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Ligands with Cycloalkane Backbones. IV. Dichloro{(S,S)-trans-diphenyl[(2-diphenylphosphinyl)cyclohexyl]phosphinic acid ester}palladium(II)†

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Abstract

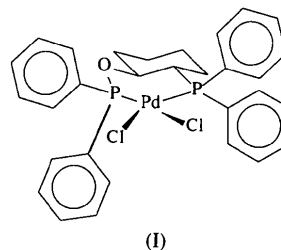
In the title compound, $[\text{PdCl}_2(\text{C}_{30}\text{H}_{30}\text{OP}_2)]$, Pd^{II} is square-planar coordinated by two chloro ligands [Pd—Cl 2.340 (1) and 2.372 (1) Å] and the two phosphorus donors [Pd—P 2.263 (1), 2.209 (1) Å] of the asymmetric chelate ligand.

Comment

The application of chiral transition metal complexes as catalysts in enantioselective transformations of organic substrates is one of the most rapidly progressing fields in chemical research. For this purpose, synthetic strategies leading to chiral chelating ligands have been developed over the last two decades. Ligand systems giving high enantiomeric excesses in catalytic reactions usually show a C_2 -symmetric arrangement of the donor fragments, forced by a rigid aromatic backbone. Since we are interested in ligands carrying two electronically dif-

† Alternative name: dichloro{diphenyl[2-(diphenylphosphino)cyclohexyloxy]phosphine-*P, P'*}palladium(II).

ferent donor centres linked by a rigid aliphatic backbone, we have developed a synthetic route using the ring opening of epoxides of cyclic olefins by various nitrogen and phosphorus nucleophiles (Barz *et al.*, 1997; Thurner *et al.*, 1997). We recently published the synthesis of new chiral chelate *P, P'*-ligands starting from *rac*-2-(diphenylphosphinyl)cyclohexanol, including structure chemical investigations of racemic dichloro{*trans*-diphenyl[(2-diphenylphosphinyl)cyclohexyl]phosphinic acid ester}palladium(II) (Thurner *et al.*, 1997). Reinvestigation of the crystalline material obtained by slow diffusion of diethyl ether into a solution of the racemic title compound in CH_2Cl_2 showed that, besides the known racemic modification, crystals of a second species are formed. Structural investigations proved that the individual crystal we obtained occupies the chiral space group $P2_1$ and resulted in the structure determination of the (*S, S*)-enantiomer, (I), which we present here. Since we started from a racemic mixture [(*S, S*)- and (*R, R*)-] of the chelate ligand, crystals with the (*R, R*)-configuration must be formed in equimolar amounts.



All bond lengths and angles concerning the slightly distorted square-planar Pd centre are similar to those in the racemic modification, which includes one additional molecule of CH_2Cl_2 per formula unit. Owing to the electronegative O atom at the phosphinite group, the

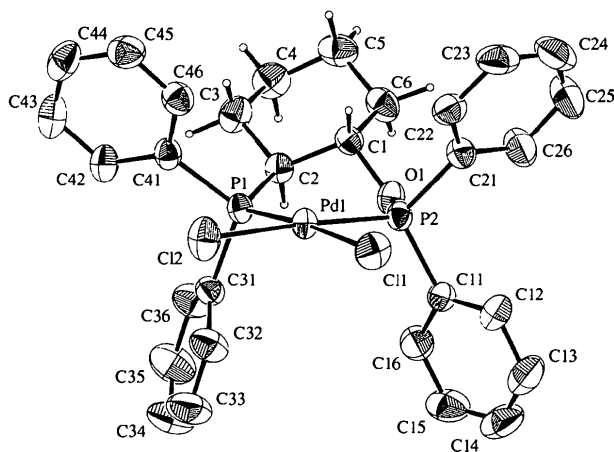


Fig. 1. PLATON (Spek, 1990) plot of the molecular structure of (I) with displacement ellipsoids drawn at the 50% probability level. The H atoms of the phenyl rings have been omitted for clarity.

distance Pd—P1 (phosphine) is about 0.054 Å longer than Pd—P2 (phosphinite) (Bouaoud *et al.*, 1987). As a result of the different *trans* influences of the P-donor moieties, the distance Pd—Cl2 (*trans* to P2) is about 0.032 Å longer than Pd—Cl1 (*trans* to P1). The energetically favoured chair conformation of the cyclohexane ring forces the six-membered palladium-containing ring, formed by coordination of the ligand, into an envelope conformation and leads to a pseudo-C₂ symmetrical orientation of the phenyl rings.

