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, [PdCl2(C18H15P)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-[PdCl2(PPh3)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 P1 (Ferguson et al., 1983) [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 P21/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.

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 PdII metal centre is observed, with principal geometry details given in Table 1. These dimensions are in accord with those found for related complexes,
metal-organic compounds

Experimental

The complex trans-[PdCl₂(PPh₃)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

\[ [\text{PdCl}_2(C_{18}H_{15}P)_2] \]

\[ \gamma = 63.926 (1)^\circ \]
\[ V = 1581.34 (8) \text{ Å}^3 \]
\[ Z = 2 \]
\[ \text{Mo Kα radiation} \]
\[ \mu = 0.88 \text{ mm}^{-1} \]
\[ T = 294 \text{ K} \]
\[ 0.12 \times 0.09 \times 0.04 \text{ mm} \]

Data collection

Nonius KappaCCD diffractometer
Absorption correction: gaussian
\( I = 0.073 \)
\( S = 1.01 \)
7114 reflections
4370 reflections with \( I > 2\sigma(I) \)
\( R_{	ext{int}} = 0.073 \)

Reﬁnement

\( R(F^2 > 2\sigma(F^2)) = 0.046 \)
\( wR(F^2) = 0.128 \)
373 parameters
H-atom parameters constrained
\( \Delta P_{	ext{max}} = 0.92 \text{ e Å}^{-3} \)
\( \Delta P_{	ext{min}} = -0.90 \text{ e Å}^{-3} \)

Table 1

Selected geometric parameters (Å, °).

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<tbody>
<tr>
<td>Pd1—Cl1</td>
<td>2.2996 (11)</td>
<td>Pd2—Cl2</td>
<td>2.2950 (11)</td>
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<tr>
<td>Pd1—P1</td>
<td>2.3247 (10)</td>
<td>Pd2—P2</td>
<td>2.3540 (10)</td>
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<tr>
<td>Cl1—Pd1—P1</td>
<td>92.41 (4)</td>
<td>Cl2—Pd2—P2</td>
<td>88.31 (4)</td>
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</table>

Table 2

Hydrogen-bond geometry (Å, °).

Cg1 and Cg2 are centroids of rings C11–C16 and C21–C26, respectively.

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<tr>
<td>D—H—A</td>
<td>D—H—A</td>
<td>D—H—A</td>
<td>D—H—A</td>
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<tr>
<td>C235—H235—C2i</td>
<td>0.93</td>
<td>2.80</td>
<td>3.637 (6)</td>
<td>151</td>
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<tr>
<td>C123—H123—Cg1iv</td>
<td>0.93</td>
<td>2.91</td>
<td>3.762 (7)</td>
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<td>C114—H114—Cg2iv</td>
<td>0.93</td>
<td>2.89</td>
<td>3.705 (5)</td>
<td>147</td>
</tr>
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</table>

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

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

Data collection: COLLECT (Nonius, 2000); cell refinement: SCALEPACK (Otwinski & Minor, 1997); data reduction: DENZO (Otwinski & 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).

In molecule 1, \( \text{trans} \) chloride ligands are in an eclipsed conformation relative to the triphenylphosphane ligands, with the Cl1—Pd1—P1—Cl21 torsion angle near zero \([1.09 (19)°]\), whereas in molecule 2, a gauche conformation is present with \( \text{Cl2—Pd2—P2—Cl2} \) 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 [010] direction (Fig. 2). In other crystal structures of \( \text{trans} \)-[PdCl₂(PPh₃)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).

Figure 3

The crystal assembly of form (III) of \( \text{trans} \)-[PdCl₂(PPh₃)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, \( \text{trans} \) chloride ligands are in an eclipsed conformation relative to the triphenylphosphane ligands, with the Cl1—Pd1—P1—Cl21 torsion angle near zero \([1.09 (19)°]\), whereas in molecule 2, a gauche conformation is present with a Cl2—Pd2—P2—Cl21 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 [010] direction (Fig. 2). In other crystal structures of \( \text{trans} \)-[PdCl₂(PPh₃)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).
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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.

References