Crystal structure of chlorido[diphenyl(thiophen-2-yl)phosphine-κP]gold(I)

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The crystal structure of the title compound, [AuCl(C_{16}H_{13}PS)], is reported. The molecular structure features a nearly linear arrangement of the chloride and phosphino ligands around the gold(I) center, with a P—Au—Cl bond angle of 179.42 (9)°. The Au—P and Au—Cl bond lengths are 2.226 (2) and 2.287 (2) Å, respectively. The geometry of the groups bonded to the phosphorus atom of the ligand is a slightly distorted tetrahedron. The phenyl and thienyl rings of the ligand are extensively disordered, with the thienyl refined over all three possible positions on the phosphorus atom. The relative occupancy ratio between these positions was found to be 0.406 (3):0.406 (2):0.188 (2). One of the major thienyl ring positions with the relative occupancy of 0.406 was modeled as two rotational isomers around the C—P bond with a relative occupancy ratio of 0.278 (3):0.128 (3). Intermolecular C—H⋯π interactions present in the crystal lattice link molecules of the title compound together to form a complex three-dimensional network.

1. Chemical context

The incorporation of triarylphosphines as ligands in metal complexes has led to a multitude of species capable of, for example, catalyzing organic transformations, binding to biological targets, and combating cancer. The synthesis of unsymmetric triarylphosphines has the potential to add additional functionality and selectivity to the resultant metal–ligand complexes. If we consider gold(I)–PAR₃ complexes, structural diversity of the phosphine ligand has led to properties such as selective catalysis for cycloisomerization reactions (Christian et al., 2017), triboluminescence (Kuchison et al., 2009), and enzyme inhibition (Zhang et al., 2014; Fonteh & Meyer, 2009). To this end, our group has been developing synthetic routes to unsymmetric triarylphosphines, their chalcogenide derivatives and the resultant metal–ligand complexes (Luster et al., 2022). While attempting to prepare a complex between gold(I) and the selenide derivative of diphenyl-2-thienylphosphine, we isolated single crystals of the title compound as a decomposition product.
2. Structural commentary

The structure of compound I was solved in the orthorhombic space group $P2_12_12_1$ with a Flack parameter of $-0.002$ (Parsons et al., 2013). The phosphorus–gold and chloride–gold bond lengths are 2.226 (2) and 2.287 (2) Å, respectively. The phenyl and thienyl rings of the ligand are disordered, with the thienyl ring being distributed over all three possible positions at the P atom. The relative occupancy ratio between these positions was found to be 0.406 (3):0.406 (2):0.188 (2). Furthermore, the thienyl ring position with a relative occupancy of 0.406 (3) was modeled as two rotational isomers around the C—P bond with a relative occupancy ratio of 0.279 (3):0.128 (3) (see the Refinement section for further details of the treatment of the disorder). The atom-labeling scheme for the predominant moiety (Part 1: phenyl rings C1–C6 and C14–C19 as well as thienyl ring S1C and C1–C4C) is shown in Fig. 1.

The coordination geometry of the gold center is nearly linear with a P1—Au1—Cl1 bond angle of 179.42 (9)$^\circ$. With regard to the phosphine ligand, for the most prevalent moiety the P—C bond lengths are 1.769 (7), 1.786 (7) and 1.874 (14) Å. The geometry around the phosphorus atom P1 resembles a tetrahedron with a $\tau_4$ descriptor for fourfold coordination of 0.95 (where 0.00 = square planar, 0.85 = trigonal pyramidal, and 1.00 = tetrahedral; Yang et al., 2007). The C—P—C bond angles range from 105.3 (6) to 106.9 (11)$^\circ$, and the Au—P—C bond angles range from 111.9 (5) to 113.6 (3)$^\circ$ for the most prevalent moiety.

3. Supramolecular features

Individual molecules of the title compound are held together through intermolecular C—H···π interactions (Table 1). In

![Figure 1](image1)

The molecular structure of the title compound I, with the atom-labeling scheme. Displacement ellipsoids are drawn at the 30% probability level, all hydrogen atoms have been omitted and only the predominant Part 1 is shown for clarity.

![Figure 2](image2)

The C—H···π interactions (solid, blue lines) found in crystals of the title compound that form helices that run along the a-axis direction, depicted using a ball-and-stick model with standard CPK colors (Au = tan, hydrogen = light pink). The chlorine atoms, phenyl ring C1–C6, and any hydrogen atom not involved in a C—H···π interaction have been omitted for clarity. Only Part 1 is shown. Symmetry codes as in Table 1.

