Transition-metal–Carbon Bonds. Part 46.[1] Cyclopalladation and Cycloplatination of N-Alkyl-N-nitrosoanilines

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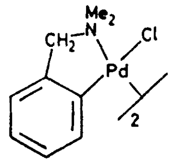
N-Methyl-N-nitrosobenzylamine (Q) is not cyclo-(*ortho*-)palladated by $Na_2[PdCl_4]$ but gives a complex of type $[PdCl_2Q_2]$. In contrast N-methyl-N-nitrosoaniline is readily *ortho* palladated to give the chloro-bridged complex $[Pd_2\{(NO)N(CH_3)C_6H_4\}Cl_2]$ (4a). This was converted into a mononuclear acetylacetonate (5a) and into species $[Pd\{(NO)N(CH_3)C_6H_4\}ClL]$, L = PPh_3 (crystal structure determined), PMe_2Ph, or pyridine, (6a), (6b), or (6c) respectively. With two moles of PPh_3 per palladium the Pd–NO bond is broken giving the σ-aryl species $[Pd\{C_6H_4N(NO)CH_3\}Cl(PPh_3)_2]$ (7a), the crystal structure of which has also been determined. With 1,2-bis(diphenylphosphino)ethane (dppe), (4a) gives the ion $[Pd\{(NO)N(CH_3)C_6H_4\}(dppe)]^+$ isolated as its tetraphenylborate salt (8a). Some palladated derivatives of N-ethyl-N-nitrosoaniline and (4-methoxy)-N-methyl-N-nitrosoaniline were made similarly. With $K_2[PtCl_4]$ N-methyl-N-nitrosoaniline gives a red material which was not obtained pure but which gave a mononuclear acetylacetonate $[Pt\{(NO)N(CH_3)C_6H_4\}(acac)]$ (5c) and bis-phosphine complex $[Pt\{C_6H_4N(NO)CH_3\}Cl(PPh_3)_2]$ (7d) analogous to the palladium complex. N-Ethyl-N-nitrosoaniline reacted similarly. Crystals of (6a) are triclinic, space group $P\bar{1}$, with a = 9.990(2), b = 15.195(3), c = 9.276(2) Å, α = 104.05(2), β = 97.92(2), γ = 89.47(2)°, and Z = 2. Those of (7a) are monoclinic, space group $P2_1/c$, with a = 12.047(2), b = 21.794(4), c = 16.402(2) Å, β = 108.54(1)°, and Z = 4. Both compounds crystallise with a molecule of CH_2Cl_2. Least-squares refinements gave final R values of 0.089 for (6a) and 0.083 for (7a).

COPE and FRIEDRICH[2] showed that N,N-dimethylbenzylamine was rapidly cyclopalladated with $Li_2[PdCl_4]$ to give (1). Since then cyclopalladation of tertiary amines has been used extensively in organic syntheses including natural products.[3,4] However, it was shown [2,5] that benzylamine or N-methylbenzylamine did not cyclopalladate but gave only complexes of the type $[PdCl_2(amine)_2]$. Since secondary amines are very readily converted to their N-nitroso-derivatives with nitrous acid we have investigated the possibility of cyclopalladating such derivatives. Since the N-nitroso-group is readily removed, *e.g.* by zinc and acetic acid, this could be, in effect, a method of cyclopalladating a secondary amine.† However, spectral evidence on free N-nitrosamines shows the existence of *syn* and *anti* isomers due to restricted rotation around the N–N bond indicating that the dipolar resonant structure (2) makes a significant contribution to the overall structure.[6-8] Thus although there are three potential co-ordinating atoms on an N-nitrosamine ligand the 'amine' nitrogen might be expected to be poorly co-ordinating whereas either the nitrogen or the oxygen of the NO group could be co-ordinated. Brown and Coates[9] prepared complexes of the type *trans*-$[Pd(R_2NNO)_2Cl_2]$ (R = Me, Et, or Bu^n) and suggested that the oxygen was the donor atom, although a crystal-structure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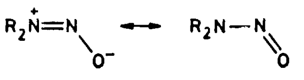

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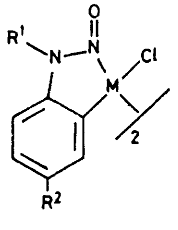
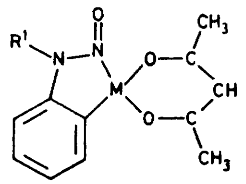
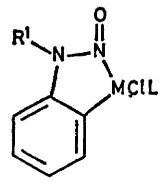


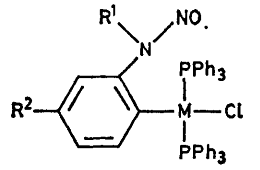
(4a) R¹ = CH₃, R² = H, M = Pd
(4b) R¹ = C₂H₅, R² = H, M = Pd
(4c) R¹ = CH₃, R² = OCH₃, M = Pd



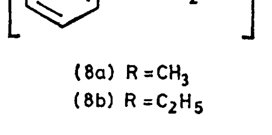
(5a) R¹ = Me, M = Pd
(5b) R¹ = Et, M = Pd
(5c) R¹ = Me, M = Pt



(6a) R¹ = CH₃, M = Pd, L = PPh₃
(6b) R¹ = CH₃, M = Pd, L = PMe₂Ph
(6c) R¹ = CH₃, M = Pd, L = py



(7a) R¹ = CH₃, R² = H, M = Pd
(7b) R¹ = C₂H₅, R² = H, M = Pd
(7c) R¹ = CH₃, R² = OCH₃, M = Pd
(7d) R¹ = CH₃, R² = H, M = Pt
(7e) R¹ = C₂H₅, R² = H, M = Pt



