DALTON
FULL PAPER

Palladium(II) and platinum(II) derivatives with N,O ligands

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The preparation of a series of Pd(II) and Pt(II) derivatives with three N,O hybrid ligands 1-(2-pyridyl)ethyldiphenylphosphine oxide, L^1; (2-pyridyl)methyldiphenylphosphine oxide, L^2 and 2-pyridyldiphenylphosphine oxide, L^3 is described. Depending on the ligand to metal molar ratio, either 1 : 1 $[LMCl_2]$ $\{[L^1PdCl_2]$ **1**, $[L^2PdCl_2]$ **2**, $[L^3PdCl_2]$ **3**, $[L^1PtCl_2]$ **4**$\}$ or 2 : 1 $[L_2MCl_2]$ $\{[L^1{}_2PdCl_2]$ **5**, $[L^2{}_2PdCl_2]$ **6**, $[L^1{}_2PtCl_2]$ **7**$\}$ adducts are obtained. In addition, an ionic species $[L^1{}_2Pd][PF_6]_2$ **8**, has been isolated by treatment of complex **5** with $AgPF_6$. The structures in the solid state of compounds **5b**·MeOH·H_2O, **6**·MeOH and **4**·CH_2Cl_2 have been solved by X-ray diffraction. The structures of *trans*-$[L^1{}_2PdCl_2]$ **5b** (one of the diastereomers of **5**) and *trans*-$[L^2{}_2PdCl_2]$ **6** are rather different, the former being a chiral molecule (*R*,*R* enantiomer) with a C_2 axis perpendicular to the plane of the metal, the latter, **6**, being a centrosymmetric molecule. In both the species the ligand is bonded through the nitrogen atom. In complex $[L^1PtCl_2]$ **4**, the ligand is coordinated through the N and O atoms to form a six-membered ring which adopts a boat-like conformation. The structure reveals a fairly short interaction between one hydrogen atom of the Me group in an axial position and the platinum atom, Pt · · · H 2.69 Å. Short contacts Pd · · · H are also observed in the structures of compounds **5b** and **6**. Some aspects of the reactivity of the new species are discussed.

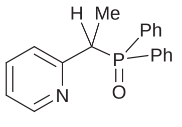
Introduction

The coordination of ligands containing different donor atoms to transition metal ions has been a topic of interest for many years.[1] In recent years much work has been devoted to so-called hemilabile hybrid ligands,[2] *i.e.* ligands having one of their donor sites with little affinity toward the acceptor, so as to be easily removed from the coordination sphere of the metal. Complexes with ligands able to produce a vacancy in the coordination of the metal without complete dissociation should be potential catalytic precursors in synthetic processes.[3] In this context the interaction of typical soft acceptors such as Rh(I), Pd(II) or Pt(II) with ligands having a P,N[4] or a P,O[5] set of donors has been extensively studied. Among the P,N ligands, special attention has been devoted to pyridylphosphines,[6] whereas much less investigated is the behaviour of the corresponding pyridylphosphine oxides. At present, as far as we know, the literature concerning the coordination of these ligands is restricted to the synthesis and structural characterization of $[L^3PtBr_4]$[7] [$L^3 = Ph_2P(O)py$-2], to a kinetic study on the dynamic behaviour of the Pd(II) complexes $[L^3Pd(C_6F_5)Br]$ and $[L^3Pd(C_6F_5)_2]$,[8] and to a study on the coordination behaviour of the same ligand towards Fe(III)[9] and Co(II).[10] In addition, a rhodium–L^3 system has been investigated in hydroformylation reactions.[11] Here we present a study on the reactivity of palladium(II) and platinum(II) ions with the ligands $Ph_2P(O)CH(Me)py$-2 (L^1), $Ph_2P(O)CH_2py$-2 (L^2) and $Ph_2P(O)py$-2 (L^3), which have different chain lengths between the donor atoms and different substituents at the carbon atom of the chain.

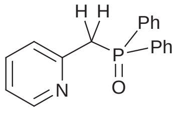
A preliminary report of part of this work has been given.[12]

Results and discussion

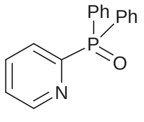
The N,O ligands 1-(2-pyridyl)ethyldiphenylphosphine oxide (racemic form), L^1; (2-pyridyl)methyldiphenylphosphine oxide, L^2 and 2-pyridyldiphenylphosphine oxide, L^3 have been prepared according to established methods (see Experimental section).[13]



L^1



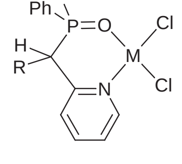
L^2



L^3

1 : 1 Adducts, $[LMCl_2]$

The reaction of L^1 and L^2 with $Na_2[PdCl_4]$ or $K_2[PtCl_4]$ (molar ratio ligand : metal = 1 : 1) in methanol solution affords the complexes $[L^1PdCl_2]$ **1**, $[L^2PdCl_2]$ **2** and $[L^1PtCl_2]$ **4** in moderate to good yields. The analytical data and the conductivity measurements are consistent with neutral 1 : 1 adducts $[LMCl_2]$.



M=Pd, R = Me **1**
M=Pd, R = H **2**
M=Pt, R = Me **4**

Spectroscopic IR and NMR evidences mainly support a chelating behaviour of the ligands. In the IR spectra the P=O stretching vibrations are strongly shifted to lower wavenumbers with respect to the free ligand (see Table 2 and Experimental section) indicating a weakening of the P=O bond consistent with coordination of the oxygen atom.[14] The $^{31}P\{^1H\}$ NMR spectra show at room temperature only one resonance, remarkably deshielded compared to that of the free ligand (Tables 1 and 2). On the other hand the deshielding of the H(6) proton in the ^1H NMR spectra and the shift of the pyridine ring

Table 1 ^1H and ^{31}P NMR data[a]

