o-Nitrophenylpalladium(II) Complexes. Crystal and Molecular Structures of *cis*-[Pd{*o*-$C_6H_4N(O)O$}$_2$] and *cis*-[Pd{*o*-$C_6H_4N(O)O$}(*o*-$C_6H_4NO_2$)(py)]†

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Bis(*o*-nitrophenyl)mercury reacts with palladium dichloride in molar ratios of 2:1 or 1:1 to give *cis*-[Pd{*o*-$C_6H_4N(O)O$}$_2$] or [{Pd[*o*-$C_6H_4N(O)O$](μ-Cl)}$_2$], respectively. The first product reacts with some unidentate (L) or bidentate (L–L) ligands to give [Pd{*o*-$C_6H_4N(O)O$}(*o*-$C_6H_4NO_2$)L] [L = Ph_3P=$CHCO_2Me$, pyridine (py), 3-bromopyridine, or 4-cyanopyridine] or [Pd(*o*-$C_6H_4NO_2$)$_2$(L–L)] [L–L = 1,10-phenanthroline, 2,2′-bipyridine, 1,2-bis(diphenylphosphino)ethane, or bis(diphenylphosphino)methane] or with $PdCl_2$, Cl_2, $PhICl_2$, or HgX_2 to give [{Pd[*o*-$C_6H_4N(O)O$](μ-X)}$_2$] (X = Cl or Br). The chloro complex reacts (*i*) with unidentate ligands L (molar ratio 1:2) to give [{Pd(*o*-$C_6H_4NO_2$)L(μ-Cl)}$_2$] (L = PPh_3 or $AsPh_3$), (*ii*) with cyclo-octa-1,5-diene (cod) to give [Pd(*o*-$C_6H_4NO_2$)Cl(cod)], and (*iii*) with thallium acetylacetonate, Tl(acac), to give [Pd{*o*-$C_6H_4N(O)O$}(acac)]. The crystal structure of *cis*-[Pd{*o*-$C_6H_4N(O)O$}$_2$] consists of molecules, with square-planar co-ordination, stacked parallel to the (001) plane with alternate Pd ··· Pd distances of 3.465(1) and 3.209(1) Å. The Pd–C [2.033(5) Å (av.)] and Pd–O [2.144(14) Å (av.)] bond lengths are normal, while the C–N [1.390(4) Å (av.)] are shorter than those found in unidentate nitroaryl ligands. The structure of [Pd{*o*-$C_6H_4N(O)O$}(*o*-$C_6H_4NO_2$)(py)] shows a square-planar co-ordination around the palladium atom with a *cis* configuration of the phenyl groups. The only significant differences between both types of *o*-nitrophenyl ligands are shorter C–N [1.428(6) Å] and longer N–O(Pd) [1.265(5) Å] bond distances in the chelating than in the unidentate ligand [1.464(5) and 1.222(5) (av.) Å, respectively].

Organomercury compounds, together with stoicheiometric or catalytic amounts of palladium complexes, have interesting applications in organic synthesis.[1] The processes are believed to occur through transmetallation reactions giving organopalladium complexes which, although not isolated, are believed to be the active species reacting with the organic substrates. Therefore we think that a better understanding of these reactions would be reached by isolating the product(s) of such transmetallation reactions. Such an isolation would require a proper choice of the organic group to be transferred from mercury to palladium.

This type of transmetallation reactions has been used as a method of synthesis of mono-organopalladium complexes [*e.g.* R_2Hg (or RHgX) + $PdX_2 \longrightarrow$ RPdX].[2] Diorganopalladium derivatives can be obtained by redox transmetallation reactions [*e.g.* $R_2Hg + Pd^0 \longrightarrow R_2Pd$ + Hg].[2b,3] We are using arylmercury(II) compounds as transmetallating agents to prepare aryl complexes of tin,[4] gold,[5,6] rhodium,[7] platinum,[8] and palladium.[9] One of the aryl groups we are transferring is *o*-nitrophenyl.[6–8] This is one of the best examples of the synthetic utility of organomercurials because *o*-nitrophenyl-lithium is very unstable[10] and, probably for this reason, scarcely used although some synthetic applications have recently been described.[11] A common feature of all these *o*-nitrophenyl complexes is their thermal and chemical stability.

The reactions between bis(*o*-nitrophenyl)mercury and $[AuCl_4]^-$, $PtCl_2$, or $[PtCl_4]^{2-}$ led always[6,8] to diaryl complexes even when an 1:1 molar ratio was used. We have interpreted this result assuming that monoarylated complexes were not intermediates in these transmetallation reactions, which is not the case when other organomercury compounds are used.[2a,5,12] This unusual behaviour is, in this paper, more solidly established allowing us to propose a way by which these transmetallation reactions occur. A different behaviour of $PdCl_2$ with respect to the other metallic substrates has allowed us to prepare the first‡,[13] cyclometallated mono(*o*-nitrophenyl) complexes. Interesting differences in behaviour between bis(*o*-nitrophenyl)-palladium and -platinum are also reported here.

Although a *cis* geometry was supposed for all the platinum(II) complexes we recently reported,[8a] we were not able to get good crystals to establish the structure of [Pt{*o*-$C_6H_4N(O)O$}$_2$]. In

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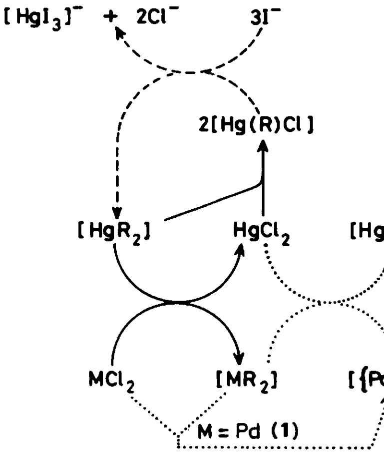
† *cis*-Bis(*o*-nitrophenyl-*C′O*)palladium(II) and *cis*-(*o*-nitrophenyl-*C′*)-(*o*-nitrophenyl-*C′O*)(pyridine)palladium(II).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

‡ In 1982 we reported[6a] that we had prepared some of the present complexes. Difficulties with the *X*-ray crystal structure of [Pd{*o*-$C_6H_4N(O)O$}$_2$] prevented publication of these results until now. The complex [Pt{*o*-$C_6H_4N(O)O$}Cl{S(O)Me_2}] has recently been reported,[13] although with little experimental detail, by a low yield orthometallation reaction.