Table 1

| C—H···π interactions (Å, $^\circ$). |
|---|---|---|---|---|
| $D$—H $\cdot$···$A$ | $D$—H | $H$···$A$ | $D$···$A$ | $D$—H···$A$ |
| C2C—H2C···Cg2$^i$ | 0.95 | 2.80 | 141 | 4 (1) |
| C2C—H2C···Cg4$^i$ | 0.95 | 2.79 | 139 | 4 (1) |
| C3D—H3D···Cg1$^i$ | 0.95 | 2.87 | 141 | 4 (1) |
| C3D—H3D···Cg3$^i$ | 0.95 | 2.85 | 141 | 4 (1) |
| C8—H8···Cg2$^i$ | 0.95 | 2.80 | 141 | 4 (1) |
| C8—H8···Cg4$^i$ | 0.95 | 2.77 | 130 | 4 (1) |
| C18—H18···Cg1$^i$ | 0.95 | 2.96 | 129 | 4 (1) |
| C18—H18···Cg3$^i$ | 0.95 | 2.95 | 128 | 4 (1) |

Symmetry codes: (i) $-x + 1, y + \frac{1}{2}, z + \frac{1}{2}$; (ii) $-x, -y + 1, z - \frac{1}{2}$.
Part 1, these interactions exist between the C14–C19 phenyl ring and the hydrogen atom C2C(H2C) of the thiényl ring as well as between hydrogen atom C18(H18) and the S1/C1/C2/C3 thienyl ring. These intermolecular C—H···π interactions link the molecules together to form helices that propagate along the a-axis direction (Fig. 2). The helices are then held together through C—H···π interactions to form a complex 3D network (Fig. 3). The remainder of the intermolecular C—H···π interactions present in this structure are not exclusive to Part 1, and are listed in Table 1.

4. Database survey
A search of the Cambridge Structural Database (CSD, Version 5.42, November, 2020; Groom et al., 2016) for structures containing a P—Au bond where the phosphorus atom bears one thienyl ring resulted in 14 hits. Structures IHUJUQ (Ho & Tiekink, 2003) and IHUJUQ01 (Monkowius et al., 2003) are closely related to compound I, with a linear arrangement of chloride and one tris(2-thienyl)-substituted phosphine ligand bound to a gold(I) atom. Another related structure is IWAYUC (Yang et al., 2016), which contains a diphenylphosphino-3-thienyl-1H-imidazole ligand again bound to a gold(I) atom that also bears a chloride. Finally, structure YAHPUT (Stott et al., 2005) features a terthiophene-substituted diphenylphosphinogold(I)–chloride complex.

5. Synthesis and crystallization
A small vial was charged with diphenyl(2-thienyl)phosphine selenide (10-15 mg; Luster et al., 2022) and a stoichiometric amount of chloro(tetrahydrothiophene)gold(I). The solids were dissolved in 1 mL of CDCl3, and the reaction mixture was transferred to an NMR tube. Crystals of compound I were grown serendipitously via slow evaporation of the solvent.

6. Refinement
Crystal data, data collection and structure refinement details are summarized in Table 2. All hydrogen atoms were placed in calculated positions and refined as riding: C—H = 0.95–1.00 Å with Uiso(H) = 1.2Ueq(C). The electron density corresponding to the disordered phenyl rings and the thiényl ring was modeled over three parts. In the model, electron density corresponding to the thiényl ring was found at three positions on the phosphorus atom. In one of these positions, the thiényl ring was also found to be present as two rotational isomers corresponding to a 180° rotation around the C–P bond. The relative occupancies of each position of the thiényl ring were refined, while the total occupancy of all thiényl sites as well as the occupancy sum of each site were constrained to unity using SUMP commands. The thiényl occupancy rates refined to be

![Figure 3](https://via.placeholder.com/150)

The crystal packing of the title compound as viewed down the a-axis, depicted using a ball-and-stick model with standard CPK colors (Au = tan, Cl = green, H = light pink). Intermolecular C—H···π interactions are shown with solid, blue lines. For clarity any hydrogen atoms not involved in a C—H···π interaction have been omitted. Only Part 1 is shown.

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<th>Table 2</th>
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Computer programs: APEX2 and SAINT (Bruker, 2013), SHELXT2018/2 (Sheldrick, 2015a), SHELXL2019/2 (Sheldrick, 2015b), CrystalMaker (Palmer, 2007), and OLEX2 (Dolomanov et al., 2009; Bourhis et al., 2015).

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**Research Communications**

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0.406 (2):0.278 (3):0.128 (3):0.188 (2) for the sites of S1C, S1B, S1A and S1D. Bond lengths and angles of all four thienyl moieties were restrained to be similar to each other using SHELXL (Sheldrick, 2015b) SAME commands with an esd of 0.001 Å. For the pivot moiety with the highest occupancy (S1C/C1C–C4C), distance restraints were used to ensure a model with bond lengths and angles that agree with known values. Bonds of the thienyl ring were restrained using DFIX commands to be 1.70 (S1C—C1C), 1.34 (C1C—C2C, C3C—C4C) and 1.41 (C2C—C3C) Å with an esd of 0.002 Å in SHELXL (Sheldrick, 2015b). The less occupied thienyl rings A and B were also restrained to be planar and coplanar with the P atom using FLAT commands. All P1—Cipso distances were restrained to be similar to each other using SADI commands. The atoms of each phenyl ring C1–C6, C7–C13 and C14–C15 were constrained to resemble an ideal hexagon with C—C bond lengths of 1.39 Å using SHELXL AFIX 66 commands. Lastly, $U_{ij}$ components of all C, S and P atoms were restrained to be similar to each other for atoms closer than 2.0 Å with an esd of 0.002 Å².