				δ (^1H)					
Compound	Solvent	T/°C		CH_3	CH_2	CH	H(6)	Aromatics	δ (^{31}P)
$[L^1PdCl_2]$ **1**	$CDCl_3$	+20		2.46 br		4.97 br	9.04 d br	7.22–7.98	49.7
	$CDCl_3$	−50	α (2)	2.86 dd (7.1) [16.6]		4.95 m (nr)[nr]	8.97 d	7.09–8.29	50.3
			β (1)	1.72 dd (6.9) [17.2]		5.72 dq (6.9) [21.4]	9.06 d		51.1
$[L^2PdCl_2]$ **2**	CD_2Cl_2	+20			4.55 d [11.9]		8.91 dd	7.06–7.85	45.4
		−85			4.09 dd br H_A (*ca.* 16) [nr]		8.85 dd br	7.2–8.0	
					5.12 dd br H_B (*ca.* 16) [*ca.* 16]				
$[L^3PdCl_2]$ **3**	CD_2Cl_2	+20					9.34 dd	7.46–8.09	60.5
$[L^1PtCl_2]$ **4**	$CDCl_3$	+20		2.11 br		5.11 br	9.25 dd	7.20–8.10	52.9
	CD_2Cl_2	−70	α (1)	2.56 dd (7.4) [17.0]		4.10 m br (nr)	9.06[b]	6.99–8.22	53.8
			β (6)	1.53 dd (7.3) [17.4]		5.63 m (7.3) [21.3]	[b]		55.1
$[L^1{}_2PdCl_2]$ **5a**	$CDCl_3$	+20	α (3)	1.91 dd (7.2) [15.0]		5.40 br	9.18 br	6.97–8.20	34.3
			β (2)	2.11 dd (7.2) [15.0]		5.80 br	8.80 br		33.6
		−20	α (2)	1.88 dd (7.2) [15.0]		5.36 m (nr)	9.18 dd	6.95–8.16	34.7
			β (1)	2.10 dd (7.2) [15.0]		5.75 m (nr)	8.80 dd		34.0
		+55		2.0 br		5.6 br	8.8–9.2 br	7.0–8.2 br	33.5
$[L^1{}_2PdCl_2]$ **5b**	$CDCl_3$	+20		1.74 dd (7.3) [14.7]		5.35 m (7.3) [nr]	9.05 dd	7.16–8.04	33.6
$[L^2{}_2PdCl_2]$ **6**	$CDCl_3$	+20			5.2 br		8.75–9.10 br	7.15–8.10	29.3 br
									29.7 br
	$CDCl_3$	+55			5.12 d [13.1]		8.90 br	7.15–8.15	29.1
	$CDCl_3$	−50	α (3)		5.14 d [13.0]		8.80	7.20–8.10	30.2
			β (2)		4.96 d [13.2]		9.00		29.6
$[L^1{}_2PtCl_2]$ **7**	$CDCl_3$	+20	α (3)	0.46 dd (7.2) [14.5]		5.54 (7.2) [7.2]	9.13	6.86–8.18	33.6
			β, γ, δ	0.75 dd (7.3) [14.6]		5.65 m[b]	8.91,[b] 8.93[b]		33.1, 34.1, 36.5
			(1 : 1 : 1)[c]	*ca.* 1.70[d]			9.26		
				1.90 dd (7.1) [15.1]					
$[L^1{}_2Pd][PF_6]_2$ **8**	CD_2Cl_2	+20	α (5)	2.21 dd (7.2) [17.0]		5.16 (7.2)[b]	8.72 dd	7.40–7.98	57.0 −143.6 ($[PF_6]^-$)
			β (2)	2.16[e]		[b]	8.75[e]		57.2

[a] Chemical shifts in ppm relative to TMS (^1H) and external 10% H_3PO_4 (^{31}P), coupling constants are given in Hz, J_{HH} in parentheses, J_{HP} in square brackets, br = broad, nr = not resolved. [b] Signals partially overlapping. [c] The signals of isomers β, γ, δ, in approximate ratio 1 : 1 : 1, are not specifically assigned. [d] Obscured by the signal of dissolved H_2O. [e] Partially obscured by the signal of isomer α.

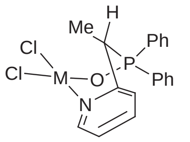
Table 2 ^1H, ^{31}P NMR and selected IR data for the ligands

	NMR[a]							
	δ (^1H)						IR[b]	
Compound	CH_3	CH_2	CH	H(6)	Other aromatics	δ (^{31}P)	P=O	CN (py)
L^1	1.58 dd (7.5) [15.8]		3.98 m (7.5) [7.5]	8.32 d	7.00–7.91	33.9	1183 s	1583 m
L^2		3.95 d [30]		8.40 d	7.05–7.90	30.4	1183 s	1581 m
L^3				8.80 d	7.35–8.34	22.0	1190 s	1590 m

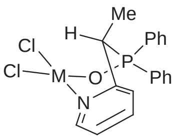
[a] Solvent $CDCl_3$, chemical shifts in ppm relative to internal TMS (^1H) or external H_3PO_4 (^{31}P), coupling constants are given in Hz, J_{HH} in parentheses, J_{PH} in square brackets. [b] IR spectra in Nujol mulls, ν_{max} in cm^{-1}.

vibrations in the IR spectra (ν_{max}/cm^{-1}: 1599, **1**; 1596, **2**; 1600, **4**; 1583, L^1; 1581, L^2) account for the coordination of the nitrogen atom.[15] At room temperature the ^1H NMR spectra indicate a non-rigid situation. Compounds **1** and **4** show broad signals for the resonances of the Me and CH protons and complex **2** one sharp signal for the CH_2 protons [δ 4.55 d, ^2J(P–H) = 11.9 Hz]. At low temperature (−85 °C) the ^1H NMR spectrum of complex **2** shows the non-equivalence of the CH_2 protons with a complex pattern consistent with an ABX system (X = ^{31}P). This behaviour is in agreement with a boat conformation of the six-membered ring.

At room temperature on the NMR time-scale the rapid upsetting of the boat results in a single set of signals, whereas at low temperature the equilibrium is frozen. In the case of the complexes **1** and **4** two conformers are expected, with a methyl (α) or a hydrogen (β) pointing toward the metal.



