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μ-Biphenyl-2,2′-dithiolato-κ^2S:S'-bis[(triphenylphosphine-κP)gold(I)]

Scott A. Larkin,[a] Jeanette A. Krause Bauer,[b] V. E. Konoplev,[c] Victor P. Dyadchenko,[c] Dmitrii A. Lemenovskii,[c] Mitchell R. M. Bruce[a]* and Alice E. Bruce[a]*

[a]Department of Chemistry, University of Maine, Orono, ME 04469-5706, USA,
[b]Department of Chemistry, University of Cincinnati, OH 45221-0172, USA, and
[c]Department of Chemistry, M. V. Lomonosov Moscow State University, Leninskiye Gory, Moscow 119992, Russia Federation
Correspondence e-mail: abruce@maine.edu

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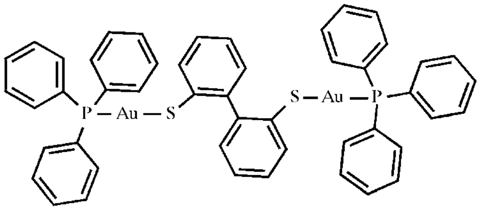
The reaction of $ClAuPPh_3$ and 1,1′-biphenyl-2,2′-dithiol in the presence of trimethylbenzylammonium chloride and K_2CO_3 in a tetrahydrofuran/methanol solution gives the title complex, $[Au_2(C_{12}H_8S_2)(C_{18}H_{15}P)_2]$. The molecule contains P—Au—S units which 'cross' with torsion angles of ~90° [P—Au—Au—P = 86.23 (5)° and S—Au—Au—S = 95.62 (5)°]. The intra- and intermolecular Au···Au distances [3.9064 (3) and 6.3797 (5) Å, respectively] are outside the range for typical Au···Au interactions. However, the Au atoms appear to be drawn together, leading to a significant bending of the P—Au—S angles [170.24 (5) and 169.52 (5)°].

Comment

Interest in gold chemistry has increased exponentially in recent years to include diverse topics such as catalysis (Grisel *et al.*, 2002), liquid crystals (Jana *et al.*, 2002), antiviral activity (Dinger & Henderson, 1998) and novel luminescence (Lee & Eisenberg, 2003; Mohamed *et al.*, 2003; Yam *et al.*, 2003; White-Morris *et al.*, 2003). An important factor fueling this growth involves gold–gold interactions, which, at about 30 kJ mol^{-1} (Schmidbaur *et al.*, 1988; Narayanaswamy *et al.*, 1993; Harwell *et al.*, 1996), have been increasingly used to engineer specific molecular properties. Gold–sulfur complexes have been of special interest because soft sulfur ligands are predicted to promote gold–gold interactions (Pyykko *et al.*, 1994). Dithiol ligands, such as 1,1′-biphenyl-4,4′-dithiol or 1,1′-biphenyl-2,2′-dithiol, are interesting because of their potential to facilitate the formation of gold arrays. Phosphine–gold–dithiolate complexes utilizing 1,1′-biphenyl-4,4′-dithiol provide examples of how steric factors influence the formation of such solid-state gold arrays. When the phosphine is tricyclohexylphosphine, there are no discernible sub-van der Waals contacts between Au atoms, but when the phosphine is tri-*p*-tolylphosphine, an aurophilicity-based one-dimensional array is formed (Ehlich *et al.*, 2002). The 1,1′-biphenyl-4,4′-dithiol ligand has also been used to form SAMs (self-assembled monolayers) on gold surfaces (de Boer *et al.*, 2003). An examination of structures containing biphenyl with sulfur attached at the 2- and 2′-positions shows no structure containing gold coordinated to the 1,1′-biphenyl-2,2′-dithiol ligand (Cambridge Structural Database, Version 5.25 of November 2003; Allen, 2002).



