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Synthesis and characterization of square-planar palladium(II), platinum(II) and rhodium(I) complexes with a chiral pyridylphosphine hybrid ligand

Sergio Stoccoro,[a] Giorgio Chelucci,[a] Antonio Zucca,[a] Maria Agostina Cinellu,[a] Giovanni Minghetti *,[a] and Mario Manassero *,[b]

[a] *Dipartimento di Chimica, Università di Sassari, via Vienna 2, I-07100 Sassari, Italy*
[b] *Dipartimento di Chimica Strutturale e Stereochimica Inorganica, Università di Milano, Centro CN via Venezian 21, I-20133 Milano, Italy*

The complexes [PdLCl$_2$] **1**, [PtLCl$_2$] **2**, [PtL(SnCl$_3$)Cl] **3** and [RhL(CO)Cl] **4**, where L is the chiral pyridylphosphine 4-(diphenylphosphinomethyl)-2,2-dimethyl-5-(2-pyridyl)-1,3-dioxolane, have been synthesized and characterized by IR, NMR and FAB mass spectra. The structure of compound **1** has been solved by X-ray diffraction: the ligand is co-ordinated through both the P and N atoms to form a seven-membered ring which adopts a chair conformation. One of the hydrogen atoms of the backbone is located 2.72(3) Å over the palladium atom in a pseudo-axial position. Spectroscopic evidence supports a chelating behaviour of the ligand also in compounds **2** and **3**. The behaviour of the L ligand in the rhodium(I) species **4** is discussed.

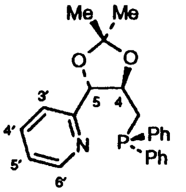
The co-ordination behaviour of bidentate compounds containing both P and a hard donor such as N has been a topic of interest in recent years.[1] These compounds are expected to display a variety of co-ordination modes well beyond those of the traditional P–P or N–N ligands. With a soft metal centre the hard nitrogen atom is likely to be weakly co-ordinated and hence easily displaceable. In addition, with P–N ligands, species more electron-rich than those with analogous P–P ligands should be achieved. As a consequence, in the resulting complexes both co-ordinative unsaturation and oxidative addition should be favoured. The latter properties can strongly affect the ability of a species to act as a precursor in a catalytic process.[2]

Among the P–N compounds of which the co-ordination behaviour has been studied, special attention has been devoted to pyridylphosphines: a review published in 1993 listed 188 references.[3] Most of the work concerns 'short bite' compounds, such as 2-(diphenylphosphino)pyridine, which have been extensively used in the stepwise synthesis of homo- and heterodinuclear complexes.[4] Less investigated have been compounds potentially able to chelate giving stable five-, six- or seven-membered rings.[5] A compound of this type, 4-(diphenylphosphinomethyl)-2,2-dimethyl-5-(2-pyridyl)-1,3-dioxolane (L) which has a backbone similar to that of the classic diop [2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane, *i.e.* 4,5-bis(diphenylphosphinomethyl)-2,2-dimethyl-1,3-dioxolane], has recently been synthesized by some of us.[6] We deemed it worthwhile to evaluate its behaviour with d^8 metal ions, namely Pd^{II}, Pt^{II} and Rh^{I}, and here report the first results. A preliminary account of this work has been given.[7]

Results and Discussion

The chiral compound L was obtained from dimethyl (+)-L-tartrate in enantiomerically pure form through the complex reaction sequence described previously.[6]