(8a) R = CH₃
(8b) R = C₂H₅

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† N-Nitrosamines are carcinogenic and require care in handling.

determination of a dialkylnitrosamine complex has not been performed. Some *C*-nitroso-palladium complexes have been prepared, *e.g.* of types $[Pd(NOC_6H_4NR_2\text{-}p)_2X_2]$ (R = Me or Et and X = Cl, Br, or I) and it was suggested on the basis of i.r. evidence that co-ordination was *via* the nitrogen atom of the nitrosyl group.[10] This was confirmed by a crystal-structure determination on *trans*-$[Pd(NOC_6H_5)Cl_2]$.[11] These results therefore suggested that *N*-methyl-*N*-nitrosobenzylamine might not cyclopalladate but the possibility of cyclopalladating *N*-alkyl-*N*-nitrosoanilines was worthy of investigation.

RESULTS AND DISCUSSION

We find that *N*-methyl-*N*-nitrosobenzylamine with $Na_2[PdCl_4]$ in methanol readily gives the non-cyclopalladated complex, *trans*-$[Pd\{(ON)N(CH_3)CH_2Ph\}_2Cl_2]$, but attempts to effect palladation by using a 1 : 1 proportion of nitrosamine to palladium salt in the presence of sodium acetate led to decomposition (metallic palladium). Characterizing data for the complex are in Tables 1 and 2. The observed molecular weight in chloroform *viz.* 310 and 314 is much lower than the calculated value of 478. This probably arises from dissociation of the ligand to give some bridged complex.

TABLE 1

Microanalytical and molecular-weight data

	Compound	Analysis (%) [a]				M [b]
		C	H	N	Cl	
	$[Pd\{(ON)N(CH_3)CH_2Ph\}_2Cl_2]$	39.95 (40.25)	4.3 (4.2)	11.5 (11.7)	15.15 (14.85)	310, 314 (478)
(4a)	$[Pd_2\{(NO)N(CH_3)C_6H_4\}_2Cl_2]$	30.45 (30.35)	2.65 (2.55)	10.0 (10.1)	12.6 (12.8)	
(5a)	$[Pd\{(NO)N(CH_3)C_6H_4\}(acac)]\cdot 0.5CH_2Cl_2$	40.55 (40.65)	4.00 (4.05)	7.7 (7.75)		
(6a)	$[Pd\{(NO)N(CH_3)C_6H_4\}Cl(PPh_3)]\cdot CH_2Cl_2$	50.3 (50.0)	3.8 (3.9)	4.8 (4.5)	16.25 (17.05)	
(7a)	$[Pd\{C_6H_4N(NO)CH_3\}Cl(PPh_3)_2]\cdot CH_2Cl_2$	59.5 (59 6)	4.45 (4.45)	3.0 (3.15)	11.75 (12.0)	
(6b)	$[Pd\{(NO)N(CH_3)C_6H_4\}Cl(PMe_2Ph)]$	43.3 (43.4)	4.45 (4.35)	6.55 (6.75)	8.7 (8.55)	
(6c)	$[Pd\{(NO)N(CH_3)C_6H_4\}Cl(py)]$	40.5 (40.5)	3.45 (3.4)	11.6 (11.8)	10.05 (9.95)	
(8a)	$[Pd\{(NO)N(CH_3)C_6H_4\}(dppe)][BPh_4]$	71.45 (71.35)	5.4 (5.35)	2.75 (2.9)		
(5b)	$[Pd\{(NO)N(C_2H_5)C_6H_4\}(acac)]$	43.9 (44.0)	4.65 (4.55)	7.6 (7.9)		349 (355)
(7b)	$[Pd\{C_6H_4N(NO)(C_2H_5)\}Cl(PPh_3)_2]$	65.1 (64.8)	4.9 (4.8)	3.25 (3.45)	4.15 (4.35)	784 (816)
(8b)	$[Pd\{(NO)N(C_2H_5)C_6H_4\}(dppe)][BPh_4]$	71.95 (71.6)	5.6 (5.5)	2.6 (2.85)		
(4c)	$[Pd_2\{(NO)N(CH_3)(C_6H_3OCH_3\text{-}4)\}_2Cl_2]$	31.3 (31.8)	3.1 (2.95)	8.75 (9.1)	11.8 (11.55)	
(7c)	$[Pd\{(C_6H_3OCH_3\text{-}4)N(NO)CH_3\}Cl(PPh_3)_2]$	63.55 (63.55)	4.75 (4.75)	3.15 (3.35)	4.4 (4.25)	794 (832
(5c)	$[Pt\{(NO)N(CH_3)C_6H_4\}(acac)]$	33.55 (33.55)	3.25 (3.3)	6.4 (6.5)		
(7d)	$[Pt\{(NO)N(CH_3)C_6H_4\}Cl(PPh_3)_2]\cdot 0.5CH_2Cl_2$	54.2 (54.2)	4.0 (4.05)	2.9 (2.85)	10.5 (10.9)	
(7e)	$[Pt\{(NO)N(C_2H_5)C_6H_4\}Cl(PPh_3)_2]$	58.4 (58.45)	4.45 (4.35)	2.6 (2.85)	4.05 (3.9)	853 (904)

[a] Calculated values are given in parentheses. [b] Determined in chloroform on an Hitachi–Perkin-Elmer apparatus, model 115.

$$2[Pd\{(ON)N(CH_3)CH_2Ph\}_2Cl_2] \rightleftharpoons [Pd_2\{(ON)N(CH_3)CH_2Ph\}_2Cl_4] + 2PhCH_2N(CH_3)NO$$