Scheme 1. Probable steps involved in the synthesis of complexes (1) and (2) (R = o-$C_6H_4NO_2$). ——, general pathway (M = Pd, Pt, or $AuCl_2^-$); – – – –, additional pathway in the presence of I^-; · · · ·, specific pathway for $PdCl_2$

this paper we report the crystal structure of its palladium homologue which has interesting features. This structure determination and also that of $[Pd\{o\text{-}C_6H_4N(O)O\}(o\text{-}C_6H_4NO_2)(py)]$ (py = pyridine) give additional data about the influence of the type of co-ordination of the nitrophenyl group on some structural parameters.

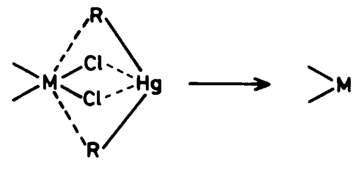
The only previously reported[14] o-nitrophenylpalladium complex, $[Pd(o\text{-}C_6H_4NO_2)Cl(PPh_3)_2]$, was obtained by an oxidative-addition reaction. The organomercury(II) route can also be used to prepare this complex but we will show that this method allows the synthesis of a greater variety of types of arylpalladium complexes with the functionalized o-nitrophenyl group.

Results and Discussion

Synthesis.—The reaction between $PdCl_2$ and $[Hg(o\text{-}C_6H_4NO_2)_2]$ (1:2, in refluxing ethanol) leads to the dark green complex $[Pd\{o\text{-}C_6H_4N(O)O\}_2]$ (1) and $[Hg(o\text{-}C_6H_4NO_2)Cl]$. Given that this mercury complex symmetrizes to $[HgR_2]$ (in the following sometimes R is used instead of o-$C_6H_4NO_2$ to simplify formulae) in the presence of I^-, $2[Hg(R)Cl] + 3I^- \longrightarrow [HgR_2] + [HgI_3]^- + 2Cl^-$, complex (1) can be obtained better from $PdCl_2$, $[HgR_2]$, and NaI in the molar ratio 1:1:3 (see Scheme 1). The complex [Hg(R)Cl] does not react with $PdCl_2$ alone but it does in the presence of NaI.

When a $PdCl_2$:$[HgR_2]$ molar ratio of 1:1 is used (in refluxing ethanol) a dark green complex is first observed which slowly changes to an orange one, $[\{Pd[o\text{-}C_6H_4N(O)O](\mu\text{-}Cl)\}_2]$ (2). If the reaction is stopped after 10 min, (1) is the only organopalladium complex isolable. Therefore both aryl groups seem to be transferred simultaneously from $[HgR_2]$ to $PdCl_2$, as we suggested previously[8a] for the reaction between $PtCl_2$ and $[HgR_2]$. In this case the 1:1 reaction gave only $[PtR_2]$. The transmetallation reaction between $[HgR_2]$ and $[AuCl_4]^-$ led also to a diarylgold(III) complex, cis-$[AuR_2Cl_2]^-$, even with a 1:1 molar ratio.[6a]

We suggest the reaction pathway, shown in Scheme 1, which is valid just for R = o-$C_6H_4NO_2$ and where M is a d^8 ion because: (*i*) other diarylmercury compounds[2a,5,12] react giving first monoaryl and then diaryl complexes; (*ii*) even the analogous $[Hg(C_6H_3Me\text{-}2,NO_2\text{-}6)_2]$ does not arylate $PdCl_2$ and only monoaryl complexes were obtained[9] with $[Pd_2Cl_6]^{2-}$;



(A)

and (*iii*) the reaction[6b] between $[AuCl_2]^-$ and $[Hg(o\text{-}C_6H_4NO_2)_2]$ (1:2) gives only $[Au(o\text{-}C_6H_4NO_2)Cl]^-$. A binuclear MHg complex, such as (A), could be an intermediate giving, as observed, a *cis*-diaryl complex.

A different pathway, in which a monoaryl complex [not necessarily (2)] would be an intermediate, cannot be ruled out. If such an intermediate were formed its arylation to give (1) would be very fast so that it would not be detectable. If (2) were the intermediate it should react with $[HgR_2]$ to give (1) as we have demonstrated in a separate reaction.