The compound [PdLCl$_2$] **1** was synthesized in fairly good yield (*ca.* 80%) from *trans*-[Pd(PhCN)$_2$Cl$_2$]. Analytical data, conductivity measurements and FAB mass spectra indicate that **1** is a 1:1 L:PdCl$_2$ adduct. Spectroscopic evidence (IR and NMR) is consistent with a monomeric species containing a chelating P–N ligand. In the IR spectrum (Nujol) the observation of ν(CN) (pyridine) at 1605 cm^{-1}, compared with 1589 cm^{-1} for free L, confirms co-ordination of the nitrogen atom.[5b,g] Bands at 345 and 284 cm^{-1} can be assigned to ν(Pd–Cl) *trans* to N and P, respectively. Evidence for co-ordination of the nitrogen atom in solution was obtained from the NMR spectra; ^{1}H, ^{31}P-{^{1}H} and ^{13}C-{^{1}H} data are collected in Tables 1 and 2. In the ^{1}H spectrum the resonances of both H^5 and H$^{6'}$ are shifted downfield with respect to free L, in agreement with the formation of a ring. Particularly remarkable is the shift of H^5 (Δδ 1.58 ppm) suggesting that the seven-membered ring adopts a conformation which allows the H^5 [H(4) in crystal structure] atom to approach the metal centre.[8]



The structure of compound **1** in the solid state has been solved by X-ray diffraction. It consists of the packing of discrete [PdLCl$_2$] molecules with normal van der Waals contacts, with the exception of a short Pd···H interaction, which will be discussed later. An ORTEP[9] view of the molecule with the atom labelling scheme is shown in Fig. 1 and selected bond distances and angles, are given in Table 3.

The palladium atom displays a slightly distorted square-planar co-ordination with maximum deviations from the best plane of +0.036(3) Å for the N atom and of −0.045(1) Å for the P atom. The dihedral angle between the PdCl(1)Cl(2) and PdPN planes is 3.5(4)°. The bite angle of the bidentate ligand is 89.63(7)°, very close to the ideal value of 90°. The bond lengths to the metal atom are all as expected and can be compared with corresponding values observed in [PdCl$_2$(*o*-Ph$_2$PC$_6$H$_4$CH$_2$OCH$_2$C$_5$H$_4$N-2)] **5**,[5g] where the palladium atom is also bonded to two chlorine atoms and a P–N bidentate ligand, with the nitrogen atom belonging to a substituted pyridine ring. The bidentate ligand forms with the metal a nine-membered ring.

The two Pd–Cl bond lengths in the present compound **1** are Pd–Cl(1) 2.277(1) and Pd–Cl(2) 2.360(1) Å. The lengthening of the latter is due to the *trans* influence of the phosphorus atom. Corresponding distances in **5** are 2.282(2) and 2.351(1) Å. The

Table 1 Proton NMR data[a]

	L		**1** [PdLCl$_2$]		**2** [PtLCl$_2$][b]		**3** [PtL(SnCl$_3$)Cl][c]		**4** [RhL(CO)Cl]	
CH$_3$	1.47 (s) 1.52 (s)		1.56 (s) 1.66 (s)		1.55 (s) 1.65 (s)		1.58 (s) 1.66 (s)		1.54 (s) 1.64 (s)	
CH$_2$	2.47 (m)	(8.5, 14.2) [2.9]	3.23 (m)	(4.6, 14.2) [18.3]	3.34 (m)	(10.7, 13.9) [8.5]	3.30 (m)	(10.4, 14.1) [8.3]	3.11 (m)	(6.1, 11.0, 13.5)
	2.77 (m)	(3.4, 14.2) [2.2]	3.37 (m)	(10.5, 14.2) [8.0]	3.51 (m)	(4.4, 13.9) [15.4]	3.79 (m)	(4.3, 14.1) [15.4] (78)[e]	3.46 (m)	(n. r.)[d]
CH^4	4.05 (m)	(3.4, 8.3, 8.5) [8.3]	3.89 (m)	(4.6, 8.3, 10.5) [1.7]	3.86 (m)	(4.4, 8.3, 10.7) [1.4]	4.05 (m)	(4.3, 8.3, 10.4) [1.7]	3.82 (m)	(4.2, 8.3, 11.0) [1.4]
CH^5	4.88 (d)	(8.3)	6.46 (d)	(8.3)	6.55 (d)	(8.3)	6.28 (d)	(8.3)	6.29 (d)	(8.3)
CH$^{6'}$	8.54		9.04		9.17	(35)[e]	8.89	(33)[e]	8.89	
Aromatics	7.2–8.6		7.2–9.1		7.2–9.2		7.3–9.0		7.2–8.9	