In the ^1H n.m.r. spectrum (in $CDCl_3$), in addition to signals ascribed to the mononuclear complex, low-intensity signals corresponding to the *syn* and *anti* forms of the free nitrosamine are observed as are low-intensity signals which might have been due to the binuclear complex. Brown and Coates[9] similarly observed dissociation of dialkylnitrosamines from complexes of the type $[Pd\{(ON)NR_2\}_2Cl_2]$. Thus, our results are in agreement with the ' amine ' nitrogen in *N*-methyl-*N*-nitrosobenzylamine being poorly co-ordinating. We next studied *N*-methyl-*N*-nitrosoaniline which we found was readily cyclopalladated by $Na_2[PdCl_4]$ in methanol to give the chloro-bridged binuclear complex (4a). The best yield was obtained with two moles of nitrosamine per palladium atom: with one mole in the presence of sodium acetate much palladium metal formed. Treatment of this chloro-bridged complex (4a) (which was very insoluble) with thallium(I) acetylacetonate gives the mononuclear acetylacetonate (5a) (see Tables 1 and 2 for characterizing data). This acetylacetonate complex (5a) was sufficiently volatile for its mass spectrum to be determined. The observed molecular-ion isotope distribution pattern was centred at $m/e = 340$ and in good agreement with the calculated pattern. Treatment of the chloro-bridged complex $[Pd_2\{(NO)N(CH_3)C_6H_4\}_2Cl_2]$ (4a) with triphenylphosphine (one mole per palladium atom) gave a mixture of the expected mononuclear complex (6a) and the bis-phosphine complex (7a), in which the palladium–nitrogen bond has been broken. The crystalline mixture could readily be separated manually. The bis-phosphine complex (7a) was more readily prepared and in high yield by heating the bridged complex (1a) with 2.2 moles of triphenylphosphine per palladium atom. Characterizing data are in Tables 1 and 2.

The structures of both (6a) and (7a) were determined by *X*-ray diffraction and are shown in Figures 1 and 2. The monophosphine complex (6a) is seen to be a chelate

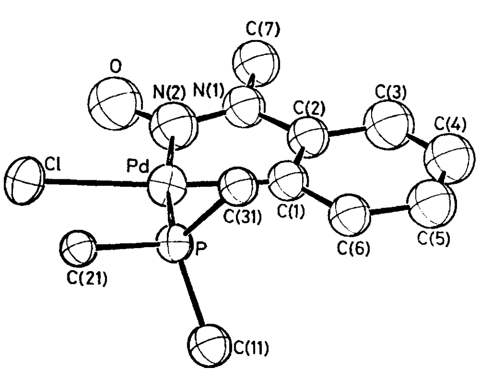

FIGURE 1 ORTEP drawing showing the molecular structure and atom numbering of compound (6a). Only C(1) of each phenyl group is shown

complex with bonding to palladium through the nitrosyl nitrogen and the *ortho*-carbon of the phenyl substituent with all atoms of the nitrosamine chelate system (except the methyl hydrogens) approximately coplanar. In the bis-phosphine complex the nitroso-group is no longer co-ordinated [although the Pd $\cdots$ N(2) distance of 2.88 Å may indicate a weak interaction]. The large U values for C(7), N(2), and O may indicate a high amplitude libration about the C(2)–N(1) bond and possibly some positional disorder between the methyl and nitrosyl groups attached to N(1). Bond lengths and angles with their estimated standard deviations are given in Table 3. In both structures the short N(1)–N(2) bond lengths suggest contribution from the $\overset{+}{N}$=N–O$^-$ resonance structure as well as the N–N=O form; the very short N–N bond in (7a) may be partly the effect of the high thermal motion of N(2).

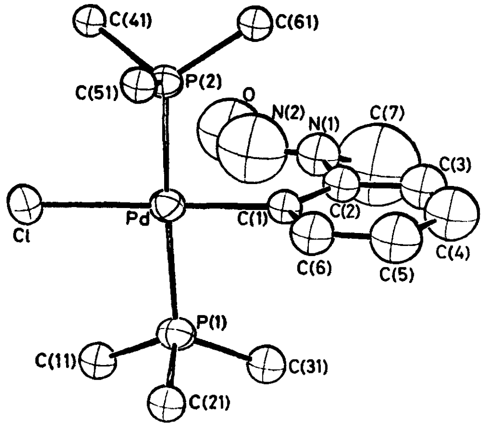

FIGURE 2 ORTEP drawing showing the molecular structure and atom numbering of compound (7a). Only C(1) of each phenyl group is shown

TABLE 3

Bond lengths (Å) and angles (°) with estimated standard deviations in parentheses

(*a*) Monophosphine complex (6a)

Pd–Cl	2.371(4)	Cl–Pd–P	93.8(1)
Pd–P	2.263(3)	Cl–Pd–N(2)	92.3(4)
Pd–C(1)	2.031(15)	P–Pd–C(1)	95.4(4)
Pd–N(2)	2.088(12)	N(2)–Pd–C(1)	78.5(5)
P–C(11)	1.829(16)	Pd–C(1)–C(2)	112.2(10)
P–C(21)	1.823(14)	C(1)–C(2)–N(1)	117.8(12)
P–C(31)	1.829(16)	C(2)–N(1)–N(2)	114.5(10)
C(1)–C(2)	1.391(19)	C(2)–N(1)–C(7)	123.7(11)
C(2)–N(1)	1.427(18)	N(2)–N(1)–C(7)	121.5(11)
N(1)–N(2)	1.276(19)	N(1)–N(2)–O	117.8(11)
N(1)–C(7)	1.480(18)	Pd–N(2)–N(1)	116.5(8)
N(2)–O	1.243(18)	Pd–N(2)–O	125.6(9)