α



β

In one of the conformers the signal of the CH_3 protons is strongly deshielded with respect to the free ligand (Δδ = 1.28 ppm) whereas in the other conformer it is the CH proton that undergoes a remarkable downfield shift (Δδ = 1.74 ppm). Likewise in complex **2** one of the two protons (δ 5.12) is strongly deshielded with respect to the the other (δ = 4.09) and to the free ligand (δ 3.95).

Note that in the platinum complex **4**, no coupling is observed between ^{195}Pt and ^{31}P, as previously observed for other P–O–Pt systems in six-membered rings.[16]

Assignment of the resonance to conformers α and β, respectively, is in agreement with the data reported in relation to weak interactions between d^8 metal ions and C–H protons in axial position.[17]

A weak interaction between a hydrogen atom and the metal has been confirmed, in the solid state, by the resolution of the structure of complex **4**.

The crystal structure of **4**·CH_2Cl_2 consists of the packing of [L^1PtCl_2] and dichloromethane molecules in the molar ratio 1 : 1, with no unusual van der Waals contacts. Principal bond parameters are reported in Table 3. An ORTEP[18] view of the [L^1PtCl_2] molecule is shown in Fig. 1. The Pt atom is in a square planar coordination with a slight pyramidal distortion, maximum distances from the best plane being +0.022(1) Å for Pt and −0.016(6) Å for N(1). The Pt–Cl(1) and Pt–Cl(2) bond lengths are 2.267(2) and 2.289(2) Å, respectively, suggesting that the *trans* influence of the oxygen atom is slightly lower than that of nitrogen. They can be compared with the Pd–Cl(1) distance, 2.277(1) Å, found in [$PdLCl_2$] **9**, where L is a chiral pyridylphosphine[6i] and the Cl atom is *trans* to a pyridinic nitrogen atom. The Pt–N(1), 2.030(6) Å, and Pt–O, 2.037(5) Å, are very similar and can be compared with the Pd–N bond length, 2.039(3) Å, found in **9**. The P–O distance, 1.527(5) Å, is longer than that observed when the oxygen atom is not coordinated [compare for instance 1.492(3) Å in **5b**·MeOH·H_2O and 1.485(2) Å in **6**·MeOH]. The six-membered metallacycle is in a boat conformation, with the methyl group in an axial position (see Fig. 1). The methylic hydrogen atom H(83) lies at 2.69 Å from the Pt atom, a distance shorter than the sum of the corresponding van der Waals radii (1.20–1.45 Å for hydrogen and 1.70–1.80 Å for platinum).[19] In the boat-like six-membered

Table 3 Selected bond distances (Å) and angles (°) with e.s.d.s in parentheses for **4**·CH_2Cl_2 (*a*), **5b**·MeOH·H_2O (*b*) and **6**·MeOH (*c*)

(*a*)			
Pt–Cl(1)	2.267(2)	Pt–Cl(2)	2.289(2)
Pt–O	2.037(5)	Pt–N(1)	2.030(6)
P–O	1.527(5)	Pt···H(83)	2.69
Cl(1)–Pt–Cl(2)	91.5(1)	Cl(1)–Pt–O	178.6(2)
Cl(1)–Pt–N(1)	92.2(2)	Cl(2)–Pt–O	89.5(2)
Cl(2)–Pt–N(1)	175.8(2)	O–Pt–N(1)	86.8(2)
(*b*)			
Pd–Cl	2.299(1)	Pd–N(1)	2.036(3)
P–O	1.492(3)	Pd···H(7)	2.66
Cl–Pd–Cl′	178.5(1)	Cl–Pd–N(1)	90.3(1)
Cl–Pd–N(1′)	89.7(1)	N(1)–Pd–N(1′)	176.5(1)
(*c*)			
Pd–Cl	2.298(1)	Pd–N(1)	2.035(2)
P–O	1.485(2)	Pd···H(71)	2.61
Cl–Pd–N(1)	89.9(1)	Cl–Pd–N(1′)	90.1(1)

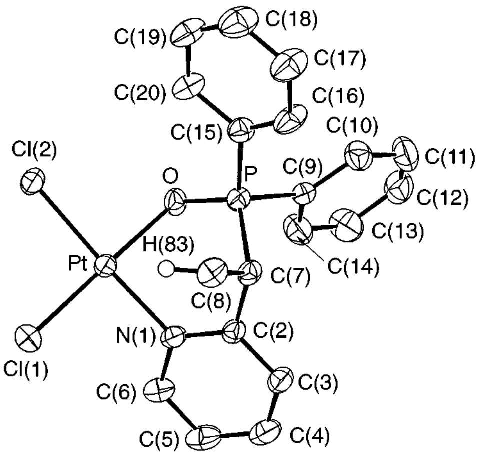


Fig. 1 An ORTEP view of compound **4**. Ellipsoids are drawn at the 30% probability level.

ring the best plane of atoms P, O, N(1) and C(2) forms dihedral angles of 43.1(3) and 44.8(4)° with the Pt–O–N(1) and P–C(7)–C(2) planes, respectively.

The third ligand, L^3, was used with the aim of comparing the stability of a five-membered N,O ring with respect to a six-membered one. By reaction with $Na_2[PdCl_4]$ or *trans*-$[(PhCN)_2PdCl_2]$, the species $[L^3PdCl_2]$ **3** was obtained in good yield. Spectroscopic data are in agreement with a chelating behaviour of the ligand.

2:1 Adducts, $[L_2MCl_2]$

When the reaction between $Na_2[PdCl_4]$ and L^1 or L^2 is carried out with a 2:1 L:Pd ratio, adding the solution of $Na_2[PdCl_4]$ to the solution of the ligand (*i.e.* in the presence of an excess of ligand), complexes $[L^1{}_2PdCl_2]$ **5** and $[L^2{}_2PdCl_2]$ **6** are obtained. In the IR spectra no significant shift of the P=O stretching vibration is observed, suggesting that the oxygen atom is not involved in the coordination. The absorptions at 348 (**5**) and 345 (**6**) cm^{-1} are indicative of a *trans* disposition of the chlorine atoms, as usually observed for $[L_2PdCl_2]$ derivatives[20] (L = pyridine or substituted pyridines).