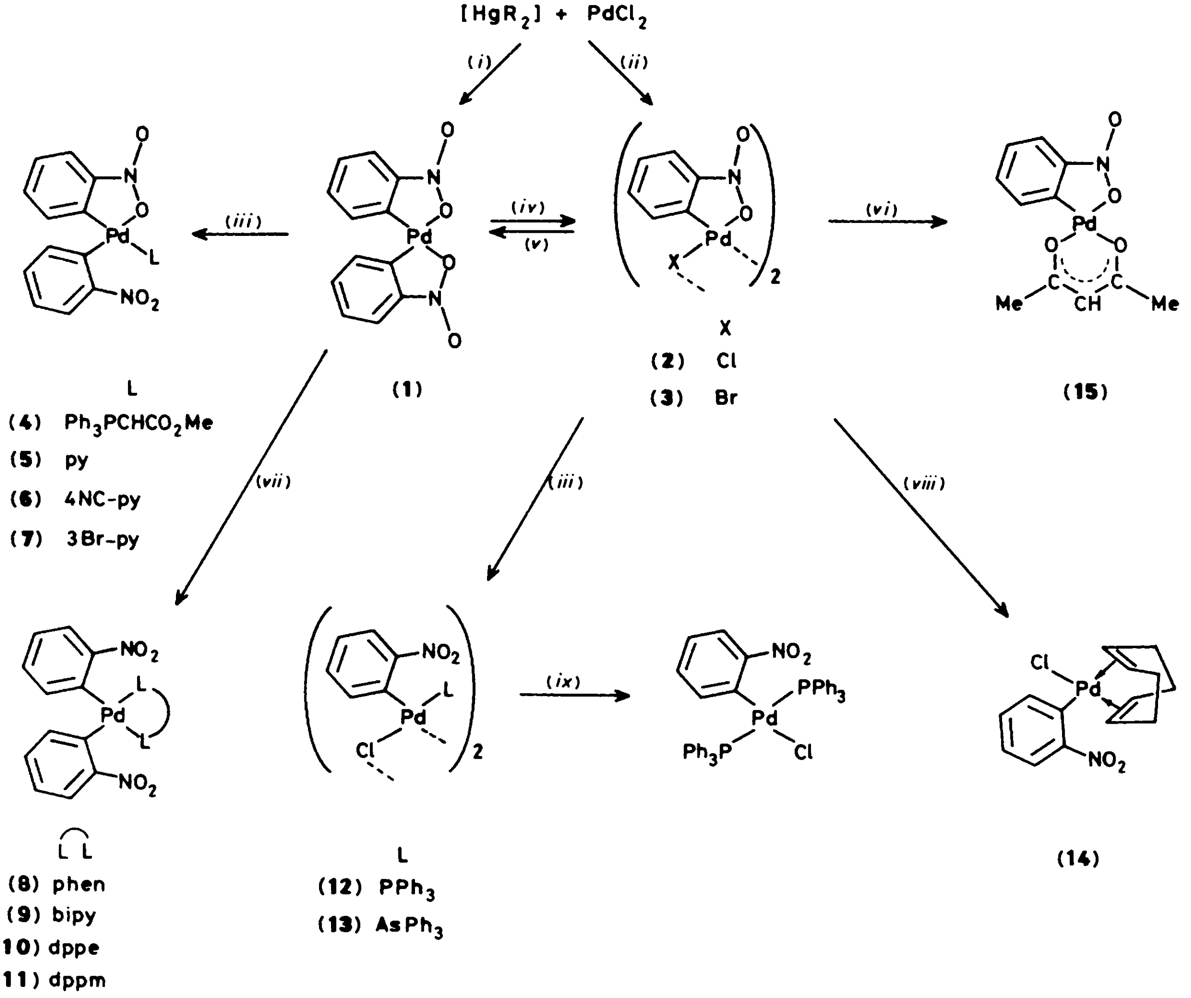
The differences between Scheme 1 and that proposed[8a] for $PtCl_2$ are the reactions between $[PdR_2]$ and $HgCl_2$ or $PdCl_2$ giving complex (2) which do not occur in the case of platinum. Both reactions have been independently verified, showing that the arylation power of $[PdR_2]$ is similar to that of the mercury derivative and both are superior to that of $[PtR_2]$. Such a difference in transmetallation ability has been shown previously[2c] with other aryl groups. Complex (2) can also be prepared by treating (1) with chlorine (in CCl_4) or with $PhICl_2$.

Arylation of $HgBr_2$ with (1) gives the orange complex $[\{Pd[o\text{-}C_6H_4N(O)O](\mu\text{-}Br)\}_2]$ (3), but when trying to prepare the corresponding iodo-derivative, by treatment of (1) with HgI_2, only PdI_2 was isolated.

Complex (1) reacts with an excess of the unidentate ligands L [$Ph_3P{=}CHCO_2Me$, pyridine (py), 4-cyanopyridine (4NC-py), or 3-bromopyridine (3Br-py)] to give yellow-orange, orange, or red solutions from which the red complexes $[Pd\{o\text{-}C_6H_4N(O)O\}(o\text{-}C_6H_4NO_2)L]$ (4)—(7) can be isolated (see Scheme 2). The ligands (L–L) 1,10-phenanthroline (phen), 2,2′-bipyridine (bipy), 1,2-bis(diphenylphosphino)ethane (dppe), and bis(diphenylphosphino)methane (dppm) react with (1) in ⩾1:1 molar ratio to give yellow solutions from which the yellow complexes $[Pd(o\text{-}C_6H_4NO_2)_2(L\text{–}L)]$ (8)—(11) can be isolated. Complexes (10) and (11) are mononuclear in $CHCl_3$ [Found (calc.): (10), *M* 792 (748); (11), *M* 763 (734)].

From these observations, and given that the same colours are observed for corresponding types of platinum complexes, it can be concluded that the presence of a chelating o-nitrophenyl group in these complexes results in red to orange colours, while when both aryl groups are unidentate the complexes are yellow. This allows us to interpret some reactions in solution. Thus, complex (1) is only slightly soluble in most organic solvents, but addition to its suspensions in acetone or dichloromethane of some of the following ligands in ligand to metal molar ratios ⩾2:1, MeCN, 2Br-py, 2NC-py, $2,4Me_2$-py, Cl^-, Br^-, or CN^- (as the NMe_4^+, NEt_4^+, or K^+ salts, respectively), gives red solutions, probably containing $[Pd\{o\text{-}C_6H_4N(O)O\}(o\text{-}C_6H_4NO_2)L]^{n-}$ (n = 0 or 1). Addition of cyclo-octa-1,5-diene (cod) gives a yellow solution, probably containing $[PdR_2(cod)]$. However, two different behaviours were observed when trying to isolate such complexes. Concentration of these solutions and addition of n-hexane or diethyl ether give (*i*) red (L = Cl^-, Br^-, CN^-, or $2,4Me_2$-py) or yellow (L–L = cod) complexes that on attempted recrystallization or even when drying in air on the filter (L–L = cod) revert to (1), or (*ii*) directly (1) even in the presence of excess of the added ligand.

Even the different colours observed for the solutions that lead



Scheme 2. Syntheses and proposed structures of complexes (1)—(15) (R = o-$C_6H_4NO_2$). (*i*) Molar ratio Hg:Pd = 2:1; (*ii*) molar ratio 1:1; (*iii*) +L; (*iv*) +HgX_2 (X = Cl or Br), −[Hg(R)X]; or +$PdCl_2$, or + Cl_2IPh, or + Cl_2; (*v*) +HgR_2, −[Hg(R)Cl]; (*vi*) +Tl(acac); (*vii*) + L–L; (*viii*) +cod; (*ix*) +PPh_3

to complexes (4)—(7) can be interpreted as a consequence of the presence, in solution, of different amounts of complexes of the type $[Pd(o\text{-}C_6H_4NO_2)_2L_2]$. In the case of the pyridine reaction the first crop of crystals obtained contains some yellow crystals. However, recrystallization of this mixture gives complex (5). This particular reaction shows the main difference in reactivity between $[PdR_2]$ and $[PtR_2]$. The platinum complex gives, in solution and in the solid state, yellow $[PtR_2(py)_2]$, although on recrystallization or even in the solid state this reverts finally to red $[\overline{Pt\{o\text{-}C_6H_4N(O)O}\}(o\text{-}C_6H_4NO_2)(py)]$. In addition, though both complexes react with cod, only the platinum one can be isolated and, finally, the platinum complex reacts with CO while (1) does not. Therefore, cleavage of the O–Pd bonds is more difficult than of the corresponding O–Pt ones.