Acknowledgements

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References

Crystal structure of chlorido[diphenyl(thiophen-2-yl)phosphine-κP]gold(I)

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Computing details
Data collection: APEX2 (Bruker, 2013); cell refinement: SAINT (Bruker, 2013); data reduction: SAINT (Bruker, 2013); program(s) used to solve structure: SHELXT2018/2 (Sheldrick, 2015a); program(s) used to refine structure: SHELXL2019/2 (Sheldrick, 2015b); molecular graphics: CrystalMaker (Palmer, 2007); software used to prepare material for publication: OLEX2 (Dolomanov et al., 2009; Bourhis et al., 2015).

chlorido[diphenyl(thiophen-2-yl)phosphine-κP]gold(I)

Crystal data
[ AuCl(C₁₆H₁₃PS) ]
Mr = 500.71
Orthorhombic, P 2₁2₁2₁
a = 10.0322 (13) Å
b = 12.0784 (15) Å
c = 12.9412 (16) Å
V = 1568.1 (3) Å³
Z = 4
F(000) = 944

Data collection
Bruker APEXII CCD
diffractometer
φ and ω scans
Absorption correction: multi-scan
(SADABS; Krause et al., 2015)
T̂ min = 0.474, T̂ max = 0.745
33335 measured reflections

Refinement
Refinement on F²
Least-squares matrix: full
R[F² > 2σ(F²)] = 0.025
wR(F²) = 0.059
S = 1.08
3075 reflections
341 parameters
837 restraints
Primary atom site location: dual
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
w = 1/σ²(Fo²) + (0.0234P)² + 0.2535P)
where P = (Fo² + 2Fc²)/3
(Δ/σ)max = 0.001
Δρ max = 1.02 e Å⁻³
Δρ min = −0.53 e Å⁻³
Absolute structure: Flack x determined using
1149 quotients [(I+)-(I-)]/[/(I+)+(I-)] (Parsons et al., 2013)
Absolute structure parameter: −0.002 (6)
Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

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### Atomic displacement parameters (Å²)

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Geometric parameters (Å, °)

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S1D—C1D—P1  121.1 (11)  C1—C2—C3  120.0
C2D—C1D—P1  132.8 (13)  C3—C2—H2  120.0
C2D—C1D—S1D  106.1 (14)  C2—C3—H3  120.0
C1D—C2D—H2D  123.1  C2—C3—C4  120.0
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C12—C11—H11  120.0  C3C—C4C—H4C  124.1

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Au1—P1—C1B—C2B  132 (3)  C12—C7—C8—C9  0.0
Au1—P1—C1C—C2C  −33 (3)  S1A—C1A—C2A—C3A  4 (3)
Au1—P1—C1C—C3C  152.2 (14)  C1A—S1A—C4A—C3A  1 (2)
Au1—P1—C1C—C4C  −33 (3)  C1A—C2A—C3A—C4A  −3 (3)
P1—C14—C15—C16  179.0 (7)  C2A—C3A—C4A—S1A  1 (3)
P1—C14—C19—C18  −179.0 (7)  C4A—S1A—C1A—P1  −179 (3)
P1—C1D—C2D—C3D  −177 (4)  C4A—S1A—C1A—C2A  −3 (2)
P1—C7—C8—C9  −179.1 (13)  S1B—C1B—C2B—C3B  −7 (2)
P1—C7—C8—C9  −179.1 (13)  C1B—P1—C7—C8  93.0 (13)


### Hydrogen-bond geometry (Å, °)

Cg1, Cg2, Cg3, and Cg4 are the centroids of the S1/C1–C4, S1D/C1D–C4D, C7–C12, and C14–C19 rings, respectively.

<table>
<thead>
<tr>
<th>D—H···A</th>
<th>D—H</th>
<th>H···A</th>
<th>D···A</th>
<th>D—H···A</th>
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<tr>
<td>C2—H2C···Cg2^i</td>
<td>0.95</td>
<td>2.80</td>
<td>141</td>
<td>4 (1)</td>
</tr>
<tr>
<td>C2—H2C···Cg4^i</td>
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<td>2.79</td>
<td>139</td>
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<tr>
<td>C3D—H3D···Cg1^ii</td>
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<td>2.87</td>
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</tr>
<tr>
<td>C3D—H3D···Cg3^iii</td>
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<td>2.85</td>
<td>141</td>
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</tr>
<tr>
<td>C8—H8···Cg2</td>
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<td>131</td>
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<tr>
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<tr>
<td>C18—H18···Cg1^ii</td>
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<td>129</td>
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</tr>
<tr>
<td>C18—H18···Cg3^iii</td>
<td>0.95</td>
<td>2.95</td>
<td>128</td>
<td>4 (1)</td>
</tr>
</tbody>
</table>

Symmetry codes: (i) −x+1, y+1/2, −z+3/2; (ii) −x+3/2, −y+1, z−1/2.