[a] Spectra recorded at room temperature, solvent CDCl$_3$ unless otherwise stated, coupling constants in Hz [*J*(H–H) in parentheses, *J*(P–H) in square brackets]. [b] CH(5′) δ 7.25; CH(4′), 7.73; CH(3′), 7.55; assignment based on a correlation (COSY) experiment (CD$_2$Cl$_2$). [c] Solvent CD$_2$Cl$_2$. [d] Not resolved. [e] *J*(Pt–H).

Table 2 ^{13}C-{^{1}H} and ^{31}P-{^{1}H} NMR data[a]

^{13}C	L	[PdLCl$_2$]	[PtLCl$_2$][b]	[PtL(SnCl$_3$)Cl][c]	[RhL(CO)Cl]
CH$_3$	26.73 27.29	26.76 27.23	26.74 27.29	26.72 27.37	26.78 27.28
CH$_2$	31.56 (15.1)	31.93 (26.2)	31.69 (35.3)	31.99 (36.5) (20.8)[d]	36.23 (24.7)
C^4, C^5	79.84 (13.1) 84.08 (9.1)	n.o.[e] 82.10 (5.0)	76.25 (5.1) 81.81 (3.0)	76.72 (4.8) 82.04 (2.8) (25)[d]	77.5 (n.o.)[f] 82.51 (4.3)
C(CH$_3$)$_2$	109.66	110.89	110.64	111.59	110.31
C$^{2'}$	158.27	159.24	159.48	159.30	159.83
C$^{3'}$, C$^{5'}$	120.63 122.75	121.93 125.34	122.61 C(3) 125.61 C(5)	122.92 (26)[d] 126.52 (29.5)[d]	120.77 123.95
C$^{4'}$	136.65	139.64	139.27	140.97	138.82
C$^{6'}$	148.95	153.68	154.46	152.42 (17)[d]	151.88
CO					188.46 (18.6) (71.7)[g]
^{31}P	−21.76	9.23	−10.83 (3725)[h]	−14.54 (3609)[h] (228)[i]	23.30 (170)[j]

[a] Spectra recorded at room temperature, solvent CDCl$_3$ unless otherwise indicated, coupling constants (Hz) in parentheses [*J*(C–P) unless otherwise indicated]. [b] Assignment based on correlation (COSY) and heteronuclear correlation (HETCOR) experiments. [c] Solvent CD$_2$Cl$_2$. [d] *J*(Pt–C). [e] Not observed, possibly hidden by the solvent. [f] Partially hidden by the solvent. [g] *J*(Rh–C). [h] *J*(Pt–P). [i] *J*(P–^{117,119}Sn). [j] *J*(Rh–P).

Table 3 Selected bond distances (Å) and angles (°) with estimated standard deviations (e.s.d.s) in parentheses for compound **1**

Pd–Cl(1)	2.277(1)	Pd–Cl(2)	2.360(1)
Pd–P	2.263(1)	Pd–N	2.039(3)
P–C(11)	1.828(3)	N–C(6)	1.350(4)
C(4)–C(5)	1.540(5)	C(4)–C(6)	1.505(4)
C(5)–C(11)	1.514(5)	Pd ··· H(4)	2.72(3)
Cl(1)–Pd–Cl(2)	91.21(4)	Cl(1)–Pd–P	92.42(3)
Cl(1)–Pd–N	177.91(8)	Cl(2)–Pd–P	175.02(3)
Cl(2)–Pd–N	86.77(8)	P–Pd–N	89.63(7)
Pd–P–C(11)	109.7(1)	Pd–N–C(6)	124.1(2)
C(5)–C(4)–C(6)	111.8(3)	C(4)–C(5)–C(11)	116.9(3)
N–C(6)–C(4)	116.9(3)	P–C(11)–C(5)	116.3(2)

