metal-organic papers

## cis-Dichlorobis(tri-2-furylphosphine)palladium(II) dichloromethane hemisolvate

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Key indicators

Single-crystal X-ray study

T = 100 K

Mean σ(C–C) = 0.005 Å

Disorder in main residue

R factor = 0.031

wR factor = 0.073

Data-to-parameter ratio = 14.3

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

In the title compound, cis-[PdCl$_2$\{P(C$_4$H$_3$O)$_3$\}$_2$]·0.5CH$_2$Cl$_2$, where P(C$_4$H$_3$O)$_3$ is tri-2-furylphosphine, the Pd^{II} centre shows a slightly distorted square-planar geometry with the two chloro ligands in cis positions. Pd—P bond lengths are 2.2329 (10) and 2.2613 (9) Å and Pd—Cl bond lengths are 2.3393 (9) and 2.3501 (10) Å. The P—Pd—Cl angles are 89.07 (4) and 175.28 (4)°. The average effective cone angle for the tri-2-furylphosphine was calculated to be 149°.

Comment

Transition metal complexes containing phosphine, arsine and stibine ligands have been widely investigated in various fields of organometallic chemistry (Spessard & Miessler, 1996). As part of a systematic investigation involving complexes with the general formula $trans$-[$MX_2(L)_2$] (M = Pt or Pd; X = halogen, Me, Ph; L = group 15 donor ligand), crystals of the title compound, (I), were obtained. The current compound is one of the few (ca 26) reported cis-[$MX_2(L)_2$] complexes (Cambridge Structural Database; Version 5.27, January 2006 update; Allen, 2002).
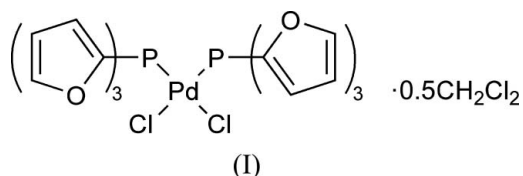
[PdCl$_2(L)_2$] (L = tertiary phosphine, arsine or stibine) complexes can be conveniently prepared by the substitution of 1,5-cyclooctadiene (COD) in [PdCl$_2$(COD)]. The title compound, cis-[PdCl$_2$\{P(C$_4$H$_4$O)$_3$\}$_2$]·0.5CH$_2$Cl$_2$, (I), crystallizes in the monoclinic space group $C2/c$ (Z = 8). Each pair of equivalent ligands is mutually cis. The geometry is slightly distorted square planar and the Pd atom is displaced 0.0403 (5) Å out of the coordination plane (r.m.s. deviation = 0.1281 Å). All cis angles in the coordination plane are close to the ideal value of 90° (Table 1). Some weak interactions were observed and are reported in Table 2.

The most widely used method for determining steric behaviour of a ligand at a metal centre is by calculating the cone angle, as described previously (Tolman, 1977). For the current study, actual M−P distances were used, resulting in effective cone angles, Θ_E (Otto $et\ al.$, 2000). The substituents of the phosphine may have different orientations, resulting in variations in cone-angle sizes. For example, the cone angles for
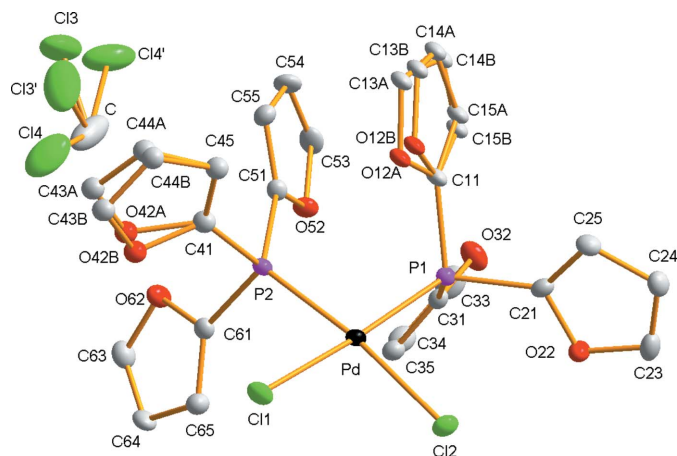
Figure 1
The asymmetric unit of (I), showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity. For the C and O atoms, the first digit indicates ring number and the second digit indicates the position of the atom in the ring. All disorder components are shown.

PPh$_3$ were reported to have a mean value of 148° with a standard deviation of ±5° and a spread from 129 to 168° (Bunten *et al.*, 2002). Data of this sort attest to the ability of phosphine ligands to adjust specifically to their individual environment in the solid state. This effect is here demonstrated by our finding two different cone angles, 154 and 144°, for the two phosphine ligands (average 149°). As a result of the disorder in the molecule, two more cone angles of 151 and 145° (average 147°) were found for the minor components of the disorder.

In Table 3, the title compound is compared with other closely related Pd^{II} complexes from the literature which contain two chloro and two tertiary phosphine ligands in a *cis* geometry. The Pd—Cl and Pd—P bond lengths fit well into the typical ranges for complexes of this kind.