The ^1H NMR spectrum of **5** at room temperature is rather complex showing three sets of signals. Taking into account that L^1 has a stereogenic centre (asymmetric carbon atom), three stereoisomers are possible, two isomers are chiral and together constitute a pair of enantiomers (*R*,*R*; *S*,*S*). The third isomer is diastereomeric to the two above mentioned isomers and is a *meso* compound.[21] In addition, other signals could originate from hindered rotation of the ligand around the Pd–N bonds, as previously observed for Pd(II) derivatives with 2-benzylpyridines.[22]

The two diastereomers **5a** and **5b** were separated taking advantage of the different solubility in methanol. The more soluble fraction, **5b**, shows in the ^1H NMR spectrum one set of sharp signals: in particular a double doublet at δ 1.74 (J_{HH} = 7.3 Hz and J_{PH} = 14.7 Hz) for the Me group and a multiplet at δ 5.35 (J_{HH} = 7.3 Hz, J_{PH} not resolved) for the CH protons. The H(6) proton is deshielded ($\Delta\delta$ = 0.73 ppm) as usually observed for a pyridine coordinated *cis* to a chlorine atom. The $^{31}P\{^1H\}$ NMR spectrum shows only one signal at δ 33.6 confirming that only one definite species is present.

To provide definitive characterization of diastereomer **5b** and to determine the solid-state stereochemistry, a single-crystal X-ray diffraction study was undertaken. Compound **5b** was found to be one of the chiral diastereomers (*R*,*R* enantiomer).

Crystals of **5b**·MeOH·H_2O consist of the packing of $[L^1{}_2PdCl_2]$, methanol and water molecules in the molar ratio 1:1:1, with no unusual van der Waals contacts. Principal bond parameters are reported in Table 3. An ORTEP view of the $[L^1{}_2PdCl_2]$ molecule is shown in Fig. 2. The molecule possesses crystallographic C_2 symmetry, with the two-fold axis perpendicular to the best plane of the metal coordination and passing through the Pd atom. The essentially square-planar coordination of the metal atom displays a slight pyramidal distortion, with maximum distances from the best plane of +0.037(1) and −0.025(3) Å for Pd and N(1), respectively. The Pd–Cl, 2.299(1), and Pd–N(1), 2.036(3) Å, bond lengths are in the range observed for similar systems: see for instance Pd–Cl(1) 2.297(1) Å in $[PdCl_2\{Me_2C(pz)_2\}]$ **10** (Hpz = pyrazole),[23] where the Cl atom is *trans* to a pyrazolic nitrogen atom, and Pt–N 2.013(3) and 2.021(3) Å in $C_{24}H_{28}N_2O_8Pt$,[24] where two substituted pyridines are *trans* to each other. The P–O bond length, 1.492(3) Å, is almost coincident within three e.s.d.s with that found in free Ph_3PO, 1.46(1) Å.[25] The C(7) and C(7′) asymmetric carbon atoms display *R* absolute configurations, and their H(7) and H(7′) hydrogen atoms lie at 2.66 Å from the Pd atom, a rather short interaction, similar to that found in $[L^1PtCl_2]$ **4**, and discussed above. With respect to the best plane of atoms Cl, N(1), Cl′ and N(1′) the Pd, H(7) and H(7′) atoms lie on the same side, and the same is true for Pt and H(83) in $[L^1PtCl_2]$ **4**, with respect to the best plane of atoms Cl(1), Cl(2), O and N(1), thus suggesting that these metal–hydrogen interactions are attractive in nature and are responsible for the pyramidal distortion of the metal coordination.

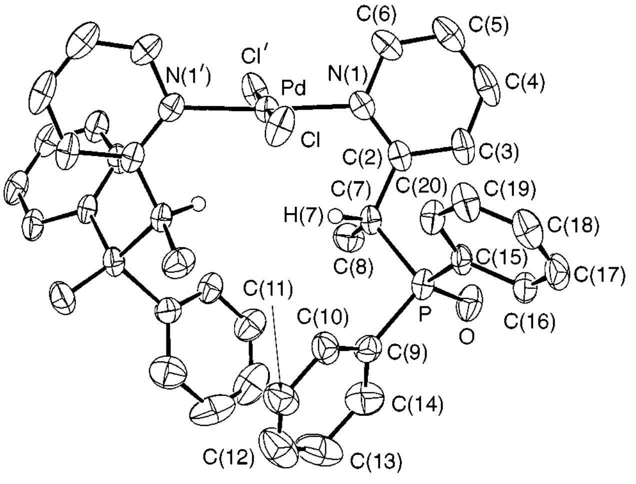
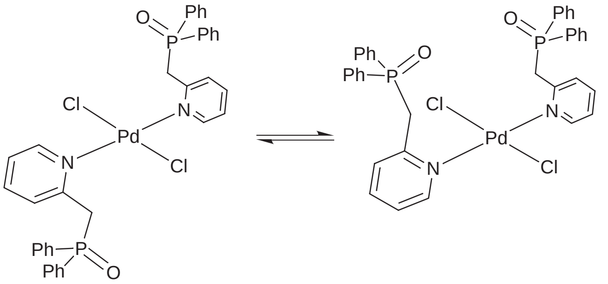


Fig. 2 An ORTEP view of compound **5b**. Primed atoms are related to unprimed ones by the symmetry operation $-x, y-x, 1/3-z$. Ellipsoids as in Fig. 1.

The fraction less soluble in MeOH, **5a**, has a more complex, temperature dependent ^1H NMR spectrum. At room temperature two sets of broad signals are observed that turn into a single set at +55 °C ($CDCl_3$) and sharpen at −50 °C. Assuming that **5a** is the achiral diastereomer (*meso* compound) the presence of two sets of signals can be due to the presence of conformational isomers (rotamers). A similar behaviour has been observed previously for *trans*-$[(2\text{-}PhCH_2py)_2PdCl_2]$ species.[22]

With ligand L^2, having no stereogenic centres, $[L^2{}_2PdCl_2]$ **6**, analogous to **5**, is obtained.