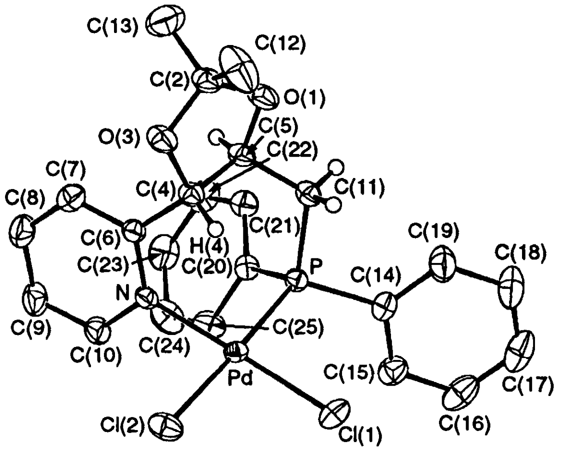


Fig. 1 An ORTEP view of [PdLCl$_2$] **1**. Thermal ellipsoids are drawn at the 30% probability level

Pd–P and Pd–N bond lengths in **1** are 2.263(1) and 2.039(3) Å, respectively [2.254(1) and 2.044(4) Å in **5**]. The seven-membered metallacycle is in a chair conformation, as can be seen in Fig. 2. Atoms Pd, P, C(4) and C(5) are substantially coplanar [maximum deviations from the best plane being +0.048(3) Å for C(5) and −0.044(3) Å for C(4)], with C(11) lying 0.696(3) Å above that plane and N and C(6) 1.497(3) and 1.380(3) Å, respectively, below it. The pyridine ring is strictly planar, with normal bond parameters. Atom H(4) is in a pseudo-axial position with respect to the metal co-ordination plane, with a Pd ··· H(4) distance of 2.72(3) Å.[8c] There is another rather short Pd ··· H contact, 2.75(4) Å, between the metal atom and the pyridine hydrogen atom H(9′) which belongs to a neighbouring molecule [H(9) is bonded to C(9) and H(9′) is related to H(9) by the symmetry operation $\frac{1}{2} + x, \frac{3}{2} - y, 1 - z$]. The Pd ··· H(9′) vector is approximately *trans* to Pd ··· H(4) [H(4) ··· Pd ··· H(9′) angle 167(1)°], so that when these metal–hydrogen interactions are taken into account the co-ordination around the Pd atom becomes distorted octahedral.

The properties of the compound [PtLCl$_2$] **2** are very similar to those of the palladium analogue. Both the IR and NMR spectra are similar to those of complex **1**. In the ^{31}P-{^{1}H} NMR spectrum a single resonance is observed at δ −10.83, with satellites due to ^{195}Pt ($I = \frac{1}{2}$, natural abundance 33.8%). The value of ^1J(Pt–P), 3725 Hz, is consistent with a phosphorus *trans* to an atom having low *trans* influence, *i.e.* Cl.[10] In the ^{1}H

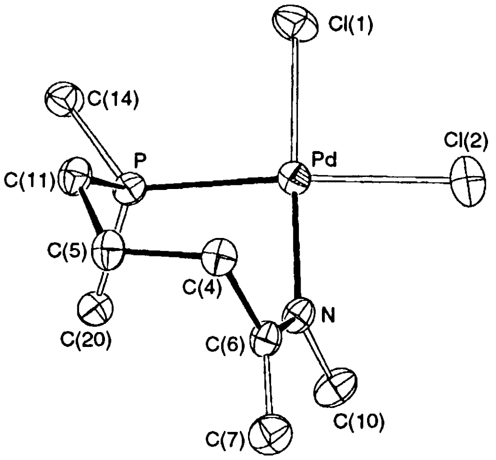
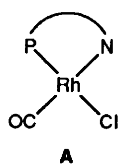


Fig. 2 Perspective view of the chair conformation of the seven-membered ring in compound **1**. Atoms not shown have been omitted for clarity

