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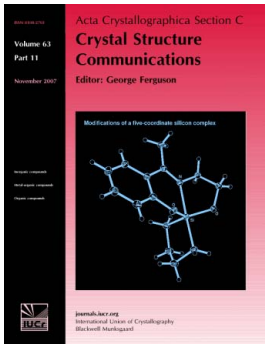

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Weak C—H···Cl—Pd interactions toward conformational polymorphism in *trans*-dichloridobis(triphenylphosphane)palladium(II)

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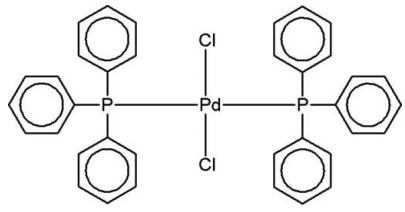
A new triclinic polymorph of the title compound, $[PdCl_2(C_{18}H_{15}P)_2]$, has two independent molecules in the unit cell, with the Pd atoms located on inversion centres. One molecule has an eclipsed conformation, whereas the second molecule adopts a *gauche* conformation. The molecules with a *gauche* conformation are involved in weak intermolecular C—H···Cl—Pd interactions with symmetry-related molecules. It is suggested that C—H···Cl—Pd interactions are mainly responsible for the existence of conformational differences, which contribute to the polymorph formation. In the crystal, there are layers of eclipsed and *gauche* molecules separated by normal van der Waals interactions.

Comment

We have previously investigated polymorphism in molecular compounds and in active pharmaceutical ingredients (APIs) (Landre *et al.*, 2010; Martins *et al.*, 2009; Corrêa *et al.*, 2006). Accordingly, as part of our ongoing effort to investigate this phenomenon in molecular crystals, we have also studied polymorphism in transition metal complexes. The complex studied here, *trans*-$[PdCl_2(PPh_3)_2]$, is commonly used as a palladium precursor in inorganic synthesis in order to obtain new derivatives presenting catalytic (Dileep & Bhat, 2010) and biological activities (Shaheen *et al.*, 2010).

This complex has previously been reported in two polymorphic forms: form (I), space group $P\overline{1}$ (Ferguson *et al.*, 1982) [with unit-cell parameters a = 9.69 (2), b = 10.325 (2), c = 9.194 (1) Å, α = 91.38 (1), β = 111.94 (1) and γ = 72.51 (1)°]; and form (II), space group $P2_1/c$ (Pons *et al.*, 2008) [with unit-cell parameters a = 9.296 (5), b = 19.889 (8), c = 10.621 (6) Å and β = 121.71 (4)°]. In addition, four solvate forms are also known with *p*-dichlorobenzene (sesquisolvate; Kitano *et al.*, 1983), chloroform (monosolvate; Stark & Whitmire, 1997), dichloromethane (monosolvate; Oilunkaniemi *et al.*, 2003) and dichloroethane (monosolvate; Steyl, 2006). In the chloroform, dichloromethane and dichloroethane solvates the Pd centre lies on an inversion centre.



trans-$[PdCl_2(PPh_3)_2]$

We report here a new polymorphic form [form (III)] of the title compound, with two independent molecules (hereafter called molecule 1 and molecule 2, Fig. 1) of the complex in the triclinic cell; in each case the Pd centre is located on a crystallographic inversion centre. With the Pd centre of each molecule lying on independent inversion centres, a square-planar coordination of the Pd^{II} metal centre is observed, with principal geometry details given in Table 1. These dimensions are in accord with those found for related complexes,

