $[Pd(C_6H_4NO_2\text{-}p)I(PPh_3)_2]$ revealed a single resonance at δ 22.6 p.p.m. in $CDCl_3$ [with respect to (w.r.t.) external H_3PO_4] due to two equivalent mutually *trans* PPh_3 ligands. $[Pd(NO_3)_2(PPh_3)_2]$ 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* PPh_3 ligands, then ^2J(P–P) coupling of *ca.* 15 Hz might have been expected. The ^{31}P n.m.r. spectrum could therefore be consistent with the presence of Ph_3PO as one of the ligands.

The nature of the new compound, $[Pd(NO_3)_2(OPPh_3)(PPh_3)]$, 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 recognised[15] as of importance in the catalysis of homogeneous hydrogenation.

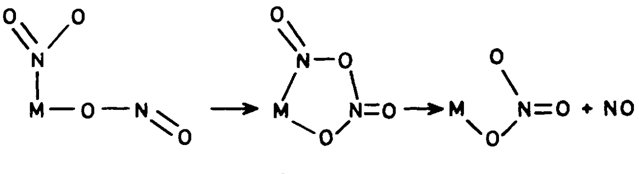
The reaction of *cis*-$[Pd(Ph)Cl(Ph_2PCH_2CH_2PPh_2)]$ with NO_2 in dichloromethane similarly resulted in cleavage of the Pd–C bond and formation of *cis*-$[PdCl(NO_3)(Ph_2PCH_2CH_2PPh_2)]$. The i.r. spectrum of this complex showed that the phenyl group was absent but that monodentate NO_3^- had been formed.

Reaction of *trans*-$[Pt(R)I(PPh_3)_2]$ (R = Ph or $C_6H_4NO_2$-*p*) with NO_2 afforded the nitrato species $[Pt(R)(NO_3)(PPh_3)_2]$ without cleavage of the Pt–C bond. These complexes could be prepared alternatively by metathetical displacement of I^- by NO_3^- using $AgNO_3$ in chloroform. The i.r. spectra of the nitrato species were consistent with the presence of the aryl ligands and with monodentate NO_3^-. The ^{31}P n.m.r. spectra of $[Pt(Ph)I(PPh_3)_2]$ and $[Pt(Ph)(NO_3)(PPh_3)_2]$ each revealed triplets [$^1J(^{195}Pt–P)$ *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 NO_2. 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] NO_2 is a fairly strong oxidising agent being comparable, in aqueous solution at least, to bromine.

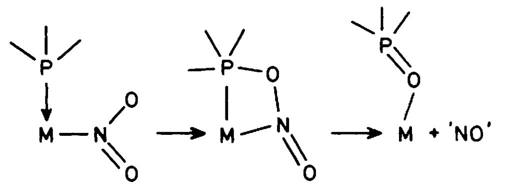
In the reactions described above, NO_2 was always present in excess, conditions generally comparable to the generation of $[PtMe_2(NO_3)_2(PMe_2Ph)_2]$ from $[PtMe_2(PMe_2Ph)_2]$.[3] If insufficient NO_2 was used in the work described here, then a mixture of nitro and nitrato complexes was formed, as indicated by i.r. spectral studies.

The formation of nitrato 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' NO_2 to a co-ordinated NO_2^- or ONO^- ligand. The intramolecular process is analogous to that proposed for the conversion of $[Pt(NO)(NO_3)(PPh_3)_2]$ into $[Pt(NO_2)_2(PPh_3)_2]$.[17] That NO_2 can act as a source of O atoms for the oxygenation of co-ordinated nitrite was demonstrated by the treatment of $[Pd(NO_2)_2(PPh_3)_2]$ and $[Pt(Ph)(NO_2)(PPh_3)_2]$ with NO_2, when $[Pd(NO_3)_2(PPh_3)_2]$ and $[Pt(Ph)(NO_3)(PPh_3)_2]$ were formed. The nature of these complexes was established by elemental analyses and i.r. spectral measurements (which clearly established the presence of NO_3^- and absence of NO_2^-) and, indirectly, by ^{31}P n.m.r. spectroscopy. The ^{31}P n.m.r. spectrum of authentic $[Pd(NO_3)_2(PPh_3)_2]$ 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 $[Pt(Ph)(NO_3)(PPh_3)_2]$ were significantly different to those of its nitro analogue.