NMR spectrum, ^{195}Pt coupling to H(6′) [^{3}J(Pt–H) 35 Hz] unambiguously demonstrates the bidentate behaviour of the ligand. The chemical shift, δ 9.17, indicates that H(6′) is strongly deshielded, as often observed when a chlorine is in the proximity of the pyridine ring.[11]

Since the activity of certain platinum complexes, *e.g.* as oxo catalysts, increases in the presence of $SnCl_3^-$,[12] the reaction of compound **2** with $SnCl_2$ has been investigated. The outcome of the reaction was the insertion of $SnCl_2$ into a platinum–chlorine bond to give [PtL($SnCl_3$)Cl] **3**. The FAB mass spectrum shows a peak at *m*/*z* 794 corresponding to $[M - Cl]^+$. Evidence for the co-ordination of the nitrogen atom is provided by the coupling of platinum to H(6′) [*J*(Pt–H) 33 Hz] observed in the ^{1}H NMR spectrum. In the ^{31}P-{^{1}H} NMR spectrum one resonance is observed at δ −14.54, with satellites due both to platinum and tin [*J*(P–Pt) 3609, *J*(P–Sn) 228 Hz], indicating that the reaction yields only one of the two possible geometrical isomers. The *J*(P–Pt) and *J*(P–Sn) values are consistent with a *trans* P–Pt–Cl arrangement. The *J*(P–Sn) values are reported to be much larger in complexes having a P-donor *trans* to the $SnCl_3^-$ ligand.[13]

The reaction of L with [{Rh(CO)$_2$Cl}$_2$] at room temperature gives compound **4**, formulated as [RhL(CO)Cl] on the basis of the analytical data. Compound **4** is not an electrolyte: thus ionic species such as [RhL$_2$][Rh(CO)$_2$Cl$_2$] or [(OC)LRh(μ-Cl)RhL(CO)]Cl are ruled out. A peak in the FAB mass spectrum at *m*/*z* 1051, corresponding to the latter cation, can arise from a vapour-phase reaction of a monomeric molecule, *M*, and a $[M - Cl]^+$ ion: no peaks due to *M* and $[M - Cl]^+$ are observed. In the IR spectrum a strong and sharp absorption at 1991 (Nujol) and 2005 cm^{-1} (CH_2Cl_2) indicates that the structure is the same in the solid state and in solution. At variance with the platinum complexes **2** and **3**, clear-cut evidence for the binding of the nitrogen atom is not provided by the ^{1}H NMR spectrum as no ^{103}Rh coupling to H(6′) is observed. Nevertheless, the resonances of the protons in the backbone of the ligand, as well as of H(6′), are remarkably shifted with respect to free L, suggesting that both the P and N atoms are involved in co-ordination. In addition, the analogies observed in the ^{1}H NMR spectra of compounds **1**–**4** are consistent with an endobidentate behaviour of the ligand L also in **4**. The set of coupling constants obtained from the ^{31}P-{^{1}H} and ^{13}C-{^{1}H} NMR spectra, ^{1}J(P–Rh) 170,[5b] ^{1}J(C–Rh) 71.7[14] and ^{2}J(C–P) 18.6 Hz is consistent with a *trans* P–Rh–Cl arrangement. In conclusion, we feel confident to consider **A** as the most likely structure for compound **4**, even if a highly symmetric dinuclear species with bridging ligands cannot be completely ruled out.



