

Aurophilic interactions in μ -*p*-phenylenediethynyl-bis-[(trimethyl phosphite)gold(I)] dichloromethane hemisolvate

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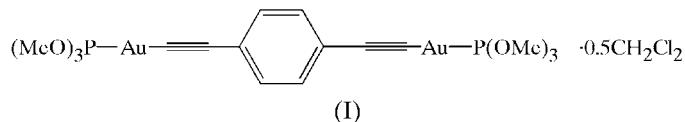
The title compound, $[\text{Au}_2(\text{C}_{10}\text{H}_4)(\text{C}_3\text{H}_9\text{O}_3\text{P})_2] \cdot 0.5\text{CH}_2\text{Cl}_2$, is a linear monomer in which each Au atom is coordinated by one acetylene and one phosphite group. Molecules are connected through aurophilic interactions, one short and one longer, approximately perpendicular to the intramolecular di(gold acetylide) unit, with an $\text{Au} \cdots \text{Au}(x, 1 - y, \frac{1}{2} + z)$ distance of 3.1733 (2) Å and an $\text{Au} \cdots \text{Au}(-x, y, \frac{1}{2} - z)$ distance of 3.5995 (3) Å. Comparison with related compounds exhibiting aurophilic interactions shows that the packing architecture is not determined by steric factors alone.

Comment

Aurophilic interactions, weakly bonding interactions between formally non-bonded gold centers, have been described and classified only in the relatively recent past (Scherbaum *et al.*, 1988). These interactions are of considerable current interest as both intra- and intermolecular motifs in gold compounds (Mohr *et al.*, 2004). These interactions have strengths similar to those of hydrogen bonding (Pyykkö, 1997) and are characterized by $\text{Au} \cdots \text{Au}$ contacts close to the sum of the van der Waals radii (3.2 Å). Ligand bulk plays an important role in the formation of intermolecular aurophilic interactions. We report here the structure of a gold–phosphite–acetylene compound, (I), that exhibits two aurophilic contacts of appreciably different length.

Compound (I), shown in Fig. 1, has a typical ‘wheel-and-axle’ structure, with two phosphite ‘wheels’ on the ends of the di(gold acetylide) ‘axle’ (Bruce *et al.*, 2002). The Au atom is linearly coordinated by the phosphite and acetylide moieties, as is typical for Au^{I} compounds. The intramolecular bond lengths and angles, detailed in Table 1, are unexceptional in compar-

ison with other known gold–acetylene and gold–phosphite complexes. Searches of the Cambridge Structural Database (Version 5.25; Allen, 2002) yield an average Au–P distance in seven $\text{Au}-\text{P}(\text{OMe})_3$ linkages of 2.254 (7) Å and an average Au–C distance of 1.99 (4) Å from 99 Au–C distances in two-coordinate gold acetylides. The analogous Au–P distances for the title compound are 2.2459 (8) and 2.2492 (8) Å, and the Au–C bond lengths are both 2.000 (3) Å.



There are two aurophilic interactions present in (I), as shown in Fig. 2. Each Au1 atom bonds intermolecularly to an $\text{Au}2(x, 1 - y, \frac{1}{2} + z)$ atom at a distance of 3.1733 (2) Å in a head-to-tail fashion. Each Au2 atom also interacts with atom $\text{Au}2(-x, y, \frac{1}{2} - z)$ of a third molecule at a distance of 3.5995 (3) Å. The intermolecular $\text{Au} \cdots \text{Au}$ contacts, shown in Fig. 2, generate a herring-bone lattice. The $\text{Au} \cdots \text{Au}$ contacts form short chains of four atoms ($\text{Au}1 \cdots \text{Au}2 \cdots \text{Au}2 \cdots \text{Au}1$) in which the angle at each Au2 atom is 149.55 (1)°. There is not an infinite chain of contacts through the crystal because each Au1 center is effectively a terminus for the aurophilic contacts.

A few related di(gold acetylide) compounds have been structurally characterized, and some exhibit aurophilic interactions, as summarized in Table 2. In the PCy_3 analog of the title compound (Chao *et al.*, 2002), all $\text{Au} \cdots \text{Au}$ distances are longer than 3.6 Å. With smaller PMe_3 ligands on the ends of a digold $\text{CC}-\text{C}_6\text{H}_2\text{Me}_2-\text{CC}$ axle, the Au atoms show aurophilic contacts of 3.1361 (9) Å (Irwin, Vittal *et al.*, 1997). In this structure, the methyl groups are in the 2- and 5-positions of the phenylene ring. A PMe_3 analog of the present compound, $[(\text{Me}_3\text{P})\text{Au}-\text{CC}-\text{Au}(\text{PMe}_3)]$ (Jia *et al.*, 1993; Liao *et al.*, 2003), with a much shorter bridge (axle) has also been reported, with $\text{Au} \cdots \text{Au}$ contacts of 3.0747 (8) Å. Two gold acetylides with capping $\text{P}(\text{OMe})_3$ ligands are known, both with a *meta* orientation of the two acetylene groups in contrast with the *para* orientation in the title compound. One compound has ethynylgold groups in the 1- and 3-positions and a methyl group in the 5-position (MacDonald *et al.*, 2000); the $\text{Au}1 \cdots \text{Au}2$ contacts are 3.2196 (9) Å. When a third

