Data collection

Stoe AED-2 four-circle diffractometer
$\omega/2\theta$ scans
Absorption correction: none
1356 measured reflections
1356 independent reflections
893 reflections with $I > 2\sigma(I)$

$\theta_{max} = 22.51°$
$h = -9 \rightarrow 9$
$k = 0 \rightarrow 10$
$l = 0 \rightarrow 12$
2 standard reflections
frequency: 60 min
intensity decay: 1.5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.116$
$S = 1.144$
1352 reflections
163 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0382P)^2 + 1.6057P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = -0.001$

$\Delta\rho_{max} = 0.27$ e Å^{-3}
$\Delta\rho_{min} = -0.30$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0010 (11)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Cu1—O3	1.895 (4)	Cu1—*OW*1	2.470 (6)
Cu1—N1	2.135 (4)		
O3—Cu1—N1	80.6 (2)	N1—Cu1—*OW*1	91.8 (2)
O3—Cu1—*OW*1	91.6 (2)		

The crystal did not diffract significantly beyond 45° in 2θ and diffraction data were not measured beyond this limit. Water H atoms were located from difference maps and refined isotropically. The remainder were included in calculated positions and treated as riding atoms using *SHELXL*93 (Sheldrick, 1993) default parameters, except that one parameter was refined for each methyl group to define its orientation.

Data collection: *DIF*4 (Stoe & Cie, 1995). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1996). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93. Molecular graphics: *PLATON*/*PLUTON* (Spek, 1990). Software used to prepare material for publication: *SHELXL*93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: MU1367). Services for accessing these data are described at the back of the journal.

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cis-Dichloro(2-diphenylphosphinoethylamine-*N*,*P*)palladium(II)

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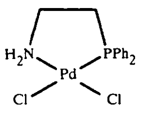
Abstract

The coordination geometry about the palladium(II) ion in [$PdCl_2\{Ph_2P(CH_2)_2NH_2\}$] is distorted square planar. Individual atoms are displaced from the $PdCl_2PN$ coordination plane by no more than 0.094 Å, while in-plane distortion of the bond angles at the metal atom is more marked. The greater *trans* influence of phosphine over amine is reflected in the mean Pd—Cl bond lengths of 2.383 Å, *trans* to P, and 2.293 Å, *trans* to N.

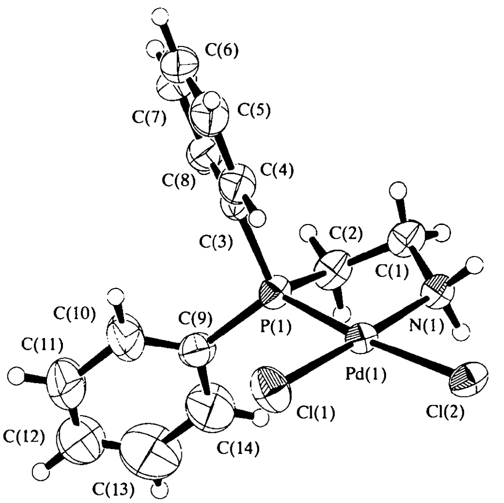
Comment

Hybrid ligands with both hard and soft donor atoms are able to form hemi-labile complexes which have been noted for their utility in catalytic systems (Bader & Lindner, 1990; Wehman *et al.*, 1995). To this end, we are currently studying the complexes of a series of tridentate Schiff base ligands having P-, N- and O-donor atoms. The title compound, (I), was obtained unexpectedly from the reaction of one of those ligands, *o*-$C_6H_4(OH)\{C{=}N(CH_2)_2PPh_2\}$ (Dilworth *et al.*, 1994), with [$PdCl_2(NCPh)_2$] in chloroform. We believe that the ligand (either free or complexed) undergoes acid-catalysed hydrolysis of the imine linkage (there is often a trace of HCl in $CHCl_3$) to give 2-diphenylphosphinoethylamine and hence its palladium chloride complex. The preparation of this compound has been noted previously (Suzuki *et al.*, 1996).