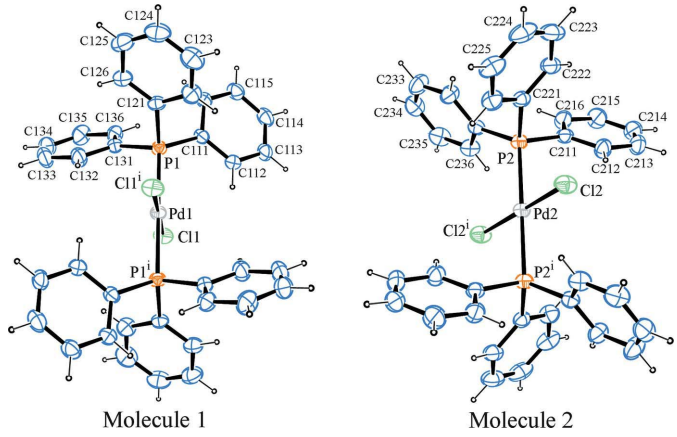


Figure 1
Views of the two independent molecules in the unit cell of the new polymorph of *trans*-$[PdCl_2(PPh_3)_2]$, with the displacement ellipsoids drawn at the 30% probability level. [Symmetry codes: (i) $-x$, $-y+1$, $-z+1$; (ii) $-x+2$, $-y$, $-z$.]

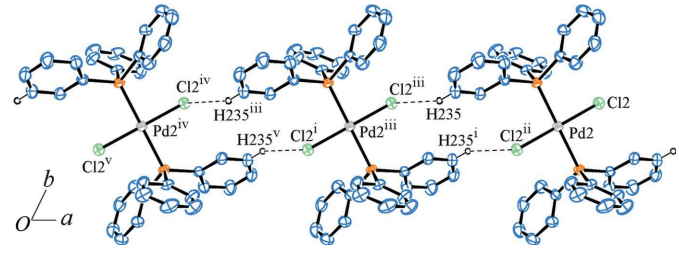


Figure 2
Intermolecular C—H···Cl interactions forming an extended chain along the *a* axis in form (III) of *trans*-$[PdCl_2(PPh_3)_2]$. [Symmetry codes: (i) $-x$, $-y+1$, $-z+1$; (ii) $-x+2$, $-y$, $-z$; (iii) $x-1$, y, z; (iv) $x-2$, y, z; (v) $-x$, $-y$, $-z$.]

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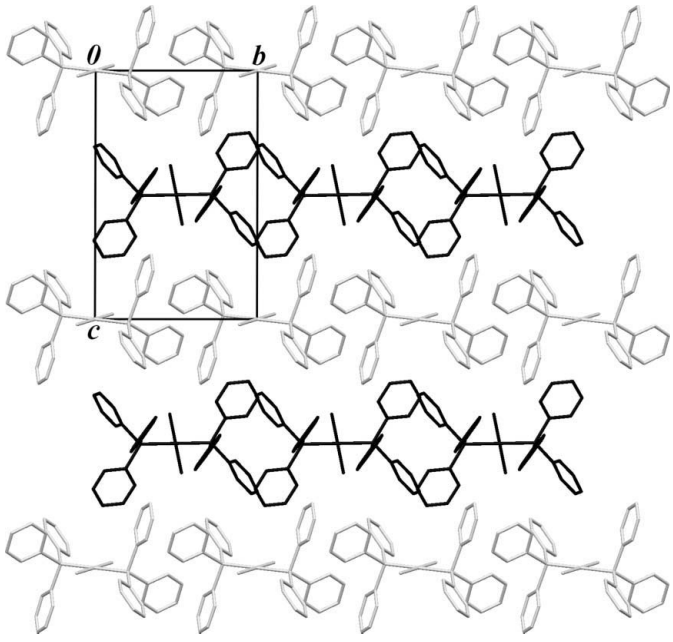

Figure 3
The crystal assembly of form (III) of *trans*-$[PdCl_2(PPh_3)_2]$ along the *a* axis, showing two independent layers formed by molecules 1 (black) and molecules 2 (grey).

including forms (I) and (II) (Ferguson *et al.*, 1982; Pons *et al.* 2008) and their solvate forms reported previously (Kitano *et al.*, 1983; Stark & Whitmire, 1997; Oilunkaniemi *et al.*, 2003; Steyl, 2006).