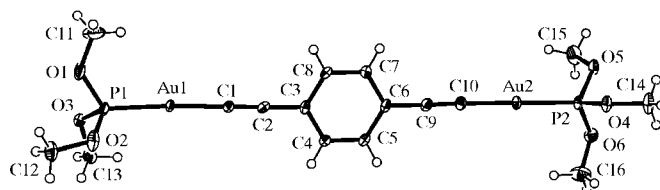
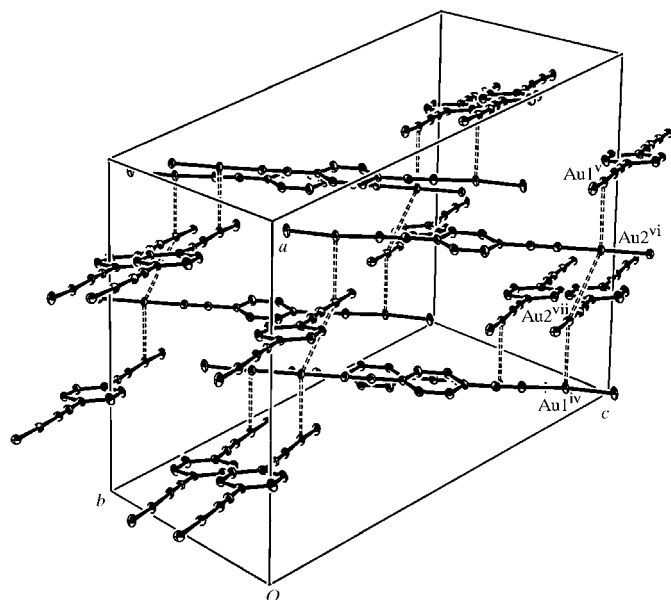


Figure 1

A view of the structure of (I), showing the atomic numbering. The dichloromethane solvent molecule has been omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level for non-H atoms.


Figure 2

A packing diagram showing the aurophilic interactions. All H atoms and phosphite methyl groups have been omitted for clarity. The short and long Au...Au contacts are shown as dashed lines. [Symmetry codes: (iv) $\frac{1}{2} + x, \frac{1}{2} + y, z$; (v) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (vi) $\frac{1}{2} - x, \frac{1}{2} - y, -z$; (vii) $\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z$.]

ethynylgold unit is present in approximate C_3 symmetry (Irwin, Manojlovic-Muir *et al.*, 1997), there is an aurophilic contact between atoms Au1 and Au3 of 3.316 (1) Å, and a much longer Au1...Au2 distance of 3.973 (1) Å.

Together with the data reported here, these structures show that in addition to the steric bulk of the ligand at the Au center, the geometric distribution of the gold acetylide units around a benzene ring also affects the formation of aurophilic contacts, as summarized in Table 2. In comparing table entry *D* with compound (I), a shorter Au...Au interaction has been achieved with similar steric bulk of the terminal ligands, because (I) has only hydrogen substituents on the central ring. Comparison of (I) and entry *E* shows the reduction in distance achieved with di- versus trisubstitution. Close aurophilic contacts require both small terminal ligands on the Au atom and fewer substituents on the benzene ring to minimize steric clashes.

Experimental

The title compound was synthesized by modification of a procedure reported by Jia *et al.* (1993). The P(OMe)₃ ligand was added to a slurry of the polymer {Au-CC-C₆H₄}_{*n*}, causing the polymer to dissolve as the phosphite breaks up the intermolecular gold-acetylene interactions. The solution was filtered and the new compound was recrystallized from CH₂Cl₂ layered with hexanes. ¹H NMR (300 MHz, CD₂Cl₂): δ 3.73 (*d*, 18H, CH₃, ²*J*_{HC} = 12.69 Hz), 7.25 (*s*, 4H, C₆H₄). ¹³C NMR (300 MHz, CD₂Cl₂): δ 52.57 (CH₃), 123.20 (*C*_{ipso}), 131.61 (CH). Acetylene C atoms were not detected, consistent with previously reported work (Liau *et al.*, 2003). UV-vis (CH₂Cl₂) [λ_{max} , nm (extinction coefficient, cm⁻¹ M⁻¹): 231 (136.000), 235 (133.000), 305 (269.000), 324 (410.000)]. Fluorescence (CH₂Cl₂) (λ_{max} , nm): excitation 346, 357, 373; emission 378, 396, 412. Analysis

calculated for C₁₆H₂₂Au₂O₆P₂: C 25.08, H 2.89, Au 51.41%; found: C 24.94, H 3.06, Au 51.30%.