Experimental

Dichloro(1,5-cyclooctadiene)palladium(II), [PdCl$_2$(COD)], was prepared according to the literature procedure of Drew & Doyle (1990). A solution of tri-2-furylphosphine (46.4 mg, 0.2 mmol) in dichloromethane (2.0 ml) was added to a solution of [PdCl$_2$(COD)] (60.3 mg, 0.1 mmol) in dichloromethane (3.0 ml). Slow evaporation of the solvent gave yellow crystals of *trans*-[PdCl$_2${P(C$_4$H$_3$O)$_3$}$_2$]·0.5CH$_2$Cl$_2$ suitable for X-ray analysis in quantitative yield.

Crystal data

[PdCl$_2$(C$_{12}$H$_9$O$_3$P)$_2$]·0.5CH$_2$Cl$_2$	$Z = 8$
$M_r = 684.09$	$D_x = 1.742$ Mg m^{-3}
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
$a = 31.3651$ (6) Å	$\mu = 1.18$ mm^{-1}
$b = 8.7024$ (2) Å	$T = 100$ (2) K
$c = 19.1498$ (4) Å	Block, yellow
$\beta = 93.695$ (1)°	0.17 × 0.09 × 0.06 mm
$V = 5216.10$ (19) Å^3	

Data collection

Bruker X8 APEXII 4K diffractometer	11733 measured reflections
ω and φ scans	4516 independent reflections
Absorption correction: multi-scan (*SADABS*; Bruker, 2004)	3584 reflections with $I > 2\sigma(I)$
$T_{min} = 0.824$, $T_{max} = 0.933$	$R_{int} = 0.036$
	$\theta_{max} = 25°$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0228P)^2 + 17.7365P]$
$R[F^2 > 2\sigma(F^2)] = 0.031$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.073$	$(\Delta/\sigma)_{max} = 0.002$
$S = 1.04$	$\Delta\rho_{max} = 0.47$ e Å^{-3}
4516 reflections	$\Delta\rho_{min} = -0.44$ e Å^{-3}
315 parameters	
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

Pd—P1	2.2329 (10)	Pd—Cl2	2.3393 (9)
Pd—P2	2.2613 (9)	Pd—Cl1	2.3501 (10)
P1—Pd—P2	93.88 (3)	P1—Pd—Cl1	175.28 (4)
P1—Pd—Cl2	89.07 (4)	P2—Pd—Cl1	84.74 (3)
P2—Pd—Cl2	171.20 (4)	Cl2—Pd—Cl1	92.96 (3)
P2—Pd—P1—C11	49.86 (13)	P1—Pd—P2—C41	−123.92 (14)
Cl2—Pd—P1—C11	−138.44 (13)	Cl1—Pd—P2—C41	51.56 (14)

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C—H0$B\cdots$O62^i	0.99	2.48	3.233 (6)	133
C13A—H13$A\cdots$O22^{ii}	0.95	2.37	3.128 (6)	136
C23—H23$\cdots$Cl2^{iii}	0.95	2.79	3.643 (4)	151
C33—H33$\cdots$Cl1^{iv}	0.95	2.8	3.442 (4)	126
C33—H33$\cdots$Cl2^{iv}	0.95	2.71	3.614 (5)	158
C63—H63$\cdots$O52^i	0.95	2.57	3.476 (4)	158
C65—H65$\cdots$Cl1	0.95	2.81	3.351 (4)	117

Symmetry codes: (i) $-x + 1, y, -z + \frac{3}{2}$; (ii) $x, y + 1, z$; (iii) $-x + \frac{3}{2}, -y - \frac{1}{2}, -z + 2$; (iv) $x, -y, z - \frac{1}{2}$.

Table 3
Comparative geometrical parameters (Å) for selected *cis*-[PdCl$_2$(L)$_2$] (L = tertiary phosphine ligand) complexes.

L	Pd—P	Pd—P	Pd—Cl	Pd—Cl	Ref.
P(2-Fur)$_3$	2.2329 (10)	2.2613 (9)	2.3393 (9)	2.3501 (10)	*a*
P(OPh)$_3$	2.2299 (11)	2.2314 (12)	2.3273 (11)	2.3354 (11)	*b*
PMePh$_2$	2.262 (2)	2.267 (2)	2.338 (2)	2.344 (2)	*c*
PMe$_2$Ph	2.260 (2)		2.362 (3)		*d*
PMe$_3$	2.256 (2)	2.259 (2)	2.359 (3)	2.378 (3)	*e*

Note: Fur is furyl. References: (*a*) this work; (*b*) Sabounchei *et al.* (2000); (*c*) Alcock & Nelson (1985); (*d*) Martin & Jacobsen (1971); (*e*) Schultz *et al.* (1992).

The methylene and aromatic H atoms were placed in geometrically idealized positions (C—H = 0.92–0.98 Å) and constrained to ride on their parent atoms, with U_{iso}(H) = 1.2U_{eq}(C). Disordered phosphine substituents were refined with complementary group occupancy

factors. These refined to 0.752 (13)/0.248 (13) for ring 1 (atoms C11, O12, C13, C14 and C15) and 0.394 (10)/0.606 (10) for ring 4 (atoms C41, O42, C43, C44 and C45). Refinement of the disorder was kept stable with bond length and displacement parameter restraints. The CH_2Cl_2 was refined with a 50% occupancy.

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT-Plus* (Bruker, 2004); data reduction: *SAINT-Plus* and *XPREP* (Bruker, 2004); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg & Putz, 2005); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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