(*b*) Bis-phosphine complex (7a)

Pd–Cl	2.395(3)	Cl–Pd–P(1)	94.0(1)
Pd–P(1)	2.328(3)	Cl–Pd–P(2)	88.8(1)
Pd–P(2)	2.312(3)	C(1)–Pd–P(1)	88.5(3)
Pd–C(1)	1.989(11)	C(1)–Pd–P(2)	88.1(3)
P(1)–C(11)	1.834(13)	Pd–C(1)–C(2)	126.5(7)
P(1)–C(21)	1.812(10)	Pd–C(1)–C(6)	117.0(7)
P(1)–C(31)	1.826(13)	C(1)–C(2)–N(1)	120.4(9)
P(2)–C(41)	1.813(10)	C(2)–N(1)–N(2)	124.3(11)
P(2)–C(51)	1.811(12)	N(2)–N(1)–C(7)	114.2(17)
P(2)–C(61)	1.826(11)	N(1)–N(2)–O	126.0(14)
C(1)–C(2)	1.381(14)	C(2)–N(1)–C(7)	116.7(14)
C(2)–N(1)	1.439(15)		
N(1)–N(2)	1.179(22)	Pd $\cdots$ N(2)	2.878(17)
N(1)–C(7)	1.498(34)		
N(2)–O	1.242(23)		

The mono-substituted dimethylphenylphosphine or pyridine complexes (6b) and (6c) respectively, were

TABLE 2

Values of ν(M–Cl) (cm^{-1}) [a] (M = Pd or Pt), ^{31}P [b] and ^{1}H [c] n.m.r. data

Compound	ν(Pd–Cl)	δ(^{31}P)	δ(^{1}H), J values, assignments
[Pd{(ON)N(CH$_3$)CH$_2$Ph}$_2$Cl$_2$]	358		
(4a)	252, 342		
(4b)	250, 342		
(5a)			2.05 (NCH_3), 2.05, 3.45 (CCH_3), 5.32 (CH)
(5b)			1.27 (t) (J = 7) (NCH$_2$CH_3), 4.07 (q) (NCH_2), 2.08 (CCH_3), 5.35 (CH)
(5c)			2.15 (NCH_3); 2.08, J(PtH) = 5.5 (CCH_3); 3.41, J(PtH) = 6.5 (CCH_3); 5.5, J(PtH) = 8 (CH)
(6a)	295	*d*	3.5 (NCH_3)
(6b) [e]	288	13.1	3.6 (NCH_3)
(6c) [e]	313		3.55 (NCH_3)
(7a)	292	*f*	2.6
(7b)	312		
(7c)	295		3.25 (OCH_3)
(7d) [e]	295	22.4 J(PtP) = 3 107	2.63 (NCH_3)
(7e) [e]	307	21.3 J(PtP) = 3 150	0.85 (t), J = 7 (NCH$_2$CH_3); 3.4 (b) (NCH_2)
(8a) [e]		60.6 (d), 44.0 (d) J(PP) = 32	1.55 (b) (NCH_3)
(8b) [e]		59.7 (d), 42.9 (d) J(PP) = 30	0.85 (t), J = 7, (NCH$_2$CH_3); 4.00 (q), (NCH_2CH$_3$)

[a] Recorded as Nujol mulls (±2 cm^{-1}). [b] Recorded at ambient temperature and 36.43 MHz in CDCl$_3$. Shifts (±0.05 p.p.m.) relative to 85% H$_3$PO$_4$. Shifts to high frequency are positive. J Values ±3 Hz. Resonances are singlets unless stated otherwise, d = doublet. [c] Recorded at 60 MHz in CDCl$_3$ unless stated otherwise. δ Values ±0.02. J Values ±1 Hz. The resonances are singlets unless stated otherwise, t = triplet, q = quartet, b = broad. [d] Very broad peak at δ = 42.7 p.p.m. at 25 °C. On cooling this splits into two and at or below −30 °C the pattern consists of a sharp peak at δ = 44.4 p.p.m. assigned to (6a) together with a peak at δ = 23.15 p.p.m. due to the bis-phosphine complex (7a). [e] Proton spectrum recorded at 100 MHz. [f] At 25 °C the resonance consists of a broad peak at δ = 22.3 p.p.m. In the presence of a *ca.* 0.2 mol proportion of PPh$_3$ to suppress dissociation, at or below −30 °C the resonance consists of a single sharp peak at δ = 23.15 p.p.m. assigned to (7a) together with a sharp peak at δ = −6.5 p.p.m. due to free PPh$_3$.

made from the chloro-bridged complex (4a) (characterizing data in Tables). The value of ν(Pd–Cl) for (6b) *viz.* 288 cm^{-1} is very similar to that of (6a) (295 cm^{-1}) and therefore almost certainly will have the same configuration, *i.e.* chlorine *trans* to carbon. The value of ν(Pd–Cl) for the pyridine complex (6c), 313 cm^{-1}, is intermediate between the values quoted for chlorine *trans* to carbon and chlorine *trans* to nitrogen [12] and we cannot assign its stereochemistry. Attempts to prepare a bis-dimethylphenylphosphine complex analogous to (7a) gave only intractable oils.

