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trans-Chloro(methyl)bis(triphenylphosphine)-palladium(II)

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.004 Å
R factor = 0.038
wR factor = 0.071
Data-to-parameter ratio = 26.4

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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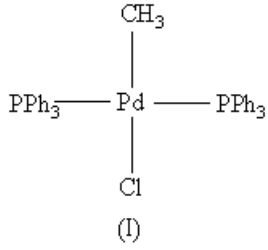
The crystal structure of the title compound, *trans*-$[PdCl(CH_3)(C_{18}H_{15}P)_2]$, was found to be isomorphous with several related platinum(II) and palladium(II) complexes. The Pd atom has a slightly distorted square-planar geometry, with most important bond lengths and angles of Pd—P = 2.3289 (7) and 2.3224 (7) Å, Pd—Cl = 2.4227 (6) Å and Pd—C = 2.054 (2) Å, and P—Pd—P = 177.38 (2)°, P—Pd—Cl = 88.97 (2) and 89.03 (2)°, and C—Pd—Cl = 175.23 (8)°.

Comment

As part of a systematic investigation of the structure–reactivity relationships for the platinum group metal complexes, crystals of (I), *trans*-chloro(methyl)bis(tripenylphosphine)-palladium(II), were prepared. The complex was found to be isomorphous with the platinum analogue (Bardi & Piazzesi, 1981), as well as with the closely related palladium and platinum triphenylarsine complexes (Rath *et al.*, 1995; Roodt *et al.*, 1995).



(I)

The Pd atom has a slightly distorted square-planar coordination environment with the phosphine ligands in a *trans* orientation. The P1—Pd—P2 angle is 177.38 (2)°, with Pd—P1 and Pd—P2 bond distances of 2.3289 (7) and 2.3224 (7) Å, respectively (see Table 1). The Pd—Cl bond is relatively long at 2.4227 (6) Å, obviously due to a strong labilizing influence of a *trans*-Me ligand [Pd—C1 2.054 (2) Å]. The C1—Pd—Cl angle of 175.23 (8)° deviates substantially from 180°. The slight distortion of the Pd square-planar coordination is also manifested in some decrease of the P1—Pd—Cl and P2—Pd—Cl [88.97 (2) and 89.03 (2)°, respectively] and a corresponding increase of the C1—Pd—P1 and C1—Pd—P2 angles [91.50 (7) and 90.63 (7)°, respectively].

All bond distances and angles within the PPh_3 ligands are within normal ranges (see Table 1). The PPh_3 groups are in almost perfectly eclipsed conformation with the biggest pseudo-torsion angle of the C_{Ph}—P1···P2—C_{Ph} type being equal to only 7.5°.

In Table 2, the title compound is compared with other closely related Pt^{II} and Pd^{II} complexes from the literature. It is

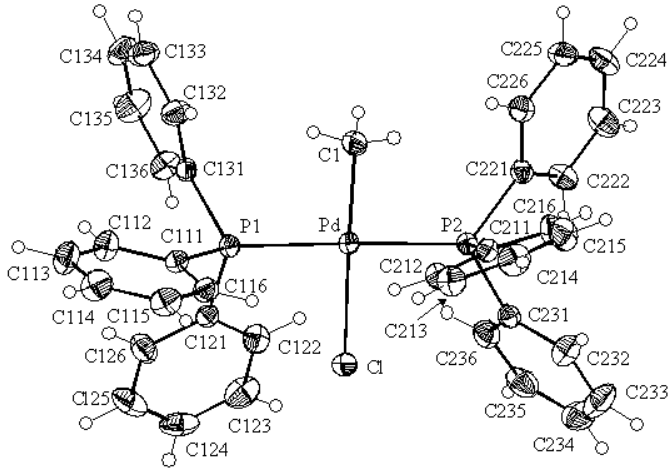


Figure 1
The structure of (I) showing the atom-numbering scheme and 30% probability displacement ellipsoids. H atoms are of arbitrary size.

noteworthy that all complexes with the general formula $[MRY(EPh_3)_2]$, where M = Pd or Pt, RY = Cl_2 or MeCl, and E = P or As, belong to one of just two types of isomorphous structures. The non-symmetric complexes with RY = MeCl are isomorphous with the title compound ($P2_1/n$, Z = 4, type I), whereas the complexes with symmetric substitution ($RY = Cl_2$) crystallize in the triclinic system, the molecule of the complex occupying a special position on the inversion centre ($P\overline{1}$, Z = 1, type II). The triclinic modification of complex $[PtMeCl(PPh_3)_2]$ (Otto *et al.*, 1995) presents a notable exception from this rule: this structure accommodates a non-symmetric molecule within the type II crystal structure, the Me group and Cl atoms being disordered over two positions related by the inversion centre.

Another observation, which follows from the data presented in Table 2, is that the Pt—L bonds are slightly shorter than the Pd—L bonds in corresponding complexes with differences of *ca* 0.030 and 0.020 Å for L = P and As, respectively. This observation could, to some extent, be explained by the difference in the covalent radii of Pd (1.380 Å) and Pt (1.370 Å) (Sheldrick, 1997). The M—Cl bonds are very similar though, while no conclusive deductions could be made concerning the M—C bond distance due to the large uncertainty associated with them.

