Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1165). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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$[Pd\{P(C_5H_{10}N)Ph_2\}_2Cl_2]$

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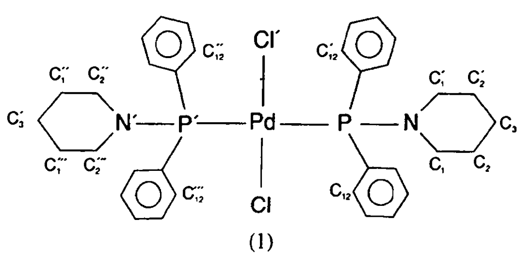
Abstract

The diphenyl(piperidino)phosphine ligands in the structure of dichlorobis[diphenyl(piperidino)phosphine]palladium, $[PdCl_2(C_{17}H_{20}NP)_2]$, coordinate to the Pd atom in a *trans* arrangement and the two Cl ligands complete the square-planar Pd coordination sphere. This arrangement is required by the crystallographically imposed $2/m$ symmetry that the molecule possesses. The Pd atom sits on a centre of inversion with the P, N and C(*para*) atoms of the piperidine group being bisected by a mirror plane. The Cl atoms define a twofold axis.

Comment

We have been studying the bidentate ligand bis(diphenylphosphino)amine, $Ph_2PN(H)PPh_2$, and its derivatives. In structural studies on complexes of bis(diphenylphosphino)amine ligands (Browning, Farrar & Frankel, 1992), the observed P—N bond lengths are significantly less than the values associated with P—N single bonds (1.77 Å) (Greenwood & Earnshaw, 1984) or the sum of the covalent radii of the P and N atoms (1.84 Å) (Shriver, Atkins & Langford, 1990). The short P—N bond lengths and the observed planarity at the N centres in the bis(diphenylphosphino)amine ligands have been the basis for proposed P—N π bonding. Our theoretical calculations on these ligands suggest that the P—N bond order is one (Browning, Farrar & Peterson, 1991). In an attempt to obtain a better estimate of a P—N single-bond length for the bisphosphinoamine ligands, we undertook the structural characterization of a complex containing bis[diphenyl(piperidino)phosphine] ligands, $Ph_2PNC_5H_{10}$. The chair conformation of the piperidine ring forces the N atom towards pyramidal geometry and thus disrupts any significant π bonding.

Bond lengths and angles for the molecule are listed in Table 2. All intermolecular contacts are greater than the sum of the van der Waals radii of the respective atom pairs. Fig. 1 is a view of the molecule (1) with H atoms omitted for clarity.



(1)

The piperidine ring is in a chair conformation with the lone pair of the N atom oriented *anti* to the Pd—P bond. Steric demands would favour the piperidine and phenyl rings to mesh forming a propeller-type arrangement, as is seen for triarylphosphines (Corbridge, 1974). The piperidine group is instead bracketed by the two phenyl groups. This

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conformation is similar to that seen in tri(piperidino)phosphine (Rømming & Sonstad, 1978) where the N-atom lone pair is *anti* to the P-atom lone pair for one piperidine group and the other two piperidine groups bracket the first with the N-atom lone pair *gauche* to the P-atom lone pair. The *gauche* conformations result in nearly planar (sp^2-hybridized) N atoms with shorter P—N bond distances [1.689 (3)–1.708 (3) Å, see Table 3] than the *anti* conformations. The *gauche* conformations also have wider C—N—C angles [111.9 (3)–112.9 (3)°] with the sum of angles around the N atoms being nearly 360° [349.9 (5)–359.9 (5)°]. The *anti* lone pairs give sp^3-hybridized N atoms; the *anti* conformations have longer P—N bond distances [1.724 (3)–1.727 (3) Å] and narrower C—N—C angles [109.8 (3)–109.9 (3)°] with more pyramidal N-atom coordination. The sums of the angles about the N atoms are 338.9 (5) and 339.6 (5)°. In the title structure, the P—N bond length is statistically the same as that of the *anti* conformation of the tri(piperidino)phosphine but the sum of angles around the N atom is 349.6 (9)° which indicates that some sp^2 character for the N atom exists [akin to the *gauche* conformation of the tri(piperidino)phosphine].