Scheme 1.

Possible mechanisms for the formation of $[Pd(NO_3)_2(OPPh_3)(PPh_3)]$ from $[Pd(C_6H_4NO_2\text{-}p)I(PPh_3)_2]$ might involve initial addition of NO_2 giving $[Pd(C_6H_4NO_2\text{-}p)I(NO_2)_2(PPh_3)_2]$, analogous to $[PtMe_2(NO_2)_2L_2]$ (L = PMe_2Ph or PEt_3).[3,4] Reductive elimination of *p*-$IC_6H_4NO_2$ would then give $[Pd(NO_2)_2(PPh_3)_2]$ which could be further oxygenated by NO_2, as shown, to give $[Pd(NO_3)_2(PPh_3)_2]$. Such a mechanism does not account for the formation of Ph_3PO, however. The phosphine oxide could arise *via* dissociation of PPh_3 from an intermediate, oxidation of the free ligand by NO_2, and recombination to give co-ordinated Ph_3PO. 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 $[Ni(NO_2)_2(PEt_3)_2]$ by CO, giving $[Ni(NO)(NO_2)(PEt_3)_2]$ and CO_2.[18]



Scheme 2.

The formation of $[Pt(R)(NO_3)(PPh_3)_2]$ might also be expected to proceed *via* the intermediate $[Pt(R)I(NO_2)_2(PPh_3)_2]$. 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 $[PtMe_2(NO_2)_2(PMe_2Ph)_2]$ and $[PtMe_2(PMe_2Ph)_2]$, which gave $[PtMe(NO_2)(PMe_2Ph)_2]$ and $[PtMe_3(NO_2)(PMe_2Ph)_2]$.[3] It is conceivable that $[Pt(R)I_2(NO_2)(PPh_3)_2]$ could

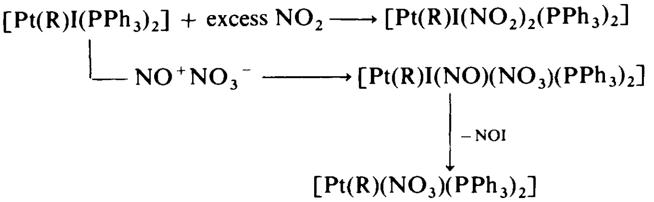
$$\begin{tikzcd}
{[Pt(R)I(PPh_3)_2] + \text{excess } NO_2} \arrow[r] & {[Pt(R)I(NO_2)_2(PPh_3)_2]} \arrow[dl] \arrow[d, "{[Pt(R)I(PPh_3)_2]}"] \\
{[Pt(R)I_2(NO_2)(PPh_3)_2]} \arrow[dr, "{-I_2, NO_2}"'] & {+\ [Pt(R)(NO_2)(PPh_3)_2]} \arrow[d, "NO_2"] \\
 & {[Pt(R)(NO_3)(PPh_3)_2]}
\end{tikzcd}$$

Scheme 3.

undergo specific reductive elimination of I_2, analogous to the loss of ethane from $[PtMe_3(NO_2)(PMe_2Ph)_2]$ and, of course, the nitro species so formed would be readily oxygenated by NO_2 to the isolated nitrato products as demonstrated by us.

In an attempt to probe the viability of $[Pt(R)I_2(NO_2)(PPh_3)_2]$ as an intermediate, we treated $[Pt(Ph)(NO_2)(PPh_3)_2]$ with I_2 in benzene at room temperature. We were unable fully to characterise the product isolated, but i.r. spectral data indicated that the phenyl group had been lost (absence of absorptions at 1 565 cm^{-1}) and that NO_2^- was still present, suggesting that $[PtI_x(NO_2)(PPh_3)_2]$ (x = 1 or 3) had been formed. This suggests that if $[Pt(R)I_2(NO_2)(PPh_3)_2]$ is an intermediate then it would be more likely reductively to eliminate RI than I_2. However, the reactions were carried out under different conditions of solvent and reagents.*