A

The chiral compound L and its *P*-oxide have been tested in the presence of rhodium(I) species as catalysts for the enantioselective hydroformylation of some functionalized olefins.[15]

Experimental

Established methods were used to prepare the compounds *trans*-[Pd(PhCN)$_2$Cl$_2$],[16] *trans*-[Pt(PhCN)$_2$Cl$_2$],[16] [{Rh(CO)$_2$Cl}$_2$][17] and L.[6] All other reagents were used as supplied. All experiments were performed under an atmosphere of purified argon. Infrared spectra were obtained as Nujol mulls on NaCl plates using a Perkin-Elmer 983 instrument, ^{1}H, ^{13}C and ^{31}P NMR spectra on a Varian VX300 spectrometer. The ^{1}H and ^{13}C spectra were referenced to internal tetramethylsilane, the ^{31}P spectra to external 85% H_3PO_4; positive chemical shifts to higher frequency. Elemental analyses were performed by the Microanalytical Laboratory of the University of Sassari. The conductivity measurements were made in dichloromethane solution using a Philips PW 9505 conductivity meter. The mass spectra were recorded on a VG 7070EQ instrument, equipped with a PDP 11-250J data system and operating under positive-ion fast atom bombardment (FAB) conditions with 3-nitrobenzyl alcohol (from Fluka). The bombarding Xe atom beam had a translational energy of 8 keV (*ca.* 1.28 × 10^{-15} J). The reported *m*/*z* values correspond to ^{195}Pt, ^{35}Cl, ^{117}Sn and ^{106}Pd. The melting points are uncorrected.

Syntheses

[PdLCl$_2$] 1. To a benzene (25 cm^3) suspension of *trans*-[Pd(PhCN)$_2$Cl$_2$] (383.6 mg, 1 mmol) was added a solution of compound L (377.2 mg, 1 mmol) in the same solvent (10 cm^3). Over 24 h the suspension disappeared and the solution was stirred at room temperature for 2 d until a pale yellow precipitate was formed. This was filtered off and washed with diethyl ether. Recrystallization from dichloromethane and diethyl ether gave pure complex **1** as a yellow crystalline solid, 81% yield, m.p. 260–261 °C (decomp.) (Found: C, 49.95; H, 4.65; N, 2.45%; M^+, *m*/*z* 553. $C_{23}H_{24}Cl_2NO_2PPd$ requires C, 49.80; H, 4.65; N, 2.45%; *M*, 553); Λ_M (5 × 10^{-4} mol dm^{-3}) = 0.2 Ω^{-1} cm^2 mol^{-1}; $\tilde{\nu}_{max}$/cm^{-1} 1605s, 1569w, 1103s, 1080s, 345s (Pd–Cl *trans* to N) and 284s (Pd–Cl *trans* to P); *m*/*z* 553 (M^+), 518 (*M* − Cl) and 483 (*M* − 2Cl).

[PtLCl$_2$] 2. To a benzene solution (25 cm^3) of *trans*-[Pt(PhCN)$_2$Cl$_2$] (315 mg, 0.667 mmol) was added a solution of compound L (251 mg, 0.667 mmol) in the same solvent (10 cm^3). The solution was refluxed for 2 d until a pale yellow precipitate was formed. This was collected and dissolved in acetone; the solution was evaporated to small volume to give a pale yellow product which was filtered off and washed with Et$_2$O, yield 70%, m.p. 272–273 °C (Found: C, 43.40; H, 3.90; N, 2.05. $C_{23}H_{24}Cl_2NO_2PPt$ requires C, 42.90; H, 3.75; N, 2.20%); Λ_M (5 × 10^{-4} mol dm^{-3}) = 0.2 Ω^{-1} cm^2 mol^{-1}; $\tilde{\nu}_{max}$/cm^{-1} 1609s, 1578w, 1104s, 1079s, 347s (Pt–Cl *trans* to N) and 294s (Pt–Cl *trans* to P); *m*/*z* 607 (*M* − Cl).