Reactions between complex (1) and some phosphine ligands [PPh_3, PMe_2Ph, or $P(OEt)_3$], $AsPh_3$ (ligand-to-metal molar ratio $\geqslant 2$), or NO gave unstable products that we were not able to characterize.

The dimeric complex (2) reacts with neutral ligands (L) (1:2) to give yellow complexes $[\{Pd(o\text{-}C_6H_4NO_2)L(\mu\text{-}Cl)\}_2]$ [L = PPh_3 (**12**) or $AsPh_3$ (**13**)]. The dimeric nature of these complexes has been confirmed by i.r. spectroscopy (see below) and by osmometry [Found (calc.): (**12**), *M* 952 (1 053); (**13**), *M* 1 075 (1 140)]. If the ligand-to-metal molar ratio used is $\geqslant 4:1$ the mononuclear complex *trans*-$[Pd(R)Cl(PPh_3)_2]$ is obtained. This is the same complex (according to i.r. spectroscopy and m.p.) reported[14] as the product of addition of RCl to $[Pd(PPh_3)_4]$. If the ligand added is cod then the yellow complex *cis*-[Pd(R)Cl(cod)] (**14**) is obtained. Finally, reaction of (**2**) with Tl(acac) gave the red complex $[\overline{Pd\{o\text{-}C_6H_4N(O)O}\}(acac)]$ (**15**) (acac = acetylacetonate). Therefore, it seems that for these monoaryl complexes their colours can also be related, in the same way as for the diaryl complexes, to the type of co-ordination of the aryl group.

All the complexes soluble in acetone, (**1**), (**2**), (**4**)—(**7**), (**14**), and (**15**), are non-conducting in this solvent. All the complexes are stable in the solid state and in solution, as well as towards atmospheric moisture and daylight. Their arylation abilities, for different organic substrates,[1] are now being investigated.

Scheme 2 summarizes all the reactions and shows the proposed structures of the complexes. Table 1 gives elemental analyses and other data for complexes (**1**)—(**15**).

I.r. Spectra.—The presence of one or both co-ordination types of the *o*-nitrophenyl group can easily be shown in the 1 400—1 200 cm^{-1} region of the i.r. spectra[7,8] where the $\nu_{sym}(NO_2)$ mode appears. If this ligand is unidentate this band is observed at around 1 330s cm^{-1}, if it is chelating, at 1 260s

Table 1. Physical and analytical data

Complex	M.p.[a] (°C)	Analysis[b] (%)			Yield (%)	$\nu_{sym}(NO_2)$/ cm^{-1}
		C	H	N		
(**1**) $[Pd\{o\text{-}C_6H_4N(O)O\}_2]$	210	41.3 (41.1)	2.40 (2.30)	7.55 (8.00)	78	1 270
(**2**) $[\{Pd[o\text{-}C_6H_4N(O)O](\mu\text{-}Cl)\}_2]$	255	27.05 (27.25)	1.30 (1.50)	4.50 (5.30)	94	1 258
(**3**) $[\{Pd[o\text{-}C_6H_4N(O)O](\mu\text{-}Br)\}_2]$	225	22.5 (23.25)	1.55 (1.30)	4.35 (4.55)	66	1 258
(**4**) $[Pd\{o\text{-}C_6H_4N(O)O\}(o\text{-}C_6H_4NO_2)(Ph_3PCHCO_2Me)]$	145	57.3 (57.85)	3.80 (3.95)	4.10 (4.10)	77	1 265, 1 330
(**5**) $[Pd\{o\text{-}C_6H_4N(O)O\}(o\text{-}C_6H_4NO_2)(py)]$	160	47.8 (47.5)	3.00 (3.05)	10.0 (9.80)	80	1 262, 1 340
(**6**) $[Pd\{o\text{-}C_6H_4N(O)O\}(o\text{-}C_6H_4NO_2)(4NC\text{-}py)]$	178	47.3 (47.55)	2.80 (2.65)	11.85 (12.3)	85	1 260, 1 330
(**7**) $[Pd\{o\text{-}C_6H_4N(O)O\}(o\text{-}C_6H_4NO_2)(3Br\text{-}py)]$	153	40.15 (40.15)	2.55 (2.40)	8.05 (8.25)	78	1 265, 1 335
(**8**) $[Pd(o\text{-}C_6H_4NO_2)_2(phen)]$	232	54.85 (54.3)	3.05 (3.00)	10.75 (10.55)	91	1 340
(**9**) $[Pd(o\text{-}C_6H_4NO_2)_2(bipy)]$	239	52.85 (52.15)	3.15 (3.15)	11.3 (11.05)	95	1 340
(**10**) $[Pd(o\text{-}C_6H_4NO_2)_2(dppe)]$	172	60.0 (60.95)	4.90 (4.30)	3.75 (3.75)	81	1 330
(**11**) $[Pd(o\text{-}C_6H_4NO_2)_2(dppm)]$	128	60.6 (60.45)	4.25 (4.10)	3.75 (3.80)	74	1 335
(**12**) $[\{Pd(o\text{-}C_6H_4NO_2)(PPh_3)(\mu\text{-}Cl)\}_2]$	257	54.7 (54.8)	2.55 (2.65)	3.80 (3.65)	89	1 330
(**13**) $[\{Pd(o\text{-}C_6H_4NO_2)(AsPh_3)(\mu\text{-}Cl)\}_2]$	220	50.35 (50.55)	3.45 (3.35)	2.35 (2.45)	71	1 330
(**14**) $[Pd(o\text{-}C_6H_4NO_2)Cl(cod)]$	169	45.1 (45.2)	4.15 (4.35)	4.20 (3.75)	80	1 325
(**15**) $[Pd\{o\text{-}C_6H_4N(O)O\}(acac)]$	178	39.75 (40.3)	3.45 (3.40)	4.05 (4.25)	63	1 262

[a] All products melt and decompose at the temperatures shown. [b] Calculated values are given in parentheses.