Experimental

The title compound was obtained by ligand exchange of [PdCl₂(C₆H₅CN)₂] with racemic 1,2-(PPh₂)(OPPh₂)C₆H₁₀ in CH₂Cl₂ and slow diffusion of diethyl ether into this solution.

Crystal data

[PdCl₂(C₃₀H₃₀OP₂)]

$M_r = 645.84$

Monoclinic

$P2_1$

$a = 14.407(1) \text{ \AA}$

$b = 8.425(1) \text{ \AA}$

$c = 11.777(1) \text{ \AA}$

$\beta = 100.93(1)^\circ$

$V = 1403.5(2) \text{ \AA}^3$

$Z = 2$

$D_x = 1.528 \text{ Mg m}^{-3}$

D_m not measured

Mo $K\alpha$ radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 25

reflections

$\theta = 17.99\text{--}23.01^\circ$

$\mu = 0.99 \text{ mm}^{-1}$

$T = 293 \text{ K}$

Octahedral

$0.4 \times 0.3 \times 0.3 \text{ mm}$

Bright yellow

Data collection

Nonius MACH-3 diffractometer

ω scans

Absorption correction:

ψ scans (North, Phillips & Mathews, 1968)

$T_{\min} = 0.639$, $T_{\max} = 0.743$

5708 measured reflections

5485 independent reflections

5234 reflections with

$I > 2\sigma(I)$

$R_{\text{int}} = 0.019$

$\theta_{\max} = 25.93^\circ$

$h = -17 \rightarrow 0$

$k = -10 \rightarrow 10$

$l = -14 \rightarrow 14$

3 standard reflections

frequency: 60 min
intensity decay: 2.1%

Refinement

Refinement on F^2

$R_1 = 0.024$

$wR_2 = 0.066$

$S = 1.124$

5485 reflections

445 parameters

All H atoms refined

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.596 \text{ e \AA}^{-3}$

$\Delta\rho_{\min} = -0.304 \text{ e \AA}^{-3}$

Extinction correction: none

Scattering factors from

International Tables for Crystallography (Vol. C)

$$w = 1/[\sigma^2(F_o^2) + (0.0424P)^2 + 0.2831P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

Absolute structure: Flack (1983)

Flack parameter = $-0.06(2)$

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

Pd1—Cl1	2.3400 (10)	P1—C41	1.819 (3)
Pd1—Cl2	2.3715 (11)	P2—O1	1.609 (3)
Pd1—P1	2.2627 (9)	P2—C11	1.803 (3)
Pd1—P2	2.2086 (9)	P2—C21	1.813 (4)
P1—C2	1.881 (3)	O1—C1	1.448 (4)
P1—C31	1.820 (3)		
Cl1—Pd1—Cl2	92.34 (4)	Pd1—P1—C2	118.93 (11)
Cl1—Pd1—P1	174.31 (4)	Pd1—P1—C31	108.74 (11)
Cl1—Pd1—P2	85.55 (4)	Pd1—P1—C41	110.87 (11)
Cl2—Pd1—P1	88.76 (3)	Pd1—P2—O1	115.19 (10)
Cl2—Pd1—P2	176.57 (4)	Pd1—P2—C11	112.73 (12)
P1—Pd1—P2	93.07 (3)	Pd1—P2—C21	117.70 (11)

The structure was solved by direct methods and refined by full-matrix least-squares techniques. All non-H atoms were refined with anisotropic displacement parameters. All H atoms were located from difference Fourier maps and refined isotropically.

Data collection: *MACH-3 Software* (Nonius, 1994). Cell refinement: *MACH-3 Software*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *PLATON* (Spek, 1990). Software used to prepare material for publication: *PLATON*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1135). Services for accessing these data are described at the back of the journal.

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