The ^1H and $^{31}P\{^1H\}$ NMR spectra of complex **6** are temperature dependent. At −50 °C two species are observed in molar ratio *ca.* 3:2; at high temperature (+50 °C) coalescence of the signals is observed. This dynamic behaviour is reminiscent of that previously described for the achiral form (*meso*) of complex **5**.



Crystals of **6**·MeOH consist of the packing of $[L^2{}_2PdCl_2]$ and methanol molecules in a molar ratio of 1:1 with no unusual van der Waals contacts. Principal bond parameters are reported in Table 3. An ORTEP view of the $[L^2{}_2PdCl_2]$ molecule is shown in Fig. 3. The molecule lies on a crystallographic inversion centre, so that the coordination around the metal atom is exactly planar. The Pd–Cl, 2.298(1), Pd–N(1), 2.035(2), and P–O, 1.485(2) Å, bond lengths are statistically coincident with those found in $[L^1{}_2PdCl_2]$ **5b**. Also in this case two hydrogen atoms bonded to C(7) and C(7′), namely H(71) and H(71′), display rather short contacts with the metal atom, 2.61 Å. If these interactions are taken into account, the coordination around the Pd atom becomes distorted octahedral.

It is noteworthy that in the case of ligand L^3, under comparable conditions, no 2:1 adduct was obtained.

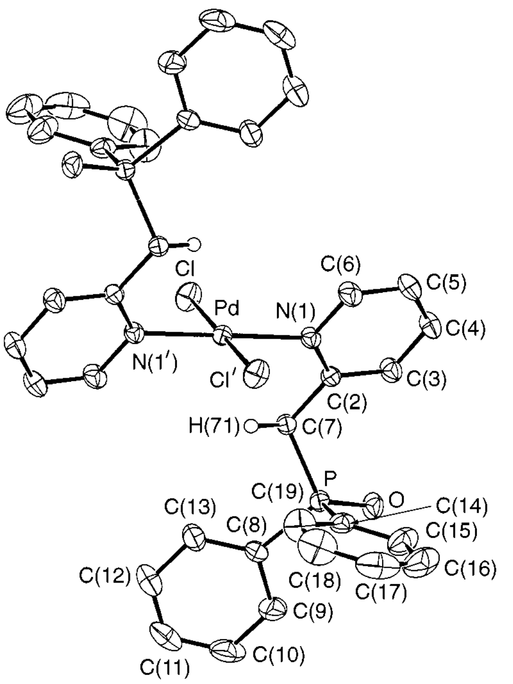
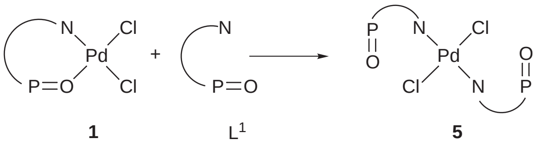


Fig. 3 An ORTEP view of compound **6**. Primed atoms are related to unprimed ones by the symmetry operation $1 - x, -y, 1 - z$. Ellipsoids as in Fig. 1.

At variance with the palladium complex **5**, in the case of the analogous platinum derivative, [$L^1{}_2PtCl_2$] **7**, we were unable to achieve separation of the species observed in solution. The $^{31}P\{^1H\}$ NMR spectrum of complex **7** shows four resonances (*ca.* 1 : 1 : 3 : 1), in a region which rules out endobidentate coordination. In the ^1H NMR spectrum, four signals are observed for the methyl protons in the range δ 0.4–2.0 and a complex multiplet for the C–H protons. More H(6) resonances (partially overlapping) around δ 9 (free ligand, δ 8.34) confirm the coordination of the pyridine ring. A rationale of the presence of more species is not easy. Tentatively, it can be assumed that, in addition to two diastereomers, geometric isomers are formed. Indeed, whereas [L_2PdCl_2] complexes are almost exclusively isolated as *trans* isomers, in the case of the corresponding platinum derivatives, both *cis*- and *trans*- isomers have been reported.

To compare the stability of a six-membered N,O ring with respect to a five-membered one, the reactions of [L^1PdCl_2] **1** and [L^3PdCl_2] **3** with L^1 and L^3, respectively, have been investigated.

The reaction of complex **1** with L^1 gives complex **5**, *i.e.* the 2 : 1 adduct, whereas the reaction of complex **3** with L^3 does not occur.



The latter behaviour is consistent with the unsuccessful attempts to obtain 2 : 1 adducts of L^3 as previously mentioned.

Reactions of [L^1PdCl_2] **1** with L^3 and of [L^3PdCl_2] **3** with L^1 give a mixture of species, including [L^3PdCl_2] and [$L^1{}_2PdCl_2$], but not the [$L^1L^3PdCl_2$] complex in the former case, and [$L^1{}_2PdCl_2$], [L^1PdCl_2] and free L^3 in the latter case (^1H and ^{31}P NMR criterion). Although an unambiguous conclusion on the relative stability of the two cycles was not achieved, at least on the basis of the reaction between the chelate complexes **1** and **3** with L^1 and L^3, respectively, it seems that coordination of oxygen is more easily displaced from a six- rather than from a five-membered ring.

The N,O ligand can be removed from complex **3** by reaction with a strong ligand such as PPh_3 (molar ratio 1 : 1) to give [$(Ph_3P)PdCl_2]_2$. Reaction with 3,5-dimethylpyridine (1 : 1) gives a complex mixture of unidentified species.