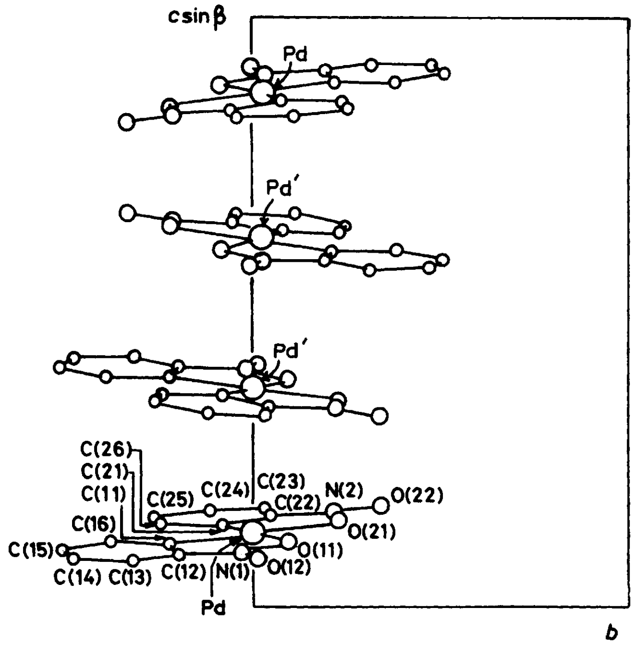


Figure 1. Unit-cell contents of complex (**1**)

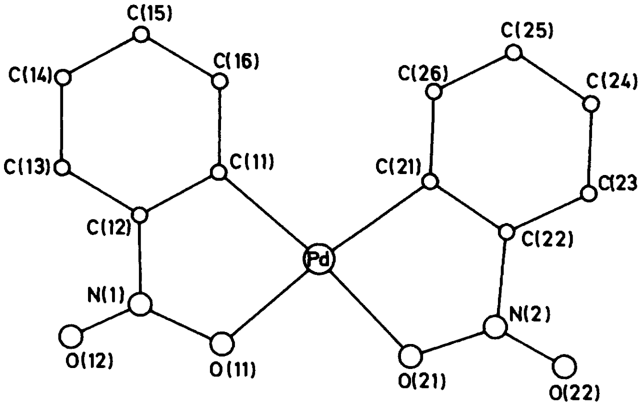


Figure 2. A view of the structure of complex (**1**) showing the atom-numbering scheme

cm^{-1} as shown in Table 1. In addition $\nu_{asym}(NO_2)$, which has low sensitivity to the co-ordination mode, appears at about 1 510vs cm^{-1}. The unidentate nature of the aryl ligands in complexes (**12**) and (**13**) (see Table 1) requires that both are binuclear.

According to the assignment of ν(PdCl) in related nitrophenylpalladium complexes,[9] we tentatively assign one of

Table 2. Bond lengths (Å) and angles (°) for complex (**1**)

C(11)–Pd	2.028(3)	N(1)–C(12)	1.394(8)
O(11)–Pd	2.158(5)	O(11)–N(1)	1.288(9)
C(21)–Pd	2.039(4)	O(12)–N(1)	1.209(11)
O(21)–Pd	2.130(5)	N(2)–C(22)	1.385(8)
Pd′ ··· Pd′	3.465(1)	O(21)–N(2)	1.247(9)
Pd ··· Pd′	3.209(1)	O(22)–N(2)	1.243(8)
O(11)–Pd–C(11)	80.6(2)	O(12)–N(1)–C(12)	123.3(7)
C(21)–Pd–C(11)	104.3(2)	O(12)–N(1)–O(11)	119.0(7)
C(21)–Pd–O(11)	175.0(2)	N(1)–O(11)–Pd	111.1(5)
O(21)–Pd–C(11)	175.6(2)	C(22)–C(21)–Pd	108.8(1)
O(21)–Pd–O(11)	95.1(2)	C(26)–C(21)–Pd	131.1(1)
O(21)–Pd–C(21)	80.0(2)	N(2)–C(22)–C(21)	120.4(3)
C(12)–C(11)–Pd	109.7(1)	N(2)–C(22)–C(23)	119.6(3)
C(16)–C(11)–Pd	130.2(1)	O(21)–N(2)–C(22)	118.1(5)
N(1)–C(12)–C(11)	120.9(4)	O(22)–N(2)–C(22)	121.2(7)
N(1)–C(12)–C(13)	119.0(4)	O(22)–N(2)–O(21)	120.7(7)
O(11)–N(1)–C(12)	117.6(7)	N(2)–O(21)–Pd	112.6(4)

Table 3. Atomic co-ordinates ($\times 10^4$; Pd, $\times 10^5$) of complex (**1**)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Pd	−748(3)	897(6)	12 688(4)
C(11)	−567(2)	2 219(5)	1 060(4)
C(12)	−1 201(2)	1 877(5)	912(4)
C(13)	−1 631(2)	3 161(5)	783(4)
C(14)	−1 428(2)	4 788(5)	801(4)
C(15)	−794(2)	5 130(5)	949(4)
C(16)	−363(2)	3 845(5)	1 078(4)
N(1)	−1 412(4)	264(9)	936(6)
O(11)	−1 001(3)	−889(6)	1 113(4)
O(12)	−1 956(4)	−91(7)	827(7)
C(21)	826(2)	810(6)	1 411(4)
C(22)	1 207(2)	−580(6)	1 563(4)
C(23)	1 850(2)	−411(6)	1 699(4)
C(24)	2 112(2)	1 148(6)	1 682(4)
C(25)	1 731(2)	2 538(6)	1 530(4)
C(26)	1 088(2)	2 369(6)	1 394(4)
N(2)	953(4)	−2 131(8)	1 600(6)
O(21)	378(3)	−2 240(6)	1 496(5)
O(22)	1 286(3)	−3 383(8)	1 727(5)

the ν(PdCl) modes of the bridge in (**2**), (**12**), and (**13**) at 270, 275, and 272 cm^{-1}, respectively. For complex (**14**) and *trans*-[Pd(R)Cl(PPh$_3$)$_2$], where the chloro ligands are terminal, ν(PdCl) appears at 320 and 295 cm^{-1}, respectively, showing a greater *trans* influence of the aryl group with respect to the olefin ligand.