Crystal data

[Au₂(C₁₀H₄)(C₃H₉O₃P)₂]₂·
0.5CH₂Cl₂
M_r = 808.69
Monoclinic, *C2/c*
a = 16.6892 (9) Å
b = 13.8568 (8) Å
c = 20.4250 (12) Å
 β = 105.2250 (10)°
V = 4557.7 (4) Å³
Z = 8

D_x = 2.357 Mg m⁻³
Mo *K*α radiation
Cell parameters from 5620
reflections
 θ = 2.5–27.5°
 μ = 13.15 mm⁻¹
T = 100 (2) K
Block, yellow
0.22 × 0.16 × 0.12 mm

Data collection

Bruker SMART CCD area-detector
diffractometer
 φ and ω scans
Absorption correction: multi-scan
(*SADABS*; Sheldrick, 1996)
*T*_{min} = 0.160, *T*_{max} = 0.301
18 988 measured reflections
5101 independent reflections

4364 reflections with *I* > 2σ(*I*)
*R*_{int} = 0.018
 θ_{max} = 27.5°
h = -21 → 21
k = -17 → 17
l = -26 → 26

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.020
wR (*F*²) = 0.052
S = 1.03
5101 reflections
262 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0223P)^2 + 20.4573P]$
where $P = (F_o^2 + 2F_c^2)/3$
(Δ/σ)_{max} = 0.002
 $\Delta\rho_{\text{max}}$ = 0.89 e Å⁻³
 $\Delta\rho_{\text{min}}$ = -0.90 e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Au1—C1	2.000 (3)	P1—O3	1.585 (2)
Au1—P1	2.2459 (8)	P2—O4	1.571 (2)
Au2—Au2 ⁱ	3.5995 (3)	P2—O5	1.583 (2)
Au2—C10	2.000 (3)	P2—O6	1.595 (2)
Au2—P2	2.2492 (8)	C1—C2	1.205 (4)
Au2—Au1 ⁱⁱ	3.1733 (2)	C2—C3	1.438 (4)
P1—O1	1.572 (3)	C6—C9	1.435 (4)
P1—O2	1.577 (3)	C9—C10	1.210 (5)
C1—Au1—P1	174.78 (10)	O3—P1—Au1	117.34 (10)
C1—Au1—Au2 ⁱⁱⁱ	89.32 (10)	O4—P2—Au2	111.09 (9)
P1—Au1—Au2 ⁱⁱⁱ	95.56 (3)	O5—P2—Au2	118.48 (9)
C10—Au2—P2	179.03 (10)	O6—P2—Au2	116.76 (10)
C10—Au2—Au1 ⁱⁱ	86.65 (9)	C2—C1—Au1	179.4 (3)
P2—Au2—Au1 ⁱⁱ	94.13 (2)	C1—C2—C3	177.9 (4)
Au1 ⁱⁱ —Au2—Au2 ⁱ	149.55 (1)	C10—C9—C6	178.7 (4)
O1—P1—Au1	120.33 (12)	C9—C10—Au2	177.5 (3)
O2—P1—Au1	109.00 (10)		

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

Table 2

Comparison of aurophilic interaction distances (Å).

Compound	Au...Au	Reference
<i>A</i> {Me ₃ PAu} ₂ μ-CC	3.0747 (8)	Liau <i>et al.</i> (2003)
<i>B</i> {Me ₂ PhPAu} ₂ μ-CC-1,3-C ₆ H ₃ Me-CC	3.124 (2), 3.146 (2)	MacDonald <i>et al.</i> (2000)
<i>C</i> {Me ₃ PAu} ₂ μ-CC-1,4-C ₆ H ₂ Me ₂ -CC	3.1361 (9)	Irwin, Vittal <i>et al.</i> (1997)
(I) {(MeO) ₃ PAu} ₂ μ-CC-1,4-C ₆ H ₄ -CC	3.1733 (2)	This work
<i>D</i> {(MeO) ₃ PAu} ₂ μ-CC-1,3-C ₆ H ₃ Me-CC	3.2196 (9)	MacDonald <i>et al.</i> (2000)
<i>E</i> {(MeO) ₃ PAu} ₃ μ-CC-1,3,5-C ₆ H ₃ -(CC) ₂	3.316 (1)	Irwin, Manojlovic-Muir <i>et al.</i> (1997)
<i>F</i> {cy ₃ PAu} ₂ μ-CC-1,4-C ₆ H ₄ -CC	< 3.6	Chao <i>et al.</i> (2002)

The title compound crystallizes as a dichloromethane hemisolvate. The solvent molecule is disordered around a twofold axis over two positions, and was refined with both C—Cl distances restrained to have the same value and isotropic displacement parameters for the C atom. All H atoms were placed in calculated positions and refined using a riding model [C—H = 0.93–0.97 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$].

Data collection: *SMART* (Bruker, 2000); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2000); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2000); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1684). Services for accessing these data are described at the back of the journal.

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