We have also studied the cyclopalladation of *N*-ethyl-*N*-nitrosoaniline. This reacted in a similar manner to *N*-methyl-*N*-nitrosoaniline to give a similar product which, however, we were unable to obtain analytically pure. It almost certainly has structure (4b) and reacted with thallium(I) acetylacetonate to give a fully characterized acetylacetonate (5b) and with triphenylphosphine to give a mononuclear bis-phosphine complex (7b). The ^{31}P n.m.r. data (Table 2) clearly show this complex to have the *trans* configuration (7b) even though the observed value of ν(Pd–Cl) *viz.* 312 cm^{-1} is rather high.

(4-Methoxy)-*N*-methyl-*N*-nitrosoaniline was similarly cyclopalladated by $Na_2[PdCl_4]$ to give the chloro-bridged complex (4c). This was also insoluble in the common organic solvents but was easily converted into the soluble bis-triphenylphosphine mononuclear complex (7c).

In view of the ease with which triphenylphosphine caused fission of the palladium–nitrogen bond we have also studied the action of 1,2-bis(diphenylphosphino)ethane (dppe) on the cyclopalladated *N*-nitrosamines. We find that treatment of either (4a) or (4b) with dppe in ethanol gives a yellow solution which, on addition of sodium tetraphenylborate gives yellow crystalline salts (8a) or (8b) respectively. Characterizing data are in the Tables. Apparently, therefore, in ethanol solution this chelating diphosphine destabilizes a palladium–chloride bond in a *trans* position more than a palladium–NO bond.

We have also attempted to prepare cycloplatinated complexes of *N*-alkyl-*N*-nitrosoanilines. Treatment of either *N*-methyl-*N*-nitrosoaniline or *N*-ethyl-*N*-nitrosoaniline with $K_2[PtCl_4]$ gave a very insoluble red microcrystalline product, contaminated with a small amount of a lighter coloured material. We could not purify these products which we refer to as material ' X ' and material ' Y ' respectively. Treatment of material ' X ' with thallium(I) acetylacetonate gave the mononuclear crystalline acetylacetonate (5c) in high yield. This substance gave a good mass spectrum with the distribution pattern of the molecular ion centred at $m/e = 429$ in good agreement with the calculated pattern. The ^{1}H n.m.r. data are given in Table 2. Materials ' X ' and ' Y ' reacted with triphenylphosphine to give the bis-phosphine complexes (7d) and (7e) respectively, see Tables 1 and 2 for characterizing data. The ^{31}P n.m.r. spectra of (7d) and (7e) consist of a broad central peak ($\omega_{\frac{1}{2}}$ *ca.* 50 Hz) with broad satellites due to coupling to platinum-195. When the solutions were cooled down the peaks sharpened and at −60 °C were very sharp ($\omega_{\frac{1}{2}} < 5$ Hz). We tentatively attribute the effect to quadrupole broadening by the nitrogen-14 nucleus.

Thus the two materials ' X ' and ' Y ' behave as if they are of the type $[Pt_2\{NON(R)C_6H_4\}_2Cl_2]$ *i.e.* analogous to compounds (4a) and (4b), R = Me or Et respectively. We cannot explain the red colour: it may be due to a solid-state interaction involving the N–N=O system. The ^{31}P resonances of the palladium complexes (6a) and (7a) were also broad at 25 °C but this was at least in part due to rapid phosphine exchange (see footnotes *e* and *f* to Table 2).

EXPERIMENTAL

The general techniques and apparatus were the same as in other recent papers from this laboratory.[13]

$[Pd\{(ON)N(CH_3)CH_2Ph\}_2Cl_2]$.—*N*-Methyl-*N*-nitrosobenzylamine (0.35 g, 2.3 mmol) was added to a solution of sodium tetrachloropalladate(II) (0.366 g, 1.05 mmol) in methanol (5 cm^3) and the resulting solution was set aside at room temperature for 24 h. The solvent was removed under reduced pressure to give a yellow solid. This was washed with water, dried, and recrystallized from dichloromethane–light petroleum (b.p. 60—80 °C) to give the product as yellow microcrystals (0.318 g, 0.665 mmol, 63%), m.p. 129—132 °C (decomp.).

$[Pd_2\{(NO)N(CH_3)C_6H_4\}_2Cl_2]$ (4a).—*N*-Methyl-*N*-nitrosoaniline (1.12 g, 8.23 mmol) was added to a solution of $Na_2[PdCl_4]$ (1.33 g, 3.92 mmol) in methanol (5 cm^3). The resultant solution was set aside at room temperature in the dark for 5 h. The product was isolated by filtration, washed with water, and dried to give orange needles (0.495 g, 0.89 mmol, 46%), m.p. 245—250 °C (decomp.), which were very insoluble in the usual organic solvents.

$[Pd\{(NO)N(CH_3)C_6H_4\}(acac)]$ (5a).—Thallium(I) acetylacetonate (0.12 g, 0.39 mmol) was added to a suspension of the chloro-bridged complex (0.10 g, 0.187 mmol) in dichloromethane (8 cm^3). The mixture was mechanically shaken for 1.5 h and the precipitate of thallium(I) chloride filtered off. The filtrate was evaporated to dryness under reduced pressure and the residue recrystallized from dichloromethane–light petroleum (b.p. 60—80 °C) to give the product as yellow microcrystals (0.095 g, 0.263 mmol, 71%), m.p. 240—245 °C (decomp.).