A second mechanism, Scheme 4, could involve the intermediacy of $[Pt(R)I(NO)(NO_3)(PPh_3)_2]$. This nitrosyl nitrate could arise by an intramolecular O-transfer reaction, *viz.* $Pt(NO_2)_2 \longrightarrow Pt(NO)(NO_3)$, although this is the reverse of that involving conversion of $[Pt(NO)(NO_3)(PPh_3)_2]$ into $[Pt(NO_2)_2(PPh_3)_2]$.[17]



$$\begin{tikzcd}
{[Pt(R)I(PPh_3)_2] + \text{excess } NO_2} \arrow[r] \arrow[d, dash] & {[Pt(R)I(NO_2)_2(PPh_3)_2]} \\
{NO^+NO_3^-} \arrow[r] & {[Pt(R)I(NO)(NO_3)(PPh_3)_2]} \arrow[d, "-NOI"] \\
 & {[Pt(R)(NO_3)(PPh_3)_2]}
\end{tikzcd}$$

Scheme 4.

Alternatively, the putative nitrosyl nitrate could arise by addition of N_2O_4 as $NO^+NO_3^-$ or $ONONO_2$, as implied in the formation of $[Pt(NO)(NO_3)(PPh_3)_2]$ from reaction of $[Pt(C_2H_4)(PPh_3)_2]$ with N_2O_4.[19] In an effort to examine the stability of nitrosyl aryl complexes, we treated $[Pt(Ph)I(PPh_3)_2]$ with NOCl and $NO^+PF_6^-$. With nitrosyl chloride, assuming that an intermediate adduct could be formed, we expected $[Pt(Ph)Cl(PPh_3)_2]$ to be the ultimate product, but we could observe no reaction after 10—15 min in dichloromethane at room temperature, nor could we detect any new product after work-up of the reaction mixture. Reaction did occur between $[Pt(Ph)I(PPh_3)_2]$ and $NO^+PF_6^-$ in acetonitrile but we were unable fully to characterise the product. I.r. studies revealed co-ordinated MeCN [ν(CN) 2 300 cm^{-1}] and the presence of PF_6^- [ν(PF) 875 cm^{-1}], as well as the absence of NO. 'Oxidation' of organometallic species by $NO^+PF_6^-$ in acetonitrile, with incorporation of MeCN but not NO^+, has been described previously.[20]

Finally, it is possible that radical substitution pathways are involved, in which I is displaced by NO_2 giving $[Pt(R)(NO_2)(PPh_3)_2]$ directly.

(iii) *Oxygen-transfer Reactions of Palladium and Nickel Complexes.*—As mentioned in sections (i) and (ii), there was no reaction between $[Pd(C_6H_4NO_2\text{-}p)I(PPh_3)_2]$ and NO, but new products were observed when NO_2 was present in the NO gas stream. In a reinvestigation of this reaction, following our successful identification of $[Pd(NO_3)_2(OPPh_3)(PPh_3)]$ as the product of the reaction of the aryl iodo complex with pure NO_2, we obtained a yellow solid from dichloromethane saturated with an NO–NO_2 mixture. An i.r. spectral examination showed that this solid was a mixture of nitro and nitrato species, that some oxidation of PPh_3 to Ph_3PO had occurred, and that the $C_6H_4NO_2\text{-}p$ group had been lost. A ^{31}P n.m.r. spectrum of the mixture in $CDCl_3$ showed three resonances, at δ 40.0, 21.6, and 18.4 p.p.m. (w.r.t. external H_3PO_4). The signals at 40.0 and 18.4 p.p.m. are very close to those observed for authentic $[Pd(NO_3)_2(OPPh_3)(PPh_3)]$ (δ 41.2 and 18.9 p.p.m.) and this indicates that this, or some very similar species, is present in the mixture. The other signal, at 21.6 p.p.m., could not be assigned, but may be due to $[Pd(NO_2)_x(NO_3)_{2-x}(OPPh_3)_y(PPh_3)_{2-y}]$. It would seem that, in this reaction, there is insufficient NO_2 to cause full oxygenation of the intermediate nitro species to the final nitrato complexes.