Finally, in order to investigate other aspects of the reactivity of these N,O ligands, an attempt has been made to synthesize ionic species [$L^1{}_2Pd]^{2+}$. It has been observed that removal of the chloride ligands from [L^1PdCl_2] by means of silver(I) ions, followed by addition of L^1, does not give the expected product. At variance, a bis-chelate species [$L^1{}_2Pd][PF_6]_2$ **8**, was obtained by removing the chloride ions with $AgPF_6$ from [$L^1{}_2PdCl_2$] **5**. This preliminary result suggests that the synthesis of these complexes requires that both the molecules of the ligand are previously bonded to the metal through the nitrogen atom: in the intermediate, arising from abstraction of the chloride ions, the coordinative unsaturation is easily filled by the oxygen atoms. IR and $^{31}P\{^1H\}$ NMR data support the endobidentate behaviour of L^1 in complex **8**.

Experimental

The ligands L^1, L^2 and L^3 were prepared according to literature methods[13] as briefly described below. $Na_2PdCl_4{\cdot}xH_2O$ (Pd 29.15%) was provided by Johnson Matthey and $K_2PtCl_4{\cdot}xH_2O$ (Pt 43.035%) by Engelhard s.r.l.

Elemental analyses were performed with a Perkin-Elmer Elemental Analyzer 240B by Mr A. Canu (Dipartimento di Chimica, Università di Sassari). Conductivities were measured with a Philips PW 9505 conductimeter. Infrared spectra were recorded with a Perkin-Elmer 983 or FT-IR Bruker IFS66 spectrophotometer using Nujol mulls or in CH_2Cl_2 solution. ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded with a Varian VXR 300 spectrometer operating at 299.9 and 121.4 MHz respectively, and are collected in Tables 1 and 2. Chemical shifts are given in ppm relative to internal TMS (^1H) and external 85% H_3PO_4 (^{31}P). Mass spectra (positive ion) were obtained with a VG 7070EQ, instrument operating under FAB conditions with 3-nitrobenzyl alcohol (NBA) as supporting matrix.

Preparation of ligands

The ligands L^1 and L^2 were prepared according to a procedure reported for the synthesis of the corresponding pyridylphosphine,[13b] by using chlorodiphenylphosphine oxide in place of chlorodiphenylphosphine. L^1 was synthesized by dropwise addition at −78 °C of a solution of BuLi in hexane to a solution of 2-ethylpyridine in Et_2O, followed by treatment with chlorodiphenylphosphine oxide; L^2 is easily accessible by dropwise addition at −78 °C of a solution of BuLi in hexane to a solution of α-picoline in Et_2O, followed by reaction with chlorodiphenylphosphine oxide in Et_2O.

Ligand L^3 was prepared from 2-pyPPh_2 by oxidation at 0 °C in acetone with H_2O_2 (30% in H_2O), according to ref. 13(*a*).

[L^1PdCl_2] 1

To a solution of $Na_2[PdCl_4]{\cdot}xH_2O$ (0.365 g, 1.00 mmol) in MeOH (20 ml) was added a methanolic solution (10 ml) of L^1 (0.307 g, 1.00 mmol). The solution was stirred for 4 h. The brick-red solution obtained was evaporated to dryness and crystallized from CH_2Cl_2–diethyl ether to give the analytical product as an orange red solid. Yield 57%, mp 230 °C (decomp.) (Found: C, 42.87; H, 3.59; N, 2.49. Calc. for $C_{19}H_{18}NOPPdCl_2{\cdot}CH_2Cl_2$: C, 42.18; H, 3.54; N, 2.46%). Λ_M (5×10^{-4} M, acetone) = 15 Ω^{-1} cm^2 mol^{-1}. FAB mass spectrum: *m*/*z* 448 (M − Cl), 413 (M − 2Cl); IR (Nujol) ν_{max}/cm^{-1}: 1599m, 1120s, 340m.

[L^2PdCl_2] 2

To a solution of $Na_2[PdCl_4]$ (0.100 g, 0.27 mmol) in water (10 ml) was added a methanolic solution (10 ml) of L^2 (0.080 g, 0.27 mmol). The mixture was stirred for 2 h. The precipitate formed was filtered, washed with water, EtOH and Et_2O to give the analytical sample as a yellow solid. Yield 89%, mp 252–254 °C (Found: C, 45.81; H, 3.64; N, 2.93. Calc. for $C_{18}H_{16}NOPPdCl_2$: C, 45.94; H, 3.43; N, 2.98%). Λ_M (5×10^{-4} M, acetone) = 13 Ω^{-1} cm^2 mol^{-1}. FAB mass spectrum: *m*/*z* 434 (M − Cl), 399 (M − 2Cl). IR (Nujol) ν_{max}/cm^{-1}: 1596m, 1126s, 325m.

[L^3PdCl_2] 3

(1) To a methanolic solution (30 ml) of $Na_2[PdCl_4]$ (0.365 g, 1.00 mmol) was added dropwise a solution of L^3 (0.279 g, 1.00 mmol) in MeOH (10 ml). The mixture was stirred for 12 h. The mustard yellow precipitate formed was filtered and recrystallized from CH_2Cl_2–Et_2O to give the analytical sample. Yield 70%.

Complex **3** was obtained also with a L^3 : Pd 2 : 1 molar ratio. The excess ligand L^3 was recovered quantitatively from the methanolic solution.

(2) To a benzenic solution (50 ml) of *trans*-[$(PhCN)_2PdCl_2$] (0.3815 g, 0.99 mmol) were added under stirring 0.279 g (1.00 mmol) of L^3. The mixture was stirred for 8 h. The precipitate formed was filtered and recrystallized from CH_2Cl_2–petroleum ether (bp range 40–60 °C) to give the analytical mustard yellow sample. Yield 92%. Mp 280 °C (decomp.) (Found: C, 44.93; H, 3.24; N, 3.22. Calc. for $C_{17}H_{14}NOPPdCl_2$: C, 44.70; H, 3.07; N, 3.07%). FAB mass spectrum: *m*/*z* 420 (M − Cl), 385 (M − 2Cl). IR (Nujol) ν_{max}/cm^{-1}: 1585w, 1120s, 339s (br).

