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Chloro(phenyl)(1*H*-pyrazole-κN^2)(triphenylphosphine-κP)palladium(II)

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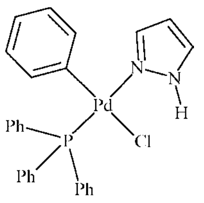
In the title compound, $[Pd(C_6H_5)Cl(C_3H_4N_2)\{P(C_6H_5)_3\}]$, the phenyl and Cl ligands lie mutually *trans*. The compound is the first structurally characterized complex with four monodentate Cl, P, N and (non-carbenoid) C ligands in a square-planar four-coordinate palladium(II) environment. The pyrazole ligand is coplanar with the latter array. The pyrazole NH group forms a bifurcated hydrogen bond to Cl, with an intra- and intermolecular component.

Comment

Ongoing interest in the catalytic behaviour of palladium(II) systems has resulted in an abundance of structurally characterized square-planar four-coordinate palladium(II) arrays with the four different donor atoms Cl, P, N and C, which form a significant component of the Cambridge Structural Database (CSD, Version 5.25; Allen, 2002), with well over 100 entries at present. Our current interest in the area has drawn our attention to the dearth of any simple baseline systems involving these atoms as simple monodentate donors; in the overwhelming majority of such systems, the pairs of N/C or N/P donors are incorporated, in consequence of various rationales, into chelates. Indeed, we have found only one such system in our CSD search and that compound is also unusual in that the C-donor is a carbene (Bertani *et al.*, 1990), a system also prominent in our present interests. Accordingly, the structure of the title complex, (I), a single crystal obtained as an unexpected decomposition product during studies of poly(pyrazol-1-yl)methane complexes of palladium, is reported here, as it contains a new array of monodentate ligand types which serves as a reference point for the studies of the above type.

The results of the present room-temperature single-crystal X-ray study of (I) are consistent with the stoichiometry and connectivity implied in the above formulation, the four monodentate ligands comprising a (square-)planar four-coordinate array about the divalent Pd atom [χ^2 Pd/Cl/P/N1/C101 670; atom deviations 0.008 (1), −0.010 (2), 0.001 (2), 0.018 (4), and −0.120 (5) Å, respectively]. One neutral molecular formula unit, devoid of crystallographic symmetry, with the Cl and phenyl donors mutually *trans*, comprises the asymmetric unit of the structure of (I) (Fig. 1). The angle sum about the Pd atom is 360.0°, the greatest deviation from orthogonality being 87.3 (2)°. Other significant geometries are presented in Table 1.



(I)

Perhaps the most interesting comparison which can be made is with the carbenoid system alluded to above. In that system, Pd—P (in PMe_2Ph) is 2.255 (2) Å [*cf.* 2.245 (1) Å in (I)], Pd—N [in aziridine, $HN(CH_2)_3$, a cyclic array with C—N—C = 88.7 (5)°] is 2.109 (5) Å [*cf.* 2.116 (4) Å in (I)], Pd—Cl is 2.363 (2) Å [*cf.* 2.417 (2) Å in (I)] and Pd—C {in $C[N(CH_2)_3]NHC_6H_4OMe$-*p*; N—C—N = 118.6 (5)°} is 1.990 (6) Å [*cf.* 1.995 (4) Å in (I)] [angle sum = 360.0°; greatest deviation from orthogonality = 91.1 (2)°]. The only notable difference is in the Pd—Cl distances, presumably to be ascribed to significant and unsurprising differences in the *trans* effects of the two types of trigonal C-donors. In both cases, the planes of the latter lie quasi-normal to the coordination plane. In (I), the interplanar dihedral angle is 89.0 (2)°, the Pd deviation δPd being 0.277 (8) Å.

The pyrazole ring [χ^2 = 0.4 and δPd = 0.025 (9) Å] is quasi-coplanar with the coordination plane [interplanar dihedral = 3.9 (2)°], perhaps in consequence of the 'protonic' H atom at N2 forming an in-plane hydrogen bond to the adjacent Cl^- ligand (Table 2), there being also a similar intermolecular contact.