In molecule 1, *trans* chloride ligands are in an eclipsed conformation relative to the triphenylphosphane ligands, with the Cl1—Pd1—P1—C121 torsion angle near zero [1.09 (19)°], whereas in molecule 2, a *gauche* conformation is present with a Cl2—Pd2—P2—C221 torsion angle of −32.25 (17)° and this is the main difference between them (Fig. 1).

In the crystal structure, there are nonclassical intermolecular C—H···Cl interactions (see Table 2) involving the Cl atoms of molecule 2 and adjacent symmetry-related aromatic C—H groups, giving rise to an extended chain in the [100] direction (Fig. 2). In other crystal structures of *trans*-$[PdCl_2(PPh_3)_2]$, the Cl atoms are involved in hydrogen bonding and as a consequence twisted conformations are observed with non-zero Cl—Pd—P—C torsion angles in the range 12.77 (10)–17.0 (2)° (Ferguson *et al.*, 1982; Kitano *et al.*, 1983; Stark & Whitmire, 1997; Oilunkaniemi *et al.*, 2003; Steyl, 2006; Pons *et al.*, 2008). Comparisons among these crystalline forms of *trans*-$[PdCl_2(PPh_3)_2]$ and the respective molecular conformations of each structure suggest that the intermolecular C—H···Cl—Pd interactions are important in establishing the conformation and crystalline form. The absence of intermolecular C—H···Cl—Pd interactions for molecule 1 and their presence for molecule 2 contribute to the existence of two conformations giving rise to this new polymorphic form. Further C—H···π interactions (see Table 2) and van der Waals contacts play a role in the crystal assembly of the new form (III), and give rise to the two independent layers formed by molecules 1 and 2 in form (III) (Fig. 3).

Experimental

The complex *trans*-$[PdCl_2(PPh_3)_2]$ was dissolved in warm ethanol with vigorous shaking. The newly prepared solution was left standing for one week at room temperature. After solvent evaporation, yellow prismatic crystals had formed on the bottom of the glass crystallizer. A well-shaped clear crystal was selected for the single-crystal X-ray diffraction experiment.

Crystal data

$[PdCl_2(C_{18}H_{15}P)_2]$
M_r = 701.84
Triclinic, $P\overline{1}$
a = 9.9830 (3) Å
b = 11.3023 (3) Å
c = 15.6037 (5) Å
α = 89.947 (2)°
β = 89.539 (1)°
γ = 63.926 (1)°
V = 1581.34 (8) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.88 mm^{-1}
T = 294 K
0.12 × 0.09 × 0.04 mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: gaussian (Coppens *et al.*, 1965)
T_{min} = 0.891, T_{max} = 0.962
27320 measured reflections
7114 independent reflections
4370 reflections with $I > 2\sigma(I)$
R_{int} = 0.073

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.128
S = 1.01
7114 reflections
373 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.92 e Å^{-3}
$\Delta\rho_{min}$ = −0.92 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Pd1—Cl1	2.2996 (11)	Pd2—Cl2	2.2950 (11)
Pd1—P1	2.3247 (10)	Pd2—P2	2.3540 (10)
Cl1—Pd1—P1	92.41 (4)	Cl2—Pd2—P2	88.31 (4)

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

*Cg*1 and *Cg*2 are centroids of rings C111–C116 and C231–C236, respectively.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C235—H235···Cl2^{i}	0.93	2.80	3.637 (6)	151
C123—H123···*Cg*1^{ii}	0.93	2.91	3.762 (7)	153
C114—H114···*Cg*2^{ii}	0.93	2.89	3.705 (5)	147

Symmetry codes: (i) $x-1, y, z$; (ii) $-x+1, -y, -z+1$.

H atoms were placed at their calculated positions using a riding model, with C—H = 0.93 Å and U_{iso}(H) = 1.2U_{eq}(C).

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG3223). Services for accessing these data are described at the back of the journal.

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