The Action of PPh_3 (1 *mol per* Pd *atom*) *on* $[Pd_2\{(NO)N(CH_3)C_6H_4\}_2Cl_2]$.—Triphenylphosphine (0.076 g, 0.29 mmol) was added to a suspension of the chloro-bridged complex in dichloromethane (8 cm^3). The mixture was boiled for 3 min to give a yellow solution and some insoluble material, which was filtered off. Ethanol (5 cm^3) was added to the filtrate which was put aside. A mixture of orange prisms and yellow needles was obtained which was separated mechanically. Thus were obtained $[Pd\{(NO)N(CH_3)C_6H_4\}Cl(PPh_3)]$ (6a) (0.089 g, 0.143 mmol, 49%) as orange prisms, m.p. 185—190 °C (decomp.), and $[Pd\{C_6H_4N(NO)CH_3\}Cl(PPh_3)_2]$ (7a) (0.51 g, 0.057 mmol, 20%) as yellow needles, m.p. 173—176 °C. This bis-triphenylphosphine complex was more readily obtained as described below.

$[Pd\{C_6H_4N(NO)CH_3\}Cl(PPh_3)_2]$ (7a).—Triphenylphosphine (0.60 g, 2.3 mmol) was added to a suspension of $[Pd_2\{C_6H_4N(NO)CH_3\}_2Cl_2]$ (0.28 g, 0.52 mmol) in dichloromethane (5 cm^3). Ethanol (5 cm^3) was then added to the resultant yellow solution. Most of the dichloromethane was boiled off giving the required product (0.84 g, 0.946 mmol, 91%).

[Pd{(NO)N(CH_3)C_6H_4}Cl(PMe_2Ph)] (6b).—Dimethylphenylphosphine (0.038 cm^3, 0.27 mmol) was added to a suspension of the chloro-bridged complex (0.07 g, 0.13 mmol) in ethanol (4 cm^3). The mixture was heated for 5 min and filtered when the required product separated on cooling as yellow needles (0.056 g, 0.134 mmol, 52%), m.p. 208—210 °C (decomp.).

[Pd{(NO)N(CH_3)C_6H_4}Cl(py)] (6c).—Pyridine (py) (0.063 cm^3, 0.78 mmol) was added to a suspension of [Pd_2{C_6H_4N(NO)CH_3}$_2Cl_2$] (0.1 g, 0.19 mmol) in dichloromethane (3 cm^3) and the mixture heated. The resultant hot solution was cooled and allowed to partially evaporate. This gave the required product as yellow needles (0.12 g, 0.337 mmol, 91%), m.p. 160 °C (decomp.).

[Pd_2{(NO)N(C_2H_5)C_6H_4}$_2Cl_2$]) (4b).—This *N*-ethyl complex was prepared in an analogous manner to its *N*-methyl analogue. Orange microcrystals, m.p. 223—225 °C (decomp.), 43% yield, were obtained. It was not obtained analytically pure.

[Pd{(NO)N(C_2H_5)C_6H_4}(acac)] (5b).—The above described complex (0.090 g, 0.155 mmol) and thallium(I) acetylacetonate (0.099 g, 0.325 mmol) were shaken together in dichloromethane (8 cm^3) for 2.5 h. The thallium(I) chloride was filtered off and the required complex was isolated from the filtrate. It formed yellow prisms from dichloromethane–light petroleum (b.p. 60—80 °C). Yield: 0.097 g (0.273 mmol, 88%), m.p. 140—146 °C.

TABLE 4

Atomic co-ordinates with estimated standard deviations in parentheses

(*a*) Compound (6a)

Pd(1)	0.202 63(13)	0.179 51(8)	0.117 36(13)
Cl(1)	0.023 6(4)	0.260 9(3)	0.018 8(4)
P(1)	0.298 0(4)	0.304 1(3)	0.285 8(4)
C(1)	0.342 1(15)	0.092 1(10)	0.177 1(16)
C(2)	0.326 4(16)	0.006 3(10)	0.079 5(16)
C(3)	0.413 1(19)	−0.065 8(12)	0.096 7(19)
C(4)	0.513 8(19)	−0.051 1(12)	0.216 3(20)
C(5)	0.532 4(18)	0.034 2(11)	0.318 2(19)
C(6)	0.445 2(16)	0.106 8(10)	0.298 6(16)
N(1)	0.215 2(13)	−0.009 3(8)	−0.038 6(13)
C(7)	0.181 2(18)	−0.098 5(11)	−0.144 7(18)
N(2)	0.138 1(14)	0.058 2(9)	−0.037 8(15)
O(1)	0.037 0(13)	0.048 3(8)	−0.135 2(13)
C(11)	0.285 7(16)	0.307 9(10)	0.482 1(16)
C(12)	0.228 3(17)	0.234 0(11)	0.518 9(18)
C(13)	0.214 8(18)	0.241 4(11)	0.675 2(19)
C(14)	0.251 6(19)	0.315 7(12)	0.774 9(20)
C(15)	0.307 4(18)	0.392 7(11)	0.745 4(18)
C(16)	0.325 4(16)	0.388 8(10)	0.595 8(16)
C(21)	0.222 9(14)	0.410 3(9)	0.261 6(14)
C(22)	0.282 5(18)	0.466 5(11)	0.188 7(18)
C(23)	0.209 0(20)	0.544 2(12)	0.161 0(20)
C(24)	0.088 5(19)	0.566 9(12)	0.214 1(19)
C(25)	0.032 6(19)	0.512 6(12)	0.290 0(19)
C(26)	0.102 2(17)	0.432 6(10)	0.317 3(17)
C(31)	0.475 9(15)	0.319 2(9)	0.267 8(15)
C(32)	0.507 1(17)	0.298 2(10)	0.119 9(17)
C(33)	0.643 8(18)	0.311 9(11)	0.095 9(18)
C(34)	0.743 8(18)	0.343 3(12)	0.217 7(19)
C(35)	0.709 0(20)	0.363 4(12)	0.363 3(20)
C(36)	0.575 1(17)	0.351 0(10)	0.390 9(17)
C(8)	0.159 6(22)	−0.188 2(14)	0.438 9(23)
Cl(2)	0.313 0(11)	−0.214 3(7)	0.337 5(12)
Cl(3)	0.113 8(17)	−0.072 6(11)	0.450 2(18)