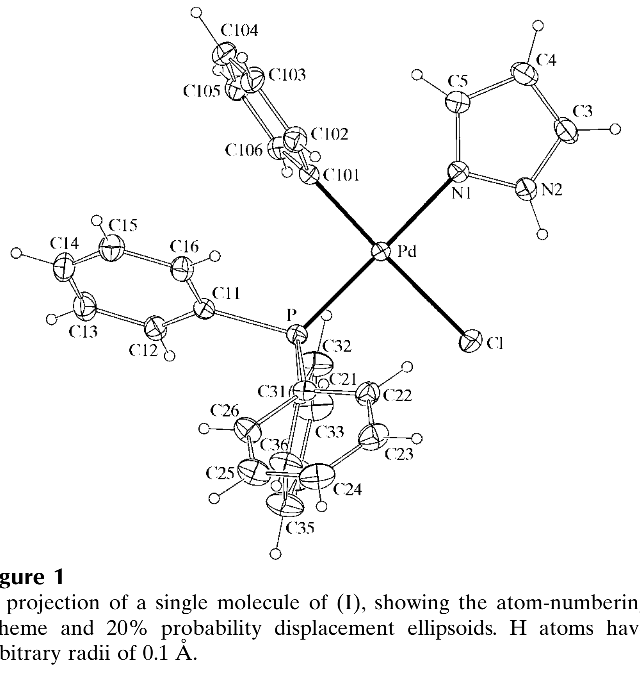


Figure 1
A projection of a single molecule of (I), showing the atom-numbering scheme and 20% probability displacement ellipsoids. H atoms have arbitrary radii of 0.1 Å.

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The Pd—N1—N2/C5 angles are quite unsymmetrical [120.1 (3) and 134.2 (3)°, respectively]. The torsion angles (Table 1) show that the triphenylphosphine is rather distorted from exact threefold symmetry, while atom C11 is quasi-coplanar with the coordination plane, perhaps accounting for the enlargement of Pd—P—C11 and C21—P—C31.

Experimental

The origin of the title compound is described in the *Comment.*

Crystal data

$[Pd(C_6H_5)Cl(C_3H_4N_2)(C_{18}H_{15}P)]$
$M_r = 549.37$
Triclinic, $P\overline{1}$
$a = 9.817$ (2) Å
$b = 10.797$ (5) Å
$c = 13.523$ (7) Å
$\alpha = 72.85$ (4)°
$\beta = 88.21$ (3)°
$\gamma = 63.55$ (3)°
$V = 1217.8$ (10) Å^3
$Z = 2$
$D_x = 1.498$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 12 reflections
$\theta = 14.5$–15.6°
$\mu = 0.96$ mm^{-1}
$T = 300$ (2) K
Fragment, colourless
0.70 × 0.52 × 0.25 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$2\theta/\omega$ scans
Absorption correction: Gaussian (*ABSORB* in *Xtal*3.5; Hall *et al.*, 1995)
$T_{\min} = 0.63$, $T_{\max} = 0.73$
4265 measured reflections
4265 independent reflections
3887 reflections with $I > 2\sigma(I)$
$\theta_{\max} = 25.0°$
$h = -11 \rightarrow 11$
$k = -12 \rightarrow 11$
$l = -16 \rightarrow 0$
6 standard reflections every 60 mins intensity decay: none

Table 1
Selected geometric parameters (Å, °).

Pd—Cl	2.4174 (15)	Pd—N1	2.116 (4)
Pd—P	2.2451 (12)	Pd—C101	1.995 (5)
Cl—Pd—P	91.18 (5)	P—Pd—C101	91.54 (13)
Cl—Pd—N1	89.96 (12)	N1—Pd—C101	87.34 (17)
Cl—Pd—C101	175.06 (14)	Pd—N1—N2	120.1 (3)
P—Pd—N1	178.86 (12)	Pd—N1—C5	134.2 (3)
Cl—Pd—P—C11	−171.9 (2)	Pd—P—C11—C16	−65.7 (5)
Cl—Pd—P—C21	66.3 (2)	Pd—P—C21—C22	−17.0 (4)
Cl—Pd—P—C31	−53.9 (2)	Pd—P—C31—C32	−36.7 (5)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2···Cl	0.92	2.44	3.060 (5)	124
N2—H2···Cl^{i}	0.92	2.58	3.229 (4)	128

Symmetry code: (i) $-x, 1 - y, 1 - z$.

Refinement

Refinement on F^2
$R(F) = 0.035$
$wR(F^2) = 0.076$
$S = 1.02$
3887 reflections
289 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F^2) + 0.48F^2]$
$(\Delta/\sigma)_{\max} = 0.003$
$\Delta\rho_{\max} = 0.80$ e Å^{-3}
$\Delta\rho_{\min} = -0.77$ e Å^{-3}

The H atoms were located in difference Fourier maps and placed in idealized positions, with C—H distances of 0.95 Å and N—H distances of 0.92 Å, and with $U_{\rm iso}$(H) = $1.25U_{\rm eq}$(C,N).

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *Xtal*3.5 (Hall *et al.*, 1995); program(s) used to solve structure: *Xtal*3.5; program(s) used to refine structure: *CRYLSQ* in *Xtal*3.5; molecular graphics: *Xtal*3.5; software used to prepare material for publication: *BONDLA* and *CIFIO* in *Xtal*3.5.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1458). Services for accessing these data are described at the back of the journal.

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