

Data collection

Stoe AED-2 four-circle diffractometer $\theta_{\max} = 22.51^\circ$
 $\omega/2\theta$ scans $h = -9 \rightarrow 9$
 Absorption correction: none $k = 0 \rightarrow 10$
 1356 measured reflections $l = 0 \rightarrow 12$
 1356 independent reflections 2 standard reflections
 893 reflections with frequency: 60 min
 $I > 2\sigma(I)$ intensity decay: 1.5%

Refinement

Refinement on F^2 $\Delta\rho_{\max} = 0.27 \text{ e } \text{\AA}^{-3}$
 $R[F^2 > 2\sigma(F^2)] = 0.045$ $\Delta\rho_{\min} = -0.30 \text{ e } \text{\AA}^{-3}$
 $wR(F^2) = 0.116$ Extinction correction:
 $S = 1.144$ *SHELXL93* (Sheldrick, 1993)
 1352 reflections Extinction coefficient:
 163 parameters 0.0010 (11)
 H atoms: see below Scattering factors from
 $w = 1/[\sigma^2(F_o^2) + (0.0382P)^2 + 1.6057P]$ *International Tables for Crystallography* (Vol. C)
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = -0.001$

Table 1. Selected geometric parameters ($\text{\AA}$, $^\circ$)

Cu1—O3	1.895 (4)	Cu1—OW1	2.470 (6)
Cu1—N1	2.135 (4)		
O3—Cu1—N1	80.6 (2)	N1—Cu1—OW1	91.8 (2)
O3—Cu1—OW1	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 *SHELXL93* (Sheldrick, 1993) default parameters, except that one parameter was refined for each methyl group to define its orientation.

Data collection: *DIF4* (Stoe & Cie, 1995). Cell refinement: *DIF4*. Data reduction: *REDU4* (Stoe & Cie, 1996). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93*. Molecular graphics: *PLATON/PLUTON* (Spek, 1990). Software used to prepare material for publication: *SHELXL93*.

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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-diphenylphosphinoethyl-amine-*N,P*)palladium(II)

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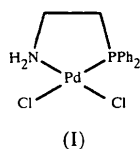
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Abstract

The coordination geometry about the palladium(II) ion in [PdCl₂{Ph₂P(CH₂)₂NH₂}] is distorted square planar. Individual atoms are displaced from the PdCl₂PN 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*-C₆H₄(OH){C=N(CH₂)₂PPh₂} (Dilworth *et al.*, 1994), with [PdCl₂(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 CHCl₃) to give 2-diphenylphosphinoethylamine and hence its palladium chloride complex. The preparation of this compound has been noted previously (Suzuki *et al.*, 1996).



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 PdCl₂NP 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{Me₂P(CH₂)₂NH₂}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.

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*-C₆H₄-(OH){C=N(CH₂)₂PPh₂} in untreated chloroform. After removal of the solvent, a small portion of the crude residue was dissolved in CDCl₃ for NMR spectroscopy. On standing for several days, yellow needles of [PdCl₂{Ph₂P(CH₂)₂NH₂}] were formed.

Crystal data

[PdCl₂(C₁₄H₁₆NP)]

M_r = 406.57

Triclinic

*P*1̄

a = 8.082 (2) Å

b = 12.554 (2) Å

c = 16.724 (5) Å

α = 74.02 (2)°

β = 85.21 (3)°

γ = 89.39 (2)°

V = 1625.5 (7) Å³

Z = 4

D_x = 1.661 Mg m⁻³

D_m not measured

Mo Kα radiation

λ = 0.71069 Å

Cell parameters from 23 reflections

θ = 16.2–18.9°

μ = 1.555 mm⁻¹

T = 295.2 K

Needle

0.80 × 0.25 × 0.05 mm

Yellow

Data collection

Rigaku AFC-7S 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 > 0.5σ(*I*)

*R*_{int} = 0.015

θ_{max} = 26.02°

h = 0 → 9

k = -15 → 15

l = -20 → 20

3 standard reflections

every 150 reflections

intensity decay: none

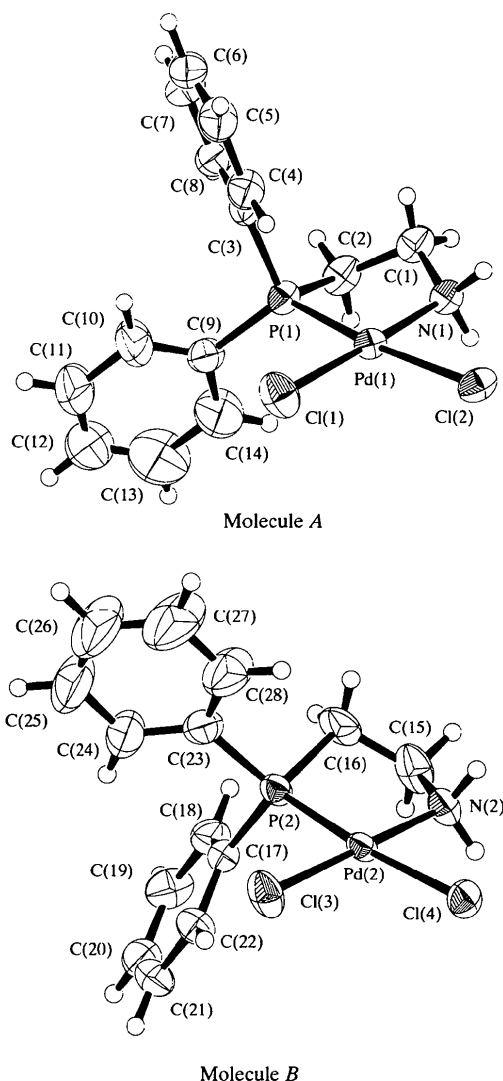


Fig. 1. ORTEP plot (Johnson, 1976) of [PdCl₂{Ph₂P(CH₂)₂NH₂}] with 40% probability ellipsoids, showing the relative conformations of the two unique molecules, *A* and *B*, in the asymmetric unit.

Refinement

Refinement on *F**R* = 0.042*wR* = 0.036*S* = 1.117

5333 reflections

343 parameters

H atoms not refined

w = 1/*σ*²(*F*)(Δ/*σ*)_{max} = 0.009Δ*ρ*_{max} = 0.52 e Å⁻³Δ*ρ*_{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* < 0.5σ(*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*_{iso} set as 1.2*U*_{eq} of the attached C atom.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *TEXSAN* (Molecular Structure Corporation, 1985, 1992). Program(s) used to solve structure: *PATY* in *DIRDIF92* (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, [Cu₃{(NO₂)₂C₆H₃COO}₆(CH₃-OH)₂]_n, is a linear polymeric chain with the dinitrobenzoate ions forming all bridges. The chain is linked across Cu(CH₃OH)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

† Alternative name: *catena*-poly[[pentakis(μ-3,5-dinitrobenzoato)-1:2κ⁸O:O';2:3κ²O:O'-dimethanol-3κ²O-tricopper(II)]-μ-(3,5-dinitrobenzoato)-1κO:κO'].