(I)

Accordingly, we now report the solid-state structure of the title complex, (I), which contains one discrete dinuclear monomer (Fig. 1). The P—Au and S—Au bond lengths are typical for gold(I)–phosphine–thiolate complexes. The intramolecular Au···Au distance [3.9064 (3) Å] precludes a typical gold–gold bonding interaction, which occurs when the distance between two Au^{I} atoms is at or slightly below the sum of the van der Waals radii (3.32 Å; Bondi, 1964). The crossed arrangement of the P—Au—S units exhibits a P—Au—Au—P torsion angle of 86.23 (5)° (Table 1). The phenyl rings of the biphenyldithiolate moiety are twisted out of the plane with respect to each other, forming a C12—C7—C6—C1 dihedral angle of 119.4 (6)°.

Structures containing biphenyl with sulfur attached at the 2- and 2′-positions reveal a wide range (2–116°) of absolute torsion angles between the phenyl rings (C2—C1—C1′—C2′ referenced to biphenyl). Some generalizations can be made by grouping these structures into subsets. In one subset, which

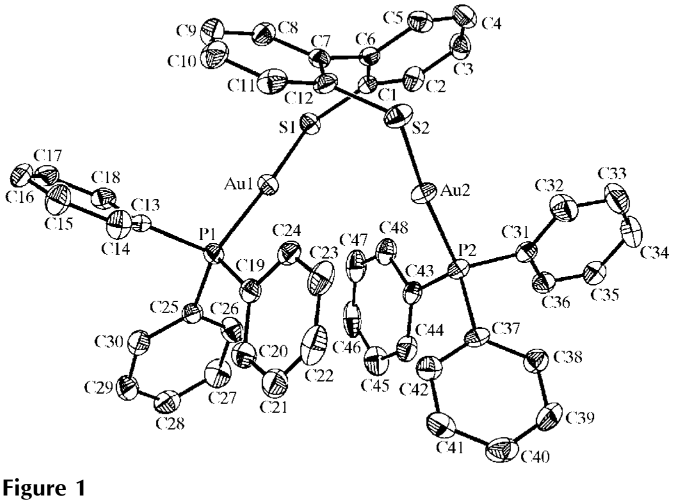


Figure 1
A view of the molecular structure of (I), with the atomic numbering scheme. Displacement ellipsoids are shown at the 50% probability level and H atoms have been omitted for clarity. [P—Au—S = 170.24 (5) and 169.52 (5)°, Au1···Au2 = 3.9064 (3) Å, S1···S2 = 5.186 (2) Å and P1···P2 = 5.529 (2) Å.]

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comprises more than half the structures, the biphenyl rings are relatively flat, with torsion angles of 2–38°. These structures are constrained by virtue of a direct bond between S atoms (*i.e.* disulfide), or by a single S, O or Se atom bridging between the 6- and 6′-positions of the biphenyl rings. Another subset of structures contains metal chelates (M = Mo, Ni, Pd, Rh, Ti, Cu and Ru), with torsion angles of 59–87°. If there are bulky groups opposite the S atoms, *i.e.* in the 6- and 6′-positions, the torsion angles between the phenyl rings tend to be ~90°. Finally, there are a few structures that contain bulky groups bonded to the S atoms (*e.g.* sulfonates), and the torsion angle can be as high as 116°. Complex (I) appears to fall into this last category. The (triphenylphosphine)gold units coordinated to sulfur are very bulky, and the torsion angle between the phenyl rings opens up to 119° in order to minimize interactions between the triphenylphosphine rings. Inspection of (I) also reveals that the Au atoms appear to be drawn together, leading to a significant bending of the P—Au—S angles [170.24 (5) and 169.52 (5)°]. However, as noted above, the long distance between the Au atoms precludes a typical gold–gold bonding interaction. Comparison with other structures shows that significant bending is observed when short gold–gold, gold–metal or gold–heteroatom interactions are present [*e.g.* Au—Au (Davila *et al.*, 1993; Crespo *et al.*, 1997), Au—Ir (Rio *et al.*, 2001), Au—Os (Leung *et al.*, 1998), Au—N (Vincert *et al.*, 2001; Wilton-Ely *et al.*, 2002) and Au—S (Wilton-Ely *et al.*, 2001; Kuz'mina *et al.*, 1993)]. These observations suggest the possibility that aurophilicity, even at these long distances, may influence the solid-state structure. In recent work, Pyykko and co-workers (Pyykko & Tamm, 1998; Pyykko, 2004) estimated the aurophilic energy as a function of the Au···Au distance, and at 3.9 Å, a gold–gold interaction is estimated to be around 3 kJ mol^{-1}. This is about one-tenth of the strength of a typical strong gold–gold interaction. Other weak interactions, such as C—H···F, which are estimated to be significantly weaker than a typical O···H hydrogen bond, have been shown to be important features for stabilizing crystal structures (Howard *et al.*, 1996; Thalladi *et al.*, 1998; Lee *et al.*, 2000).