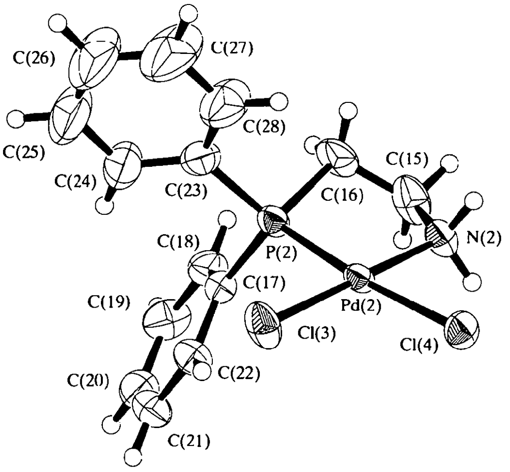


(I)

Compound (I) crystallizes with two molecules, *A* and *B*, in the asymmetric unit (Fig. 1). These differ slightly in the conformation of the ligand backbone and thus in the orientation of the phenyl groups. For molecule *A* and the inverted form of *B*, the corresponding torsion angles agree in sign but differ by up to 22° in magnitude. The largest deviations are in the torsion angles between the C(2)—P(1) or C(16)—P(2) bonds and the C_{ipso}—C_{ortho} bonds in the respective phenyl groups. The coordination sphere of each palladium ion is distorted square planar, with maximum deviations from the $PdCl_2NP$ weighted least-squares planes of 0.023 (3) and 0.094 (3) Å (means of 0.008 and 0.034 Å for the two conformations). The ligand bite angles, N(1)—Pd(1)—P(1) and N(2)—Pd(2)—P(2), are 84.96 and 85.07°, respectively, in close agreement with those observed in $[Pd\{Me_2P(CH_2)_2NH_2\}_2]^{2+}$ [83.9 (9) and 84.5 (10)°; Suzuki *et al.*, 1996], while the Cl—Pd—Cl angles are both substantially greater than 90°, as might be expected.



Molecule *A*



Molecule *B*

Fig. 1. *ORTEP*II plot (Johnson, 1976) of $[PdCl_2\{Ph_2P(CH_2)_2NH_2\}]$ with 40% probability ellipsoids, showing the relative conformations of the two unique molecules, *A* and *B*, in the asymmetric unit.

The bond lengths around each palladium ion are also worthy of note. In particular, the Pd—Cl(*trans* to P) distances [2.366 (1) and 2.400 (1) Å] are markedly greater than the Pd—Cl(*trans* to N) distances [2.289 (1) and 2.297 (1) Å]. This is in keeping with the stronger *trans*-labilizing influence of phosphine donors over amine donors, and supports the assertion that the chloride coordination sites have potentially rather different reactivities.

Experimental

The title compound was obtained by refluxing equimolar quantities of bis(benzonitrile)palladium dichloride and o-C_6H_4-(OH){C═N(CH$_2$)$_2$PPh$_2$} in untreated chloroform. After removal of the solvent, a small portion of the crude residue was dissolved in $CDCl_3$ for NMR spectroscopy. On standing for several days, yellow needles of $[PdCl_2\{Ph_2P(CH_2)_2NH_2\}]$ were formed.

Crystal data

$[PdCl_2(C_{14}H_{16}NP)]$
$M_r = 406.57$
Triclinic
$P\bar{1}$
$a = 8.082$ (2) Å
$b = 12.554$ (2) Å
$c = 16.724$ (5) Å
$\alpha = 74.02$ (2)°
$\beta = 85.21$ (3)°
$\gamma = 89.39$ (2)°
$V = 1625.5$ (7) Å^3
$Z = 4$
$D_x = 1.661$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 23 reflections
$\theta = 16.2$–$18.9°$
$\mu = 1.555$ mm^{-1}
$T = 295.2$ K
Needle
0.80 × 0.25 × 0.05 mm
Yellow

Data collection

Rigaku AFC-7*S* diffractometer
ω scans with profile analysis
Absorption correction: empirical ψ scans (North *et al.*, 1968)
$T_{min} = 0.738$, $T_{max} = 0.925$
6862 measured reflections
6382 independent reflections

5333 reflections with $I > 0.5\sigma(I)$
$R_{int} = 0.015$
$\theta_{max} = 26.02°$
$h = 0 \rightarrow 9$
$k = -15 \rightarrow 15$
$l = -20 \rightarrow 20$
3 standard reflections every 150 reflections intensity decay: none

Refinement

Refinement on F
$R = 0.042$
$wR = 0.036$
$S = 1.117$
5333 reflections
343 parameters
H atoms not refined
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{\max} = 0.009$
$\Delta\rho_{\max} = 0.52$ e Å^{-3}
$\Delta\rho_{\min} = -0.52$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Selected geometric parameters (Å, °)*