The acetylacetonato complex (**15**) shows the expected[15] bands for the chelate ligand {1 570br, vs, 1 510br, vs [also corresponding to $\nu_{asym}(NO_2)$], 1 360vs, 1 210vs, 930m, 800s, 630m, 455m, and 245vs cm^{-1}}; all these bands do not appear in the spectrum of (**1**).

Structures of Complexes (**1**) *and* (**5**).—Complex (**1**) consists of discrete molecules stacked parallel to the 001 plane with alternate Pd ··· Pd distances of 3.465(1) and 3.209(1) Å, in the range observed[16] for other stacked complexes of palladium in which metal–metal interaction has been postulated. Such weak bonding seems to be responsible for their insolubility and dark colours. As the corresponding platinum complex also has such properties it is very probable that it has the same type of structure (see Figure 1).

Each metal atom displays a distorted square-planar co-ordination (see Figure 2) with a *cis* geometry. The narrowing of the inner O–Pd–C bond angles [80.3(3)° (av.)] is reflected in the opening of the C–Pd–C bond angles [104.3(2)° (av.)]. The averages of the Pd–C and of the Pd–O bond lengths can be considered as normal[9,16b,17] (see Table 2). The average value of the C–N bond lengths [1.390(4) Å] is similar to those found[8,13] in other chelating *o*-nitrophenyl groups of platinum-(II) and -(IV) complexes. In these complexes the N–O(Pt) distances are longer than the N–O ones. The large standard deviations of these distances in complex (**1**) prevent any comparison.

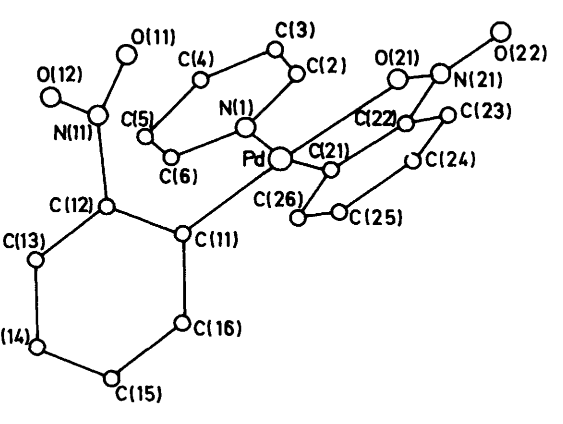


Figure 3. A view of the structure of complex (**5**) showing the atom-numbering scheme

The structure of complex (**5**) consists of discrete molecules (see Figure 3) linked by van der Waals forces. Each palladium atom is bonded (see Table 4) to two C, one N, and one O atoms at normal distances[9,16b,17,18] in a roughly planar co-ordination [the largest deviation from the mean plane is 0.057(4) Å, for O(21)] with a *cis* geometry.

The pyridine molecule and the C(2*x*) phenyl ring (see Figure 3) are almost in the co-ordination plane [dihedral angles 4.0(3) and 4.8(3)°, respectively], while the C(1*x*) phenyl ring is nearly perpendicular to it [dihedral angle 97.7(3)°]. The nitro moiety of the chelating *o*-nitrophenyl group is almost in the same plane as its phenyl ring [dihedral angle 0.8(3)°], while the unco-ordinated nitro moiety is rotated 32.1(3)° around its own phenyl ring.

The planarity and the co-ordination through the oxygen atom of the chelating ligand induces shorter C–N [1.428(6) Å] and longer N–O(Pd) [1.265(5) Å] bond distances with respect to those in the unidentate ligand [C–N 1.464(5) and N–O 1.22(5) Å (av.)] as observed in other platinum complexes (see above). We interpret these changes as a consequence of a p_z $\pi(O) \rightarrow d$ $\pi(M)$ interaction that weakens the N–O bond and leaves the $p_z(N)$ orbital more accessible to p_z $\pi(C) \rightarrow p_z\pi(N)$ bonding. The last interaction is facilitated by the planarity of the nitrophenyl group imposed by co-ordination. However this electron-withdrawing effect does not go so far as to produce either a sequence of long and short C–C bond distances in the phenyl ring (as in $[Rh\{o\text{-}C_6H_4N(O)O\}_2Cl(CO)]$[7] where there are four distances in the range 1.436(5)—1.508(7) Å and two in the range 1.233(7)—1.298(8) Å) or any significant difference in C–C bond distances with respect to the other aryl group. We had observed these two effects previously[8a] in the complex $[Pt\{o\text{-}C_6H_4N(O)O\}(o\text{-}C_6H_4NO_2)(PPh_3)]$.

Experimental

Infrared spectra were recorded in the range 4 000—200 cm^{-1} on a Perkin-Elmer 1430 spectrophotometer. Melting points were determined on a Reichert apparatus and are uncorrected. Analyses (C, H, and N) were carried out with a Perkin-Elmer 240C microanalyzer. Molecular weights were determined with a

Table 4. Bond lengths (Å) and angles (°) for complex (**5**)