TABLE 4 (*Continued*)

(*b*) Compound (7a)

Pd(1)	0.161 02(7)	0.100 24(4)	0.223 16(5)
Cl(1)	0.120 88(26)	−0.007 15(14)	0.197 92(20)
P(1)	−0.020 99(25)	0.121 63(14)	0.239 48(20)
P(2)	0.338 31(24)	0.085 42(13)	0.198 06(18)
C(1)	0.192 4(9)	0.190 2(5)	0.227 0(7)
C(2)	0.247 1(10)	0.224 7(5)	0.299 4(7)
C(3)	0.265 5(11)	0.287 4(6)	0.300 3(8)
C(4)	0.229 0(14)	0.318 8(7)	0.222 0(10)
C(5)	0.172 9(13)	0.286 7(7)	0.144 1(10)
C(6)	0.156 2(11)	0.222 0(6)	0.147 6(8)
N(1)	0.288 7(9)	0.195 9(5)	0.382 8(6)
C(7)	0.295 8(25)	0.235 8(14)	0.458 9(19)
N(2)	0.280 3(16)	0.143 0(9)	0.395 1(12)
O(1)	0.304 3(11)	0.117 6(6)	0.466 5(8)
C(11)	−0.078 7(10)	0.060 1(5)	0.291 1(7)
C(12)	−0.000 8(11)	0.023 5(6)	0.351 8(8)
C(13)	−0.044 2(12)	−0.020 3(7)	0.396 3(9)
C(14)	−0.165 9(12)	−0.026 9(6)	0.381 3(9)
C(15)	−0.245 5(12)	0.010 1(6)	0.319 5(9)
C(16)	−0.199 7(11)	0.055 2(6)	0.273 5(8)
C(21)	−0.132 0(10)	0.131 8(5)	0.135 4(7)
C(22)	−0.120 9(10)	0.095 8(5)	0.066 7(7)
C(23)	−0.204 7(11)	0.099 6(6)	−0.015 7(8)
C(24)	−0.300 8(12)	0.140 5(7)	−0.026 0(9)
C(25)	−0.317 3(13)	0.174 8(7)	0.038 8(10)
C(26)	−0.228 3(11)	0.171 2(6)	0.124 2(8)
C(31)	−0.035 4(10)	0.188 8(5)	0.302 2(7)
C(32)	−0.028 5(12)	0.246 7(7)	0.267 7(9)
C(33)	−0.033 1(13)	0.302 0(7)	0.319 2(10)
C(34)	−0.043 5(14)	0.292 0(8)	0.396 6(10)
C(35)	−0.052 5(14)	0.238 5(8)	0.430 1(10)
C(36)	−0.044 5(12)	0.182 8(6)	0.382 8(9)
C(41)	0.410 2(9)	0.015 9(5)	0.250 0(7)
C(42)	0.435 6(10)	0.010 2(5)	0.338 8(8)
C(43)	0.497 0(11)	−0.041 5(6)	0.383 2(8)
C(44)	0.529 2(10)	−0.087 1(5)	0.336 6(8)
C(45)	0.502 4(11)	−0.083 6(6)	0.247 4(8)
C(46)	0.440 4(10)	−0.031 6(5)	0.203 6(8)
C(51)	0.319 2(9)	0.076 1(5)	0.084 5(7)
C(52)	0.418 2(11)	0.076 5(6)	0.054 8(8)
C(53)	0.397 0(12)	0.068 1(6)	−0.034 9(9)
C(54)	0.282 8(12)	0.059 8(7)	−0.091 8(9)
C(55)	0.189 1(11)	0.061 7(6)	−0.064 0(8)
C(56)	0.203 0(10)	0.070 0(6)	0.026 2(8)
C(61)	0.451 5(9)	0.144 8(5)	0.230 1(7)
C(62)	0.442 7(10)	0.195 5(6)	0.175 9(8)
C(63)	0.527 6(11)	0.242 5(6)	0.199 5(9)
C(64)	0.615 9(12)	0.239 7(6)	0.277 2(9)
C(65)	0.628 4(12)	0.190 0(6)	0.330 7(9)
C(66)	0.543 4(10)	0.140 8(6)	0.307 6(8)
C(8)	0.226 4(13)	−0.099 3(7)	0.381 0(10)
Cl(2)	0.268 9(4)	−0.059 0(3)	0.480 3(3)
Cl(3)	0.265 2(7)	−0.174 6(4)	0.401 1(5)

[Pd{C_6H_4N(NO)(C_2H_5)}Cl(PPh_3)$_2$] (7b).—A mixture of the chloro-bridged complex (0.12 g, 0.206 mmol) and triphenylphosphine (0.226 g, 0.86 mmol) was heated in dichloromethane (3 cm^3). The product was isolated from the resultant solution and formed yellow prisms (0.265 g, 0.325 mmol, 79%), m.p. 182—184 °C (decomp.), from dichloromethane–methanol.

[Pd_2{(NO)N(CH_3)($C_6H_3OCH_3$-4)}$_2Cl_2$] (4c).—This was prepared in an analogous manner to its phenyl analogue (above) using (4-methoxy)-*N*-methyl-*N*-nitrosoaniline. Orange needles, m.p. 268—271 °C (decomp.), were obtained. Yield: 40%.

[Pd{(C_6H_3OMe-4)N(NO)CH_3}Cl(PPh_3)$_2$] (7c).—This was prepared in an analogous manner to its phenyl analogue. Yellow prisms, m.p. 179—181 °C (decomp.). Yield 90%.