Crystal data

$[PdCl(CH_3)(C_{18}H_{15}P)_2]$
M_r = 681.42
Monoclinic, $P2_1/n$
a = 11.8068 (4) Å
b = 23.3389 (9) Å
c = 12.3650 (5) Å
β = 111.537 (1)°
V = 3169.4 (2) Å^3
Z = 4
D_x = 1.428 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5564 reflections
θ = 2.2–24.4°
μ = 0.80 mm^{-1}
T = 293 (2) K
Prism, light yellow
0.37 × 0.24 × 0.11 mm

Data collection

Siemens SMART CCD diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
T_{min} = 0.621, T_{max} = 0.735
32 413 measured reflections
9837 independent reflections
4925 reflections with $I > 2\sigma(I)$
R_{int} = 0.076
θ_{max} = 31.7°
$h = -17 \rightarrow 17$
$k = -34 \rightarrow 32$
$l = -18 \rightarrow 18$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.071
S = 0.85
9837 reflections
372 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0243P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.43 e Å^{-3}
$\Delta\rho_{min}$ = −0.61 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Pd—P1	2.3289 (7)	P1—C121	1.825 (3)
Pd—P2	2.3224 (7)	P1—C131	1.835 (2)
Pd—Cl	2.4227 (6)	P2—C211	1.828 (2)
Pd—C1	2.054 (2)	P2—C221	1.830 (2)
P1—C111	1.827 (3)	P2—C231	1.815 (3)
C1—Pd—P1	91.50 (7)	C111—P1—Pd	115.52 (8)
C1—Pd—P2	90.63 (7)	C121—P1—Pd	109.92 (9)
P1—Pd—P2	177.38 (2)	C131—P1—Pd	119.01 (8)
C1—Pd—Cl	175.23 (8)	C211—P2—C221	103.27 (11)
P1—Pd—Cl	88.97 (2)	C211—P2—C231	107.09 (12)
P2—Pd—Cl	89.03 (2)	C221—P2—C231	100.86 (11)
C111—P1—C121	105.56 (11)	C211—P2—Pd	113.09 (8)
C111—P1—C131	101.16 (11)	C221—P2—Pd	120.36 (8)
C121—P1—C131	104.27 (11)	C231—P2—Pd	110.81 (8)
Cl—Pd—P1—C111	65.25 (9)	Cl—Pd—P2—C211	−70.73 (9)
Cl—Pd—P1—C121	−54.03 (8)	Cl—Pd—P2—C221	166.67 (10)
Cl—Pd—P1—C131	−174.08 (10)	Cl—Pd—P2—C231	49.52 (9)

Experimental

[PdMeCl(COD)] was prepared according to the literature (Chatt *et al.*, 1957; Rülke *et al.*, 1993). Crystals were obtained using the following procedure: a solution of 21 mg (0.079 mmol) of PPh_3 in 5 ml of acetone was added very carefully (so as to disturb the mixture as little as possible) to a solution of 10 mg (0.037 mmol) of [PdMeCl(COD)] in 5 ml of acetone. Light yellow prisms of the title compound soon precipitated from the reaction mixture and were collected by filtration in an almost quantitative yield. ^{1}H NMR ($CDCl_3$): 7.65–7.76 (*m*, 15H), 7.30–7.45 (*m*, 18H), −0.035 (*t*, 3H, $^3J_{P-H}$ = 12.5 Hz) p.p.m. ^{31}P NMR ($CDCl_3$) 31.2 p.p.m.

The data were collected on a Siemens SMART CCD diffractometer using an exposure time of 20 s per frame. A total of 1890 frames were collected with a frame width of 0.25° being used.

Data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1997); software used to prepare material for publication: *SHELXL*97.

Table 2
Comparative X-ray data for *trans*-[*MR*Cl(*L*)$_2$] (*M* = Pd, Pt; *R* = Me, CH_2Cl, Ph, Cl and *L* = tertiary phosphine- or arsine ligand) complexes.

Complex	*M*—*L* (Å)	*M*—C (Å)	*M*—Cl (Å)	Type[a]	Refs
[PdMeCl(PPh_3)$_2$]	2.3289 (7) 2.3224 (7)	2.054 (2)	2.4227 (6)	I	(i)
[PdMeCl($AsPh_3$)$_2$]	2.3989 (5) 2.4067 (5)	2.095 (4)	2.4086 (11)	I	(ii)
[PtMeCl(PPh_3)$_2$]	2.295 (3) 2.298 (3)	2.08 (1)	2.431 (3)	I	(iii)
[PtMeCl(PPh_3)$_2$]	2.2955 (10)	2.02 (2)	2.415 (5)	II	(iv)
[PtMeCl($AsPh_3$)$_2$]	2.3856 (9) 2.3786 (9)	2.073 (8)	2.410 (2)	I	(*v*)
[PdMeCl(PPh_2Fc)$_2$]	2.3328 (10)	2.108 (10)	2.378 (3)		(vi)
[$PdCH_2ClCl(PPh_3)_2$]	2.337 (1) 2.329 (1)	2.031 (2)	2.402 (1)		(vii)
[PdPhCl(PPh_3)$_2$]	2.316 (1) 2.324 (1)	2.016 (3)	2.407 (1)		(viii)
[Pd(Cl)$_2$(PPh_3)$_2$]	2.337 (1)		2.290 (1)	II	(ix)
[Pt(Cl)$_2$(PPh_3)$_2$]	2.3175 (12)		2.2997 (11)	II	(x)

Notes: (*a*) see *Comment* section for definition of structure types.

References: (i) this work; (ii) Rath *et al.* (1995); (iii) Bardi & Piazzesi (1981); (iv) Otto *et al.* (1995); (v) Roodt *et al.* (1995); (vi) Otto *et al.* (2000); (vii) McCrindle *et al.* (1995); (viii) Flemming *et al.* (1998); (ix) Ferguson *et al.* (1982); (x) Johansson & Otto (2000).

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