[L^1PtCl_2] 4

To an ethanolic solution (5 ml) of L^1 (111 mg, 0.36 mmol) an aqueous solution of $K_2[PtCl_4]$ (150 mg, 0.36 mmol, 10 ml) was added under vigorous stirring. The mixture was stirred for 6 days, then filtered over celite, evaporated to dryness and crystallized from CH_2Cl_2 and Et_2O to give the analytical sample as a pale yellow solid. Yield 47.3%, mp 212 °C (Found: C, 36.60; H, 3.06; N, 2.08. Calc. for $C_{19}H_{18}NOPPtCl_2\cdot CH_2Cl_2$: C, 36.47; H, 3.04; N, 2.13%). IR (Nujol) ν_{max}/cm^{-1}: 1600m, 1124s, 345s (br).

[$L^1_2PdCl_2$] 5

To a solution of L^1 (0.584 g, 1.90 mmol) in MeOH (10 ml) was added dropwise a methanolic solution (20 ml) of $Na_2[PdCl_4]\cdot xH_2O$ (0.346 g, 0.95 mmol). The yellow precipitate formed was filtered to give a first sample **5a** (0.376 g). The solution was evaporated to a small volume and treated with Et_2O. The precipitate formed was filtered to give a second sample **5b** (0.230 g).

5a: Yield 49%, mp 274 °C (decomp.) (Found: C, 56.62; H, 4.49; N, 3.35. Calc. for $C_{38}H_{36}N_2O_2P_2PdCl_2\cdot H_2O$: C, 56.35; H, 4.73; N, 3.46%). FAB mass spectrum: *m*/*z* 755 (M − Cl), 720 (M − 2Cl), 413 (M − 2Cl − L^1). IR (Nujol) ν_{max}/cm^{-1}: 1608m, 1180s, 348m.

5b: Yield 29%, mp 240–241°C (decomp.) (Found: C, 54.59; H, 4.79; N, 3.51. Calc. for $C_{38}H_{36}N_2O_2P_2PdCl_2\cdot H_2O\cdot CH_3OH$: C, 55.63; H, 5.03; N, 3.33%). IR (Nujol) ν_{max}/cm^{-1}: 1608m, 1180s, 348m.

[$L^2_2PdCl_2$] 6

To a methanolic solution (10 ml) of L^2 (0.100 g, 0.34 mmol) was added dropwise a solution of $Na_2[PdCl_4]$ (0.63 g, 0.17 mmol) in H_2O (10 ml). The yellow precipitate formed was filtered and recrystallized from CH_2Cl_2 and Et_2O to give the analytical sample. Yield 76%, mp 242–243 °C (Found: C, 55.42; H, 4.62; N, 3.39. Calc. for $C_{36}H_{32}N_2O_2P_2PdCl_2\cdot MeOH$: C, 55.83; H, 4.56; N, 3.52%). FAB mass spectrum: *m*/*z* 727 (M − Cl), 692 (M − 2Cl). IR (Nujol) ν_{max}/cm^{-1}: 1602m, 1587w, 1189s, 345m.

[$L^1_2PtCl_2$] 7

To an ethanolic solution (5 ml) of L^1 (307 mg, 1.00 mmol) an aqueous solution of $K_2[PtCl_4]$ (207 mg, 0.5 mmol, 15 ml) was added under vigorous stirring. The mixture was stirred for 3 days. The precipitate formed was filtered and washed with H_2O, EtOH and Et_2O and recrystallized from CH_2Cl_2–Et_2O to give the analytical sample as a pale yellow solid. Yield 80% (Found: C, 50.04; H, 4.28; N, 3.29. Calc. for $C_{38}H_{36}N_2O_2P_2PtCl_2\cdot H_2O$: C, 50.79; H, 4.26; N, 3.12%). IR (Nujol) ν_{max}/cm^{-1}: 1600m, 1181s, 350m (br).

[L^1_2Pd][PF_6]$_2$ 8

To a solution of **5** (0.100 g, 0.126 mmol) in CH_2Cl_2 (20 ml) 0.064 g (0.253 mmol) of $Ag[PF_6]$ in the same solvent were added. The mixture was stirred for 2.5 h in the dark. The AgCl formed was filtered: the resulting solution was evaporated to a small volume and diethyl ether was added. The precipitate formed was filtered and washed with Et_2O to give the analytical sample as a pale yellow solid. Yield 80%, mp 200 °C (Found: C, 44.91; H, 3.59; N, 2.98. Calc. for $C_{38}H_{36}N_2O_2P_4PdF_{12}$: C, 45.15; H, 3.59; N, 2.77%). Λ_M (5×10^{-4} M, CH_2Cl_2) = 24 Ω^{-1} cm^2 mol^{-1}; (5×10^{-4} M, acetone) = 220 Ω^{-1} cm^2 mol^{-1}. FAB mass spectrum: *m*/*z* 720 [M$^+$], 413 (M − L^1). IR (Nujol) ν_{max}/cm^{-1}: 1602m, 1122s.

Reaction of [L^1PdCl_2] with L^1

To a methanolic solution (30 ml) of **1** (0.100 g, 0.206 mmol) was added under vigorous stirring a solution of L^1 (0.0635 g, 0.207 mmol) in MeOH (10 ml). A yellow precipitate was formed. The mixture was stirred for 24 h and filtered to give the analytical sample, **5**. Yield 74%, mp 273 °C (decomp.) (Found: C, 57.02; H, 4.35; N, 3.50. Calc. for $C_{38}H_{36}N_2O_2P_2PdCl_2$: C, 57.63; H, 4.58; N, 3.54%).

Reaction of [L^3PdCl_2] with L^3

To a methanolic suspension (20 ml) of **3** (0.100 g, 0.22 mmol) was added under vigorous stirring a solution of L^3 (0.0610 g, 0.22 mmol) in MeOH (15 ml). After 24 h, the solid was collected and found to be unreacted [L^3PdCl_2].

The reaction was also carried out in solution (NMR tube) using a mixture of solvents [CD_2Cl_2–CD_3OD (5 : 1)]. The ^1H and ^{31}P NMR spectra showed only the presence of [L^3PdCl_2] and free ligand.