[PtL(SnCl$_3$)Cl] 3. To a stirred solution of complex **2** (128.6 mg, 0.2 mmol) in acetone (25 cm^3) was added a solution of anhydrous $SnCl_2$ (37.9 mg, 0.2 mmol) in the same solvent (5 cm^3). After 4 h the resulting pale yellow solution was evaporated to dryness and the precipitate was crystallized from dichloromethane–hexane, yield 84%, m.p. 218–219 °C

Table 4 Crystallographic data for compound **1**

Formula	$C_{23}H_{24}Cl_2NO_2PPd$
M	554.7
Colour	Yellow
Crystal system	Orthorhombic
Space group	$P2_12_12_1$ (no. 19)
a/Å	10.116(2)
b/Å	13.907(3)
c/Å	16.634(4)
U/Å^3	2340.1(9)
Z	4
F(000)	1120
D_c/g cm^{-3}	1.574
Crystal dimensions/mm	0.28 × 0.45 × 0.55
μ(Mo-Kα)/cm^{-1}	11.0
Minimum transmission factor	0.94
Scan mode	ω
ω-Scan width/°	1.80 + 0.35 tan θ
θ Range/°	3–27
Reciprocal space explored	$+h$, $+k$, $+l$ in the range θ 3–27°, $+h$, $+k$, $-l$ in the range θ 3–23°
Measured reflections	4768
Unique observed reflections with $I > 3\sigma(I)$	3818
Final *R* and *R'*[a]	0.026, 0.033
No. variables	291
Goodness of fit[b]	1.30

[a] $R = [\Sigma(||F_o - k|F_c||)/\Sigma F_o]$, $R' = [\Sigma w(F_o - k|F_c|)^2/\Sigma w F_o{}^2]^{\frac{1}{2}}$. [b] $[\Sigma w(F_o - k|F_c|)^2/(N_o - N_v)]^{\frac{1}{2}}$, where $w = 1/[\sigma(F_o)]^2$, $\sigma(F_o) = [\sigma^2(I) + (0.04I)^2]^{\frac{1}{2}}/2F_oL_p$, N_o is the number of observations and N_v the number of variables.

Table 5 Fractional atomic coordinates with e.s.d.s in parentheses for the refined atoms of compound **1**

Atom	*x*	*y*	*z*
Pd	0.045 80(2)	0.804 49(2)	0.350 02(1)
Cl(1)	0.267 74(8)	0.828 94(7)	0.339 78(7)
Cl(2)	0.019 8(1)	0.948 91(6)	0.422 80(6)
P	0.058 57(8)	0.659 97(6)	0.287 98(5)
O(1)	−0.166 5(3)	0.723 3(2)	0.093 5(1)
O(3)	−0.276 0(3)	0.840 5(2)	0.163 1(1)
N	−0.153 7(3)	0.787 7(2)	0.360 5(1)
C(2)	−0.265 0(4)	0.796 7(3)	0.086 4(2)
C(4)	−0.179 6(3)	0.802 5(3)	0.215 5(2)
C(5)	−0.145 6(3)	0.705 1(2)	0.176 7(2)
C(6)	−0.238 6(3)	0.790 4(2)	0.297 9(2)
C(7)	−0.371 4(4)	0.777 5(3)	0.310 0(2)
C(8)	−0.418 7(4)	0.757 2(4)	0.385 5(3)
C(9)	−0.332 2(4)	0.755 4(3)	0.448 8(2)
C(10)	−0.201 6(4)	0.771 8(3)	0.434 2(2)
C(11)	−0.004 6(3)	0.670 2(2)	0.185 4(2)
C(12)	−0.217 6(7)	0.867 0(4)	0.026 1(3)
C(13)	−0.396 6(6)	0.753 9(5)	0.066 7(4)
C(14)	0.220 5(3)	0.604 7(2)	0.276 5(2)
C(15)	0.295 7(4)	0.587 8(3)	0.345 0(3)
C(16)	0.420 5(4)	0.547 0(3)	0.339 1(4)
C(17)	0.469 3(4)	0.523 4(4)	0.264 7(4)
C(18)	0.396 3(5)	0.537 9(4)	0.198 1(3)
C(19)	0.270 3(4)	0.578 4(4)	0.203 2(3)
C(20)	−0.042 2(3)	0.572 0(2)	0.342 0(2)
C(21)	−0.115 0(4)	0.502 3(3)	0.303 1(2)
C(22)	−0.195 1(4)	0.440 7(3)	0.347 1(3)
C(23)	−0.203 9(4)	0.449 5(3)	0.429 5(3)
C(24)	−0.128 2(5)	0.517 0(3)	0.469 1(3)
C(25)	−0.047 0(5)	0.577 3(3)	0.425 8(2)
H(4)	−0.104(3)	0.846(2)	0.219(2)
H(5)	−0.206(4)	0.654(2)	0.196(2)
H(9)	−0.358(4)	0.746(3)	0.502(2)
H(111)	0.006(3)	0.616(3)	0.159(2)
H(112)	0.052(4)	0.719(3)	0.163(2)