The sum of the absolute values of the torsion angles of the C and N atoms of the piperidine group is 279.6 (16)° for the title compound, as compared with 331.3 (10)–338.0 (10)° for the *gauche* piperidine groups, 347.0 (10)–348.8 (10)° for the *anti* piperidine groups and 345.6 (8)° for free piperidine. For an ideal chair form, the sum should be 360° (Bucourt, 1974). Thus the piperidine ring in the title structure is flattened considerably. This suggests that partial sp^2 hybridization of the N atom does not result in a partial multiple bond to the P atom but does affect the piperidine ring.

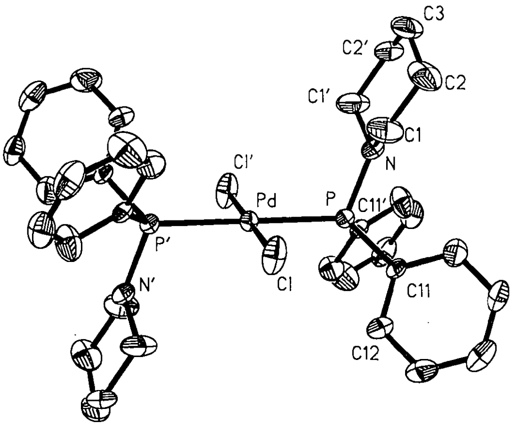

Fig. 1. View of (1) indicating the atomic labelling scheme. The displacement ellipsoids are at the 30% probability level.

We conclude that in phosphinoamine complexes a normal P—N single bond is in the range of 1.68–1.73 Å depending upon the amount of pyramidal character at the N centre.

Experimental

Crystal data

$[PdCl_2(C_{17}H_{20}NP)_2]$
$M_r = 715.9$
Orthorhombic
Pnnm
$a = 8.210$ (2) Å
$b = 12.334$ (3) Å
$c = 16.354$ (5) Å
$V = 1656.1$ Å^3
$Z = 2$
$D_x = 1.44$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 12$–$15°$
$\mu = 0.76$ mm^{-1}
$T = 298$ K
Block
0.20 × 0.20 × 0.15 mm
Colourless
Crystal source: slow evaporation from toluene/hexanes

Data collection

Enraf-Nonius CAD-4 diffractometer
ω-2θ scans [width $(1.0 + 0.35\tan\theta)°$ in ω]
Absorption correction: empirical (*DIFABS*; Walker & Stuart, 1983)
$T_{min} = 0.79$, $T_{max} = 1.30$
2120 measured reflections
1423 independent reflections

1205 observed reflections $[I > 3\sigma(I)]$
$R_{int} = 0.021$
$\theta_{max} = 25°$
$h = 0 \rightarrow 9$
$k = 0 \rightarrow 14$
$l = 0 \rightarrow 19$
2 standard reflections
frequency: 180 min
intensity variation: 9.8%

Refinement

Refinement on F
$R = 0.0455$
$wR = 0.0470$
$S = 3.26$
1205 reflections
104 parameters
H-atom parameters not refined
$w = 1/\sigma^2(F)$

$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.56$ e Å^{-3}
$\Delta\rho_{min} = -0.63$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Pd	0	0	0	0.0355 (5)
Cl	0	0	0.1400 (1)	0.071 (1)
P	0.1226 (2)	0.1698 (2)	0	0.035 (1)
N	−0.0280 (8)	0.2675 (5)	0	0.048 (2)
C(1)	−0.1208 (8)	0.2821 (5)	0.0729 (4)	0.084 (3)
C(2)	−0.2110 (8)	0.3842 (5)	0.0749 (5)	0.091 (3)
C(3)	−0.3013 (12)	0.4075 (9)	0	0.112 (6)
C(11)	0.2504 (6)	0.2064 (4)	0.0846 (3)	0.036 (2)
C(12)	0.3560 (7)	0.1301 (5)	0.1166 (4)	0.063 (2)
C(13)	0.4597 (9)	0.1593 (6)	0.1801 (4)	0.085 (3)
C(14)	0.4722 (8)	0.2643 (6)	0.2044 (4)	0.074 (3)
C(15)	0.3694 (8)	0.3407 (5)	0.1742 (4)	0.066 (2)
C(16)	0.2607 (9)	0.3133 (4)	0.1115 (4)	0.075 (3)