N(1)–Pd	2.143(4)	C(4)–C(3)	1.354(9)	C(14)–C(13)	1.368(6)	C(23)–C(22)	1.405(7)
C(11)–Pd	1.978(4)	C(5)–C(4)	1.376(9)	C(15)–C(14)	1.391(6)	N(21)–C(22)	1.428(6)
C(21)–Pd	1.973(4)	C(6)–C(5)	1.373(8)	C(16)–C(15)	1.383(6)	C(24)–C(23)	1.364(8)
O(21)–Pd	2.138(3)	C(12)–C(11)	1.397(6)	N(11)–O(11)	1.224(5)	C(25)–C(24)	1.389(9)
C(2)–N(1)	1.330(6)	C(16)–C(11)	1.399(6)	O(12)–N(11)	1.221(5)	C(26)–C(25)	1.376(7)
C(6)–N(1)	1.332(6)	C(13)–C(12)	1.380(5)	C(22)–C(21)	1.379(6)	N(21)–O(21)	1.265(5)
C(3)–C(2)	1.377(7)	N(11)–C(12)	1.464(5)	C(26)–C(21)	1.409(6)	O(22)–N(21)	1.218(5)
C(11)–Pd–N(1)	95.1(1)	C(5)–C(4)–C(3)	118.7(5)	C(15)–C(14)–C(13)	118.8(4)	N(21)–C(22)–C(21)	116.3(4)
C(21)–Pd–N(1)	172.8(2)	C(6)–C(5)–C(4)	118.7(6)	C(16)–C(15)–C(14)	120.4(4)	N(21)–C(22)–C(23)	117.3(4)
C(21)–Pd–C(11)	91.5(1)	C(5)–C(6)–N(1)	122.8(5)	C(15)–C(16)–C(11)	122.7(4)	C(24)–C(23)–C(22)	117.5(5)
O(21)–Pd–N(1)	93.8(1)	C(12)–C(11)–Pd	124.0(3)	O(11)–N(11)–C(12)	118.6(4)	C(25)–C(24)–C(23)	118.7(5)
O(21)–Pd–C(11)	171.1(1)	C(16)–C(11)–Pd	121.8(3)	O(12)–N(11)–C(12)	118.8(4)	C(26)–C(25)–C(24)	122.4(5)
O(21)–Pd–C(21)	79.6(1)	C(16)–C(11)–C(12)	114.1(4)	O(12)–N(11)–O(11)	122.6(4)	C(25)–C(26)–C(21)	121.3(5)
C(2)–N(1)–Pd	118.1(3)	C(13)–C(12)–C(11)	124.3(4)	C(22)–C(21)–Pd	114.0(3)	N(21)–O(21)–Pd	112.1(3)
C(6)–N(1)–Pd	123.9(3)	N(11)–C(12)–C(11)	120.1(4)	C(26)–C(21)–Pd	132.2(3)	O(21)–N(21)–C(22)	117.8(4)
C(6)–N(1)–C(2)	117.9(4)	N(11)–C(12)–C(13)	115.5(3)	C(26)–C(21)–C(22)	113.7(4)	O(22)–N(21)–C(22)	122.6(4)
C(3)–C(2)–N(1)	122.1(5)	C(14)–C(13)–C(12)	119.6(4)	C(23)–C(22)–C(21)	126.3(4)	O(22)–N(21)–O(21)	119.6(4)
C(4)–C(3)–C(2)	119.7(5)						

Table 5. Atomic co-ordinates ($\times 10^4$; Pd, $\times 10^5$) of complex (**5**)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Pd	14 381(2)	3 089(2)	54 425(4)
N(1)	14 201(3)	−1 006(2)	5 743(5)
C(2)	892(4)	−1 321(3)	6 977(6)
C(3)	867(5)	−2 156(3)	7 303(7)
C(4)	1 401(7)	−2 681(3)	6 360(8)
C(5)	1 945(8)	−2 365(4)	5 071(9)
C(6)	1 943(6)	−1 526(3)	4 817(7)
C(11)	2 330(3)	300(2)	3 509(5)
C(12)	3 379(3)	434(2)	3 668(5)
C(13)	4 000(3)	459(2)	2 317(5)
C(14)	3 589(4)	338(2)	701(5)
C(15)	2 546(4)	213(3)	457(5)
C(16)	1 940(3)	195(3)	1 832(6)
O(11)	3 561(3)	211(2)	6 571(4)
N(11)	3 889(3)	568(2)	5 347(4)
O(12)	4 636(3)	1 016(2)	5 468(4)
C(21)	1 412(3)	1 527(3)	5 467(5)
C(22)	875(4)	1 859(3)	6 754(6)
C(23)	783(5)	2 702(3)	7 140(9)
C(24)	1 257(6)	3 252(3)	6 143(9)
C(25)	1 789(6)	2 955(3)	4 800(9)
C(26)	1 873(5)	2 124(3)	4 463(7)
O(21)	489(2)	523(2)	7 506(4)
N(21)	390(3)	1 284(2)	7 817(5)
O(22)	−108(4)	1 501(2)	8 993(5)

Knauer vapour-pressure osmometer. Conductivities were measured with a Philips 9501 conductimeter.

All reactions were carried out at room temperature, with magnetic stirring and without any special precautions against light, air, or moisture unless otherwise stated.

cis-[$\overline{\mathrm{Pd}\{o\text{-}\mathrm{C_6H_4N(O)O}}\}_2$] (**1**).—To a suspension of [HgR_2][18] (500 mg, 1.12 mmol) in MeOH (25 cm^3) were added solid $PdCl_2$ (200 mg, 1.12 mmol) and NaI (675 mg, 0.22 mmol). The mixture was heated under reflux for 4 h. After cooling, water (100 cm^3) was added and the resulting dark green solid filtered off and washed with acetone (2 × 5 cm^3) to give crude (**1**). A solution of this product in CH_2Cl_2–MeCN (*ca.* 10:1) was filtered over $MgSO_4$ and from the resulting solution analytically pure (**1**) was obtained by addition of Et_2O.

[{$\overline{\mathrm{Pd}[o\text{-}\mathrm{C_6H_4N(O)O}}$](μ-Cl)}$_2$] (**2**).—To a solution of complex (**1**) (50 mg, 0.14 mmol) in MeCN (5 cm^3) was added solid $PdCl_2$ (25.3 mg, 0.14 mmol). After 2 h, the reaction mixture was filtered over $MgSO_4$ and the resulting solution concentrated (2 cm^3). Complex (**2**) was obtained by slow addition of Et_2O (15 cm^3).

[{$\overline{\mathrm{Pd}[o\text{-}\mathrm{C_6H_4N(O)O}}$](μ-Br)}$_2$] (**3**).—To a solution of $HgBr_2$ (65 mg, 0.18 mmol) in acetone (15 cm^3) was added solid complex (**1**) (60 mg, 0.17 mmol). The mixture was heated under reflux for 30 min. After cooling the resulting suspension was filtered off and the solid washed with acetone (2 × 5 cm^3) to give (**3**).

cis-[$\overline{\mathrm{Pd}\{o\text{-}\mathrm{C_6H_4N(O)O}}$}(*o*-$C_6H_4NO_2$)L] [L = Ph_3PCHCO_2Me (**4**), py (**5**), 4NC-py (**6**), *or* 3Br-py (**7**)].—To suspension of complex (**1**) (150 mg, 0.3 mmol) in Et_2O [for (**4**)], acetone [for (**5**)], or CH_2Cl_2 [for (**6**) and (**7**)] was added an excess of the corresponding ligand. After 1—2 h the solutions were concentrated (2 cm^3) and n-hexane added to precipitate crude complexes (**4**)—(**7**). These were recrystallized from dichloromethane–n-hexane.

cis-[Pd(*o*-$C_6H_4NO_2$)$_2$(L–L)] [L–L = phen (**8**), bipy (**9**), dppe (**10**), *or* dppm (**11**)].—To suspension of complex (**1**) (150 mg, 0.3 mmol) in acetone [for (**8**) and (**9**)] or CH_2Cl_2 [for (**10**) and (**11**)] were added stoicheiometric amounts of the ligands. After 1—2 h the complexes (**8**) and (**9**) were isolated by filtration and (**10**) and (**11**) by concentration of the corresponding solutions (2 cm^3) and slow addition of Et_2O (15 cm^3).