(decomp.) (Found: C, 33.60; H, 2.90; N, 1.65. $C_{23}H_{24}Cl_3NO_2PPtSn$ requires C, 33.15; H, 2.90; N, 1.70%); Λ_M (5 × 10^{-4} mol dm^{-3}) = 0.2 Ω^{-1} cm^2 mol^{-1}; $\tilde{\nu}_{max}$/cm^{-1} 1602s, 1569w, 1104s, 1071s, 349s, 333s and 322s; *m*/*z* 794 (*M* − Cl), 642 (*M* − $SnCl_2$) and 607 (*M* − $SnCl_3$).

[RhL(CO)Cl] 4. To a benzene solution (25 cm^3) of $[\{Rh(CO)_2Cl\}_2]$ (74.5 mg, 0.192 mmol) was added at room temperature a solution of compound L (144.5 mg, 0.384 mmol) and the mixture was stirred for 1 h. The solution was reduced to small volume and hexane was added to give a pale yellow solid. Crystallization from dichloromethane and hexane gave the pure complex **4** as a pale yellow crystalline solid, 90% yield, m.p. 194–195 °C (Found: C, 52.95; H, 4.50; N, 2.50. $C_{24}H_{24}ClNO_3PRh$ requires C, 52.05; H, 4.35; N, 2.55%); Λ_M (5 × 10^{-4} mol dm^{-3}) = 3 Ω^{-1} cm^2 mol^{-1}; $\tilde{\nu}_{max}$/cm^{-1} (CO) 1991vs (CH_2Cl_2 solution, 2005vs), 1601s, 1569w, 1099s, 1068s and 296s (Rh–Cl *trans* to P); *m*/*z* 480 [*M* − (CO + Cl)] and 1051 (2*M* − Cl).

Crystallography

Crystal data and other experimental details are summarized in Table 4 with atomic coordinates in Table 5. The diffraction analysis was carried out on an Enraf-Nonius CAD-4 diffractometer at room temperature using Mo-Kα radiation (λ = 0.710 73 Å) with a graphite-crystal monochromator in the incident beam. The calculations were performed on a PDP 11/73 computer using the SDP structure determination package[18] and the physical constants tabulated therein. A crystal decay of about 0.8% on intensities was observed at the end of data collection. The diffracted intensities were corrected for Lorentz, polarization, decay and absorption effects (ψ-scan empirical correction).[19] Scattering factors and anomalous dispersion corrections were taken from ref. 20. The structure was solved by Patterson and Fourier methods and refined by full-matrix least squares, minimizing the function $\Sigma w(F_o - k|F_c|)^2$. Anisotropic thermal parameters were refined for all the non-hydrogen atoms. The atomic coordinates and the isotropic thermal parameters of hydrogen atoms H(4), H(5), H(9), H(111) and H(112) were also refined. The remaining hydrogen atoms were placed in their ideal positions (C–H 0.97 Å, *B* = 1.20 times that of the C atom to which the atom is bonded) and not refined. The full refinement of the two structure enantiomorphs led to *R* = 0.026 and *R'* = 0.033 for the correct one, and to *R* = 0.030 and *R'* = 0.038 for the other. The final Fourier map showed a maximum residual of 0.59(8) e Å^{-3} at 0.85 Å from the palladium atom.

Complete atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

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