It is conceivable that NO, either present in a reagent gas mixture, or generated as a by-product of reaction, could function as a deoxygenating agent in a manner similar to CO, *viz.* $[Ni(NO_2)_2L_2X] + CO \longrightarrow [Ni(NO)L_2X] + CO_2$ (L = tertiary phosphine, X = halide).[21] Thus, treatment of $[Pd(NO_3)_2L_2]$ (L = PPh_3 or PEt_3) and $[Pd(Ph)(NO_3)(PPh_3)_2]$ with NO in dichloromethane afforded, after *ca.* 30 min, a mixture of species including $[Pd(NO_2)_2L_2]$ and $[Pd(Ph)(NO_2)(PPh_3)_2]$ (characterised by i.r. spectroscopy). This demonstrates that NO can indeed abstract O atoms from co-ordinated nitrate, presumably being itself converted to NO_2. This is the reverse of the reaction depicted in Scheme 1.

Reaction of $[Pd(NO_3)_2L_2]$ (L = PPh_3 or PEt_3) with CO in dichloromethane under ambient conditions afforded reasonably good yields of $[Pd(NO_2)_2L_2]$ but although we expected that $[Pd(NO_2)_2L_2]$ would undergo further reactions with CO giving nitrosyl complexes and, possibly, isocyanato derivatives, as described in the reactions of $[Pt(NO_3)_2(PEt_3)_2]$,[17] this was not observed. Further deoxygenation of NO_2^- by CO may require more vigorous conditions than we employed.

These reactions contrast with those of $[Ni(NO_3)_2(PEt_3)_2]$ which was reported[18] to react with NO in benzene after 10 min forming $[Ni(NO_3)_2(OPEt_3)_2]$. This reaction does indeed occur, although we found it took 25—30 min to effect complete conversion. The differing reactivity may be related to a structural difference between $[Ni(NO_3)_2L_2]$ (tetrahedral) and $[M(NO_3)_2L_2]$ (M = Pd or Pt; planar). However, $[Ni(NO_3)_2(PEt_3)_2]$ reacted instantly with NO_2 in benzene giving $[Ni(NO_3)_2(OPEt_3)_2]$, whereas treatment with O_2 gave only partial conversion to the phosphine oxide complex after 7—8 h.

When $[Pd(NO_3)_2(PPh_3)_2]$ was refluxed in dry toluene for 2—3 h, an orange-yellow solid could be obtained. I.r. spectral examinations of this material showed it to contain nitro groups (1 330 and 822 cm^{-1}) and some co-ordinated Ph_3PO (1 135 cm^{-1}). The product was difficult to purify and reproducible microanalytical data could not be obtained. The ^{31}P n.m.r. spectrum of the complex showed a sharp singlet at δ 23.0 p.p.m. in $CDCl_3$ (w.r.t. external H_3PO_4), and a number of peaks of very low intensity, presumably due to minor products or impurities. This major peak does not correspond to that in $[Pd(NO_2)_2(PPh_3)_2]$ or $[Pd(NO_3)_2(OPPh_3)(PPh_3)_2]$ but may be due to $[Pd(NO_2)_x(NO_3)_{2-x}(OPPh_3)_y(PPh_3)_{2-y}]$ where x = 1 or 2, *i.e.* a species related to but different from that obtained as one of the products of the reaction of NO + NO_2 with $[Pd(C_6H_4NO_2\text{-}p)I(PPh_3)_2]$.

Conclusions

While it is clear that NO does not react with $[M(R)X(PPh_3)_2]$ (M = Pd or Pt, R = Ph or $C_6H_4NO_2\text{-}p$, X = I or Cl) under ambient conditions, NO_2 does, but giving differing products depending on M. The different reaction pathways may be related to the stability of the presumed intermediate $[M(R)X(NO_2)_2(PPh_3)_2]$. We have shown that co-ordinated NO_2^- in

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* Reaction of $[Pt(Ph)(NO_2)(PPh_3)_2]$ 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: $\mathrm{M(NO_2) + NO_2 \rightleftharpoons M(NO_3) + NO}$. It is also conceivable that certain reactions of NO with low-oxidation state species which give nitro and/or nitrito species[1] may in fact be reactions involving NO_2 present in the NO reagent gas. An example of this behaviour could be the formation of $[\{Co(NO)_2(NO_2)\}_n]$ and $[Co_4(NO)_8(NO_2)_3(N_2O_2)]$ from $[Co_2(CO)_8]$ or $[Co(NO)(CO)_3]$ and NO.[22]

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