Experimental

Complex (I) was synthesized by reaction of ClAuPPh$_3$ (910 mg, 1.84 mmol) and 1,1′-biphenyl-2,2′-dithiol (200 mg, 0.92 mmol) in the presence of trimethylbenzylammonium chloride (68 mg, 0.36 mmol) and K$_2$CO$_3$ (500 mg, 3.62 mmol) in a tetrahydrofuran/methanol solution. Crystals suitable for X-ray analysis were grown from Et$_2$O/CH$_2$Cl$_2$ and were obtained as colorless plates.

Crystal data

$[Au_2(C_{12}H_8S_2)(C_{18}H_{15}P)_2]$
M_r = 1134.78
Monoclinic, $P2_1/c$
a = 20.0310 (4) Å
b = 10.2199 (2) Å
c = 20.0399 (3) Å
β = 96.303 (2)°
V = 4077.67 (13) Å^3
Z = 4
D_x = 1.848 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 6392 reflections
θ = 2.5–28.3°
μ = 7.40 mm^{-1}
T = 150 (2) K
Plate, colorless
0.20 × 0.10 × 0.04 mm

Table 1
Selected geometric parameters (Å, °).

Au1—P1	2.2605 (14)	P1—C13	1.823 (5)
Au1—S1	2.3020 (13)	P2—C31	1.806 (5)
Au2—P2	2.2565 (13)	P2—C43	1.819 (5)
Au2—S2	2.3024 (13)	P2—C37	1.823 (5)
P1—C19	1.804 (6)	S1—C1	1.777 (5)
P1—C25	1.820 (5)	S2—C12	1.779 (5)
P1—Au1—S1	170.24 (5)	C1—S1—Au1	111.05 (17)
P2—Au2—S2	169.52 (5)	C12—S2—Au2	107.15 (17)
S1—Au1—Au2—S2	95.62 (5)	P1—Au1—Au2—P2	86.23 (5)

Data collection

Bruker SMART 1K CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min}$ = 0.319, $T_{\max}$ = 0.756
42 287 measured reflections
10 002 independent reflections
6889 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.066
$\theta_{\max}$ = 28.3°
$h = -26 \rightarrow 26$
$k = -13 \rightarrow 13$
$l = -26 \rightarrow 25$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.071
S = 1.00
10002 reflections
488 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.026P)^2 + 4.627P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$ = 0.002
$\Delta\rho_{\max}$ = 1.00 e Å^{-3}
$\Delta\rho_{\min}$ = −0.92 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.00011 (3)

H atoms were positioned geometrically (C—H = 0.95 Å) and treated as riding, with $U_{\rm iso}$(H) values of $1.2U_{\rm eq}$(C). The final difference map was featureless, the highest residual electron-density peaks being approximately 0.9 Å from the Au atoms.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Siemens, 1994); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; 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: FR1487). Services for accessing these data are described at the back of the journal.

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