[{Pd(*o*-$C_6H_4NO_2$)(μ-Cl)L}$_2$] [L = PPh_3 (**12**) *or* $AsPh_3$ (**13**)].—To suspensions of complex (**2**) (100 mg, 0.19 mmol) in CH_2Cl_2 (10 cm^3) were added stoicheiometric amounts (0.38 mmol) of the ligands. After 1 h, the solutions were concentrated (3 cm^3) and Et_2O or n-hexane (15 cm^3) added to precipitate complexes (**12**) and (**13**).

cis-[Pd(*o*-$C_6H_4NO_2$)Cl(cod)] (**14**).—To a suspension of complex (**2**) (100 mg, 0.19 mmol) in CH_2Cl_2 (10 cm^3) was added cod (0.25 cm^3). After 30 min the solution was concentrated (3 cm^3) and n-hexane (20 cm^3) added to precipitate (**14**).

cis-[$\overline{\mathrm{Pd}\{o\text{-}\mathrm{C_6H_4N(O)O}}$}(acac)] (**15**).—To a suspension of complex (**2**) (52 mg, 0.1 mmol) in CH_2Cl_2 (10 cm^3) was added Tl(acac) (60 mg, 0.2 mmol). After 2 h the suspension was filtered off over $MgSO_4$ and the resulting solution concentrated (2 cm^3). Addition of Et_2O (5 cm^3) and n-hexane (10 cm^3) gave (**15**) as a crystalline solid.

Crystallography.—Complex (**1**). *Crystal data.* $C_{12}H_8N_2O_4Pd$, $M = 350.6$, monoclinic, $a = 22.072(6)$, $b = 8.129(2)$, $c = 13.280(3)$ Å, $\beta = 103.46(2)°$, $U = 2\,317(2)$ Å^3, Mo-K_α radiation ($\lambda = 0.710\,69$ Å, $\mu = 15.86$ cm^{-1}), $Z = 8$, $D_c = 2.009$ g cm^{-3}, space group $C2/c$, $F(000) = 1\,376$, room temperature.

Six different data sets were collected from the same number of crystals obtained from three different crystallization processes. The best result was obtained from an acicular crystal (0.02 × 0.02 × 0.2 mm) mounted on a Philips PW-1100 four-circle diffractometer along the longest axis in order to minimize absorption and crystal-size effects. Cell parameters were determined from 25 reflections ($4 \leqslant \theta \leqslant 12°$) and refined by least squares. Intensities were collected with Mo-K_α radiation, using the ω-scan technique, scan width 1°, and scan speed 0.1° s^{-1}. Three intensities were collected every 2 h as orientation and intensity control; no significant intensity decay was observed. 2 620 Reflections were measured in the range $2 \leqslant \theta \leqslant 25°$ ($\pm h, k, l$), 2 156 of which were independent and assumed as observed [$I \geqslant 2.5\sigma(I)$]; R_{int} (on F) = 0.043. Lorentz-polarization and absorption corrections were made.

The first structure solved was a super-structure, with a cell volume to a quarter that reported. The *o*-nitrophenyl ligands were located in disordered positions. This result was refined with the intensity set reported. Isotropic and anisotropic full-matrix least-squares refinements were carried out with the SHELX 76 program.[19] The function minimized was $\Sigma w||F_o| - |F_c||^2$, where $w^{-1} = \sigma^2(F_o) + 0.03|F_o|$; f, f', and f'' were taken from ref. 20. In order to increase the ratio of the number of reflections to the number of parameters, the benzene rings were assumed to be planar, with bond distances and angles constrained to standard values. The final R factor was 0.063 ($R' = 0.070$) for all observed reflections. Selected bond distances and angles are listed in Table 2 and final co-ordinates in Table 3.

Complex (**5**). *Crystal data.* $C_{17}H_{13}N_3O_4Pd$, $M = 429.7$, monoclinic, $a = 13.175(2)$, $b = 16.192(3)$, $c = 7.878(1)$ Å, $\beta = 93.40(2)°$, $U = 1\,677.7(8)$ Å^3, space group $P2_1/n$, $Z = 4$, $D_c = 1.701$ g cm^{-3}, Mo-K_α radiation ($\lambda = 0.710\,69$ Å, $\mu = 11.158$ cm^{-1}), $F(000) = 1\,264$, room temperature.

An equidimensional crystal (0.1 × 0.1 × 0.1 mm) was selected. The unit-cell parameters were determined from 25 reflections ($5 \leqslant \theta \leqslant 12°$) and refined by the least-squares method. Intensities were collected with Mo-K_α radiation, monochromatized by reflection from a graphite crystal. Three intensities were measured every 2 h but no significant decay was observed. 2 411 Independent reflections were measured in the range $2 \leqslant \theta \leqslant 25°$, 2 396 of which were assumed as observed [$I \geqslant 2.5\sigma(I)$]. Lorentz-polarization, but not absorption, corrections were made.

The structure was solved by direct methods using the MULTAN system of programs[21] and refined isotropically and anisotropically by the full-matrix least-squares method, using SHELX 76.[19] The function minimized was $\Sigma w||F_o| - |F_c||^2$, where $w^{-1} = \sigma^2(F_o) + 0.00346|F_o|^2$. All hydrogen atoms were located from a difference synthesis and refined with an overall isotropic thermal parameter, and the remaining atoms anisotropically. The final R factor was 0.031 ($R' = 0.037$) for all independent reflections observed. Selected bond distances and angles are listed in Table 4 and final co-ordinates in Table 5.

Acknowledgements

Financial support from the Comisión Asesora de Investigación Científica y Ténica (Spain) and a grant from the University of Barcelona (Spain) are gratefully acknowledged.

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Received 16th December 1986; Paper 6/2425