Pd(1)—Cl(1)	2.297 (1)	P(1)—C(3)	1.813 (4)
Pd(1)—Cl(2)	2.400 (1)	P(1)—C(9)	1.795 (4)
Pd(1)—P(1)	2.209 (1)	P(2)—C(16)	1.821 (4)
Pd(1)—N(1)	2.049 (3)	P(2)—C(17)	1.809 (4)
Pd(2)—Cl(3)	2.289 (1)	P(2)—C(23)	1.803 (5)
Pd(2)—Cl(4)	2.366 (1)	N(1)—C(1)	1.479 (5)
Pd(2)—P(2)	2.201 (1)	N(2)—C(15)	1.468 (6)
Pd(2)—N(2)	2.056 (3)	C(1)—C(2)	1.511 (6)
P(1)—C(2)	1.831 (4)	C(15)—C(16)	1.468 (7)
Cl(1)—Pd(1)—Cl(2)	96.27 (5)	C(2)—P(1)—C(3)	106.0 (2)
Cl(1)—Pd(1)—P(1)	91.97 (5)	C(2)—P(1)—C(9)	107.6 (2)
Cl(1)—Pd(1)—N(1)	176.87 (9)	C(3)—P(1)—C(9)	107.1 (2)
Cl(2)—Pd(1)—P(1)	171.74 (4)	Pd(2)—P(2)—C(16)	100.6 (2)
Cl(2)—Pd(1)—N(1)	86.80 (9)	Pd(2)—P(2)—C(17)	115.2 (1)
P(1)—Pd(1)—N(1)	84.96 (9)	Pd(2)—P(2)—C(23)	117.4 (2)
Cl(3)—Pd(2)—Cl(4)	93.23 (4)	C(16)—P(2)—C(17)	109.5 (2)
Cl(3)—Pd(2)—P(2)	92.53 (4)	C(16)—P(2)—C(23)	107.0 (2)
Cl(3)—Pd(2)—N(2)	176.44 (10)	C(17)—P(2)—C(23)	106.6 (2)
Cl(4)—Pd(2)—P(2)	173.94 (4)	Pd(1)—N(1)—C(1)	116.3 (3)
Cl(4)—Pd(2)—N(2)	89.25 (10)	Pd(2)—N(2)—C(15)	116.6 (3)
P(2)—Pd(2)—N(2)	85.07 (10)	N(1)—C(1)—C(2)	108.9 (3)
Pd(1)—P(1)—C(2)	100.9 (1)	P(1)—C(2)—C(1)	106.4 (3)
Pd(1)—P(1)—C(3)	112.9 (1)	N(2)—C(15)—C(16)	111.9 (4)
Pd(1)—P(1)—C(9)	121.1 (2)	P(2)—C(16)—C(15)	108.5 (3)

N(1)—C(1)—C(2)—P(1)	51.6 (4)
N(2)—C(15)—C(16)—P(2)	−45.8 (5)
C(2)—P(1)—C(3)—C(4)	−133.5 (4)
C(16)—P(2)—C(17)—C(22)	155.5 (4)
C(2)—P(1)—C(3)—C(8)	45.0 (4)
C(16)—P(2)—C(17)—C(18)	−24.7 (5)
C(2)—P(1)—C(9)—C(10)	−136.1 (5)
C(16)—P(2)—C(23)—C(24)	119.0 (5)
C(2)—P(1)—C(9)—C(14)	43.8 (6)
C(16)—P(2)—C(23)—C(28)	−65.1 (5)

Data were corrected only for Lorentz–polarization and absorption effects, and equivalent reflections were averaged. Reflections with $I < 0.5\sigma(I)$ were subsequently disregarded. The structure was solved by Patterson methods and expanded by Fourier difference syntheses. H atoms were located in a difference map. Their positions were not refined and their displacement parameters $U_{\rm iso}$ set as $1.2U_{\rm eq}$ of the attached C atom.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1985, 1992). Program(s) used to solve structure: *PATTY* in *DIRDIF*92 (Beurskens *et al.*, 1992). Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: MU1349). Services for accessing these data are described at the back of the journal.

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catena-Poly[[tetrakis(μ-3,5-dinitrobenzoato-*O*:*O*′)dicopper(II)]bis[(μ-3,5-dinitrobenzoato-*O*:*O*′)(methanol-*O*)copper(II)]]†

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Abstract

The title complex, [Cu$_3${(NO$_2$)$_2$C$_6$H$_3$COO}$_6$(CH$_3$OH)$_2$]$_n$, is a linear polymeric chain with the dinitrobenzoate ions forming all bridges. The chain is linked across Cu(CH$_3$OH)$_2$ units on symmetry centres and includes fourfold bridged pairs of Cu atoms with a Cu···Cu separation of 2.616 (2) Å. The latter Cu atoms are five-coordinated, surrounded by square pyramids of

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† Alternative name: *catena*-poly[[pentakis(μ-3,5-dinitrobenzoato)-1:2κ^8*O*:*O*′;2:3κ^2*O*:*O*′-dimethanol-3κ^2*O*-tricopper(II)]-μ-(3,5-dinitrobenzoato)-1κ*O*:κ*O*′].

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