Reaction of [L^1PdCl_2] with L^3

To a methanolic solution (15 ml) of **1** (0.0664 g, 0.137 mmol) was added under vigorous stirring a solution of L^3 (0.0390 g, 0.137 mmol) in MeOH (15 ml). The mixture was stirred for 2 h: the precipitate formed was filtered off. ^1H and ^{31}P NMR spectra ($CDCl_3$) showed a mixture of compounds [$L^1_2PdCl_2$] and [L^3PdCl_2].

Reaction of [L^3PdCl_2] with PPh_3

To a solution of **3** (0.100 g, 0.22 mmol) in dichloromethane (30 ml) was added under vigorous stirring a solution of PPh_3 (0.0575 g, 0.22 mmol) in the same solvent (20 ml). The colour of the solution turned immediately to brilliant-orange. The solution was evaporated to a small volume and diethyl ether was added. The precipitate formed was filtered off and washed with Et_2O to give the analytical sample {[$(Ph_3P)PdCl_2$]$_2$} in almost quantitative yield.

X-Ray data collections and structure determinations

Crystal data and other experimental details are summarized in Table 4. A crystal of **4**·CH_2Cl_2 was mounted on an Enraf-Nonius CAD-4 diffractometer at room temperature using

Table 4 Crystallographic data

Compound	**4**·CH_2Cl_2	**5b**·MeOH·H_2O	**6**·MeOH
Formula	$C_{20}H_{20}Cl_4NOPPt$	$C_{39}H_{42}Cl_2N_2O_4P_2Pd$	$C_{37}H_{36}Cl_2N_2O_3P_2Pd$
M	658.3	842.0	796.0
Crystal system	Monoclinic	Trigonal	Monoclinic
Space group	$P2_1/c$ (no. 14)	$P3_121$ (no. 152)	$P2_1/c$ (no. 14)
a/Å	12.753(3)	16.742(2)	10.522(2)
b/Å	14.353(4)		11.090(2)
c/Å	12.863(3)	12.798(1)	16.220(4)
β/°	100.51(2)		108.87(1)
U/Å^3	2315.0(1.0)	3106.6(6)	1791.0(7)
Z	4	3	2
T/K	298	298	298
μ(Mo-Kα)/cm^{-1}	66.7	6.9	7.9
Measured reflections (total, independent)	4040, 4040	34876, 4893	19704, 4096
Unique observed reflections with $I > 3\sigma(I)$	2558	2903	3014
Final R and R'	0.030, 0.032	0.027, 0.034	0.023, 0.031

Mo-Kα radiation ($\lambda = 0.71073$ Å) with a graphite crystal monochromator in the incident beam. Cell parameters and orientation matrix were obtained from the least squares refinements of 25 reflections in the range $3 < \theta < 23°$. A periodic monitoring of three standard reflections revealed a crystal decay, on X-ray exposure, which was evaluated as about 16.1% (on intensities) at the end of data collection. The diffracted intensities were corrected for Lorentz, polarization, decay and absorption effects (empirical correction).[26] Crystals of **5b**·MeOH·H_2O and of **6**·MeOH were mounted on a Siemens SMART CCD area detector diffractometer at room temperature using Mo-Kα radiation with a graphite crystal monochromator in the incident beam. Cell parameters and orientation matrix were obtained from the least-squares refinement of 105 (for **5b**·MeOH·H_2O) and 86 (for **6**·MeOH) reflections measured in three different sets of 15 frames each, in the range $3 < \theta < 23°$. At the end of data collections the first 50 frames, containing 264 reflections (for **5b**·MeOH·H_2O) and 242 reflections (for **6**·MeOH), were recollected to have a monitoring of crystal decay, which was not observed, so that no time-decay correction was needed. The collected frames were processed with the software SAINT,[27a] and an absorption correction was applied (SADABS[27b]) to the 34876 collected reflections of **5b**·MeOH·H_2O [4893 of which are unique with $R_{int} = 0.023$ ($R_{int} = \Sigma|F_o{}^2 - F_{mean}{}^2|/\Sigma F_o{}^2$)] and to the 19704 collected reflections of **6**·MeOH (4096 of which are unique with $R_{int} = 0.030$). The calculations were performed on an AST Power Premium 486/33 computer using the Personal Structure Determination Package[28] and the physical constants tabulated therein. Scattering factors and anomalous dispersion corrections were taken from ref. 29.

The structures were solved by Patterson and Fourier methods and refined by full-matrix least squares, minimizing the function $\Sigma w(F_o - k|F_c|)^2$. In compound **5b**·MeOH·H_2O the water molecule is in general position with an occupancy factor of 0.50, and the methanol molecule is disordered, with the oxygen atom lying on a crystallographic two-fold axis, with occupancy factor of 0.50, and the carbon atom lying in general position, with an occupancy factor of 0.50. In **6**·MeOH the solvent molecule is disordered, and lies in the proximity of a crystallographic inversion centre, with occupancy factor of 0.50. Anisotropic thermal factors were refined for all the non-hydrogen atoms of **4**·CH_2Cl_2, **5b** and **6**. The carbon and oxygen atoms of MeOH and H_2O were refined with isotropic thermal parameters, and their hydrogen atoms were neglected. The other hydrogen atoms were placed in their ideal positions (C–H = 0.97 Å, B 1.15 times that of the carbon atom to which they are attached) and not refined. For noncentrosymmetric **5b**·MeOH·H_2O full refinement of the reported structure model in space group $P3_121$ led to $R = 0.027$ and $R' = 0.034$, full refinement of the structure enantiomorph in space group $P3_221$ led to $R = 0.031$ and $R' = 0.039$. The final Fourier maps showed maximum residuals of 0.62(9) e Å^{-3} at 0.33 Å from a chlorine atom of the solvent molecule in compound **4**·CH_2Cl_2, 0.50(6) e Å^{-3} at 0.69 Å from the oxygen atom of MeOH in **5b**·MeOH·H_2O, and 0.37(5) e Å^{-3} at 0.82 Å from Cl in **6**·MeOH.

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Paper 8/05842C