[Pd{(NO)N(CH_3)C_6H_4}(dppe)][BPh_4] (8a). A suspension of 1,2-bis(diphenylphosphino)ethane (0.074 g, 0.186 mmol) and the chloro-bridged complex (4a) (0.05 g, 0.093 mmol) in ethanol was heated to give a yellow solution. Sodium tetraphenylborate (0.13 g, 0.37 mmol) was added and the resultant precipitate washed with ethanol then water and dried. The required product was obtained as yellow prisms (0.15 g, 0.156 mmol, 84%), m.p. 165—169 °C (decomp.), from dichloromethane–ethanol.

$[Pd\{(NO)N(C_2H_5)C_6H_4\}(dppe)][BPh_4]$ (8b).—This was made similarly to its *N*-methyl analogue. Yellow microcrystals from dichloromethane–ethanol, m.p. 149—150 °C (decomp.), were obtained. Yield: 88%.

The Action of N-*Methyl*-N-*nitrosoaniline on Potassium Tetrachloroplatinate*(II).—A mixture of *N*-methyl-*N*-nitrosoaniline (0.69 g, 5.09 mmol) and $K_2[PtCl_4]$ (1.01 g, 2.41 mmol) in water (12 cm^3) and methanol (5 cm^3) was mechanically shaken for 4 d in the dark. The resultant solid was filtered off, washed with water and methanol to give material ' X ' as red microcrystals, decomposing at 300 °C. Yield: 0.24 g. We were unable to purify or to characterize this material. Under the microscope it was seen to contain a small amount of lighter coloured crystals.

A similar reaction using *N*-ethyl-*N*-nitrosoaniline gave material ' Y ' as red microcrystals, melting with decomposition at 163—165 °C, which we were unable to purify or characterize.

$[Pt\{(NO)N(CH_3)C_6H_4\}(acac)]$.—A mixture of the red material ' X ' (0.074 g) (see above) and thallium(I) acetylacetonate (0.065 g, 0.213 mmol) in dichloromethane (5 cm^3) was mechanically shaken for 1 h. The precipitate of thallium(I) chloride was filtered off and the orange solution evaporated under reduced pressure. Recrystallization of the residue from dichloromethane–light petroleum (b.p. 60—80 °C) gave the product as orange prisms (0.063 g, 0.147 mmol), m.p. 200—210 °C (decomp.).

$[Pt\{(NO)N(CH_3)C_6H_4\}Cl(PPh_3)_2]$.— Triphenylphosphine (0.073 g, 0.28 mmol) was added to a suspension of material ' X ' (0.050 g) in dichloromethane (3 cm^3). Ethanol (4 cm^3) was added to the resultant red solution and most of the dichloromethane was boiled off. This gave the product as yellow needles (0.098 g, 0.101 mmol), m.p. 241—244 °C (decomp.). Yield: 75% based on triphenylphosphine.

$[Pt\{(NO)N(C_2H_5)C_6H_4\}Cl(PPh_3)_2]$.—This was prepared similarly from material ' Y ' as yellow prisms, m.p. 225—228 °C (decomp.). Yield: 57% based on triphenylphosphine.

Crystal Data.—(6a). $C_{25}H_{22}ClN_2OPPd\cdot CH_2Cl_2$, $M = 624.2$, Triclinic, $a = 9.990(2)$, $b = 15.195(3)$, $c = 9.276(2)$ Å, $\alpha = 104.05(2)$, $\beta = 97.92(2)$, $\gamma = 89.47(2)°$, $U = 1\,352.4(5)$ Å^3, $D_m = 1.56$ g cm^{-3}, $Z = 2$, $D_c = 1.533$ g cm^{-3}, $F(000) = 628$, space group $P\bar{1}$, μ(Mo-K_α) = 10.55 cm^{-1}.

(7a). $C_{43}H_{37}ClN_2OP_2Pd\cdot CH_2Cl_2$, $M = 886.5$, Monoclinic, $a = 12.047(2)$, $b = 21.794(4)$, $c = 16.402(2)$ Å, $\beta = 108.54(1)°$, $U = 4\,082(1)$ Å^3, $D_m = 1.49$ g cm^{-3}, $Z = 4$, $D_c = 1.44$ g cm^{-3}, $F(000) = 1\,808$, space group $P2_1/c$, Mo-K_α radiation, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 7.59 cm^{-1}.

Structure Analyses.—Measurements were made on a Syntex $P2_1$ diffractometer. Cell dimensions and their standard deviations for each compound were obtained by least-squares treatment of the setting angles for 15 reflections with $35 < 2\theta < 40°$. Intensities were measured in the θ—2θ scan mode for all independent reflections in the range $4 < 2\theta < 45°$ and the structure analyses used the 2 819 with $I > 3\sigma(I)$ for (6a) and the 4 230 with $I > 3\sigma(I)$ for (7a). For (6a) a further 737 reflections below this threshold were excluded, 1 134 for (7a). After correction for Lorentz, polarisation, and transmission factors, and solution of the structures by Patterson and electron-density syntheses, least-squares refinements with anisotropic temperature factors for Pd, P, and Cl only converged at $R = 0.089$, $R' = 0.105$ for (6a) and $R = 0.083$, $R' = 0.095$ for (7a). Atomic scattering factors were computed using the analytical approximation and coefficients given in ref. 14. The atomic co-ordinates and their estimated standard deviations are given in Table 4. Vibration parameters and observed and calculated structure factors are listed in Supplementary Publication No. SUP 22855 (46 pp.).*

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

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