Table 2. *Selected geometric parameters* (Å, °)

Pd—Cl	2.289 (2)	C(11)—C(12)	1.382 (7)
Pd—P	2.324 (2)	C(11)—C(16)	1.392 (7)
P—N	1.727 (6)	C(12)—C(13)	1.391 (9)
P—C(11)	1.794 (5)	C(13)—C(14)	1.36 (1)
N—C(1)	1.425 (7)	C(14)—C(15)	1.358 (9)
C(1)—C(2)	1.461 (9)	C(15)—C(16)	1.402 (9)
C(2)—C(3)	1.460 (9)		
P—Pd—Cl	90	C(2)—C3—C(2i)	114.0 (8)
Pd—P—N	108.6 (2)	P—C(11)—C(12)	119.2 (4)
Pd—P—C11	118.7 (2)	P—C(11)—C(16)	121.1 (4)
N—P—C(11)	104.1 (2)	C(12)—C(11)—C(16)	119.2 (5)
C(11)—P—C(11i)	100.9 (3)	C(11)—C(12)—C(13)	119.3 (5)
P—N—C(1)	118.1 (4)	C(12)—C(13)—C(14)	120.8 (6)
C(1)—N—C(1i)	113.4 (7)	C(13)—C(14)—C(15)	120.5 (6)
N—C(1)—C(2)	113.5 (6)	C(14)—C(15)—C(16)	119.6 (6)
C(1)—C(2)—C(3)	114.1 (6)	C(11)—C(16)—C(15)	119.9 (5)

Symmetry code: $x, y, -z$.

Table 3. *A comparison of the molecular geometry of the piperidine ring determined in this paper to those of free piperidine* (*Koman, Durcanska, Handlovic & Gazo*, 1983) *and two tri(piperidino)phosphine molecules* (*Rømming & Sonstad*, 1978)

Piperidine group 1 has the P-atom lone pair *anti* to the N-atom lone pair; groups 2 and 3 are *gauche*; the estimated standard deviations are given in parentheses following the values.

	P—N bond length (Å)	C(1)—N—C(5) angle ( )	Sum of angles about the N atom (°)	Sum of absolute values of torsion angles of the C and N atoms of the piperidine ring ( )
Free ligand		112.0		345.6
Tri(piperidino)-phosphine I, group 1	1.727 (3)	109.9 (3)	339.6 (5)	347.0 (10)
Tri(piperidino)-phosphine I, group 2	1.692 (3)	112.9 (3)	359.9 (5)	331.3 (10)
Tri(piperidino)-phosphine I, group 3	1.705 (3)	112.1 (3)	350.4 (5)	337.4 (10)
Tri(piperidino)-phosphine II, group 1	1.724 (3)	109.8 (3)	338.9 (5)	348.8 (10)
Tri(piperidino)-phosphine II, group 2	1.689 (3)	112.5 (3)	359.6 (5)	333.8 (10)
Tri(piperidino)-phosphine II, group 3	1.708 (3)	111.9 (3)	349.9 (5)	338.0 (10)
This paper	1.727 (6)	113.4 (7)	349.6 (9)	279.6 (16)

Systematic absences: $0kl$ if $k + l = 2n + 1$, $h0l$ if $h + l = 2n + 1$. The structure was solved by the heavy-atom method. A difference map showed maxima in positions consistent with the expected locations of the H atoms. In the final round of calculations the H atoms were positioned on geometric grounds (C—H = 0.96 Å) and included (as riding atoms) in the structure-factor calculations. The H atoms were assigned general isotropic displacement parameters ($U_{\rm iso}$ = 0.08 Å^2). All calculations were carried out on a PDP11/23 computer using *SDP* (B. A. Frenz & Associates, Inc., 1982), a DSP10020 computer using *SHELXS*86 (Sheldrick, 1985) and on a personal computer using *SHELXTL/PC* (Sheldrick, 1991).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71508 (8 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CD1043]

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Pentaaqua(2-furancarboxylato)nickel(II) 2-Furancarboxylate at 120 K

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Abstract

The crystal structure of $[Ni(C_5H_3O_3)(H_2O)_5](C_5H_3O_3)$ has been determined by X-ray diffraction at 120 K. One 2-furancarboxylate anion and five water molecules are in-