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A monomeric gold(I) carbanion complex with an uncoordinated thioether: [2-(methylsulfanyl)phenyl]-(triphenylphosphine)gold(I)

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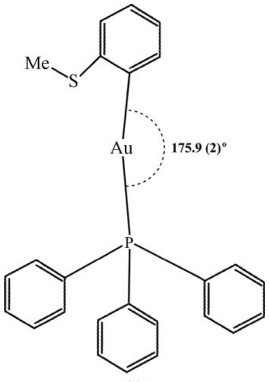
The title compound, [Au(C_7H_7S)($C_{18}H_{15}P$)], is conformationally chiral and crystallizes from benzene–hexane as individually enantiopure crystals. This mononuclear compound has the Au^I atom linearly bound to a triphenylphosphine P atom and to a phenyl C atom of a 2-(methylsulfanyl)phenyl group. The angle at the Au^I atom is 175.9 (2)°. The linear ligand coordination about the Au^I atom has geometric parameters inside the remarkably narrow range found for gold complexes bound by a phosphine ligand and by the *ortho*-C atom of a substituted phenyl group. This is the first example of gold(I) attached to a methylsulfanyl aromatic carbanion.

Comment

Gold carbanion connections are strong, as revealed by structural (Schmidbaur, 1995) and theoretical energy studies (Dargel *et al.*, 1999). However, establishing such bonds usually demands reactive carbon precursors (organolithium or Grignard reagents) (Fernandez *et al.*, 2004) with some reduction of Au^I to Au^0. This inconvenience has prompted the search for more efficient procedures to generate Au—C bonds. Partyka *et al.* (2009), using boronic acids $ArB(OH)_2$ as carbon-delivering substrates, have shown these reagents to give good yields of the desired aromatic carbanion products with LAuBr (where L is a bulky PR_3 N-heterocyclic carbene) and an assisting base. In this report, we describe a transmetallation from boron to gold using Ph_3PAuCl instead of LAuBr. The reaction provides an excellent yield of the title substituted triphenylphosphine gold(I) compound, [(Ph_3P)-Au^I(2-$C_6H_4SCH_3$)], (I), under very controllable conditions.

Efficient protocols for generating Au—C bonded products are in demand since the optical properties found for such compounds (Fackler, 2002; Gray, 2007) may be applied in opto-electronic devices (LEDs, organic LEDs or photovoltaic cells; Wong & Guo, 2008). Optical properties such as luminescence are enhanced by the heavy gold centre (spin-orbit coupling) attached to a variety of organic molecules such as pyrene (Heng *et al.*, 2007), phenyls, heteroaromatic rings (Wong *et al.*, 2007) and alkynyls (Yam *et al.*, 2003) in mononuclear (King *et al.*, 1992) and in polynuclear complexes (Hong *et al.*, 1994; Rios *et al.*, 2008).



(I)

Compound (I) is the first example of gold(I) attached to a thiomethyl aromatic carbanion. Even though the *ortho* thio unit on the ring could bond to Au^I to produce a four-membered chelate ring, the long Au1···S1 distance of 3.246 (3) Å shows that this does not happen. Connectivity of S to Au of a neighbouring molecule is apparently hindered by the phenyl rings of the phosphine, which obviate any aurophilic interactions [Au···Au = 6.986 (4) Å]. The propeller organization of the phenyl rings on the phosphine lowers the symmetry of the molecule (with no improper rotations), making it chiral.

From what is expected to be a racemic mixture of the product, only one of the two conformational enantiomers is present in the crystal structure (Fig. 1), so the crystalline

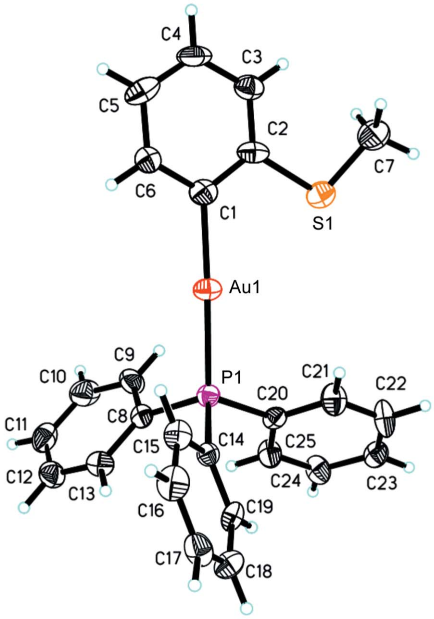


Figure 1
The structure of (I), showing the almost linear P—Au—C arrangement. Displacement ellipsoids are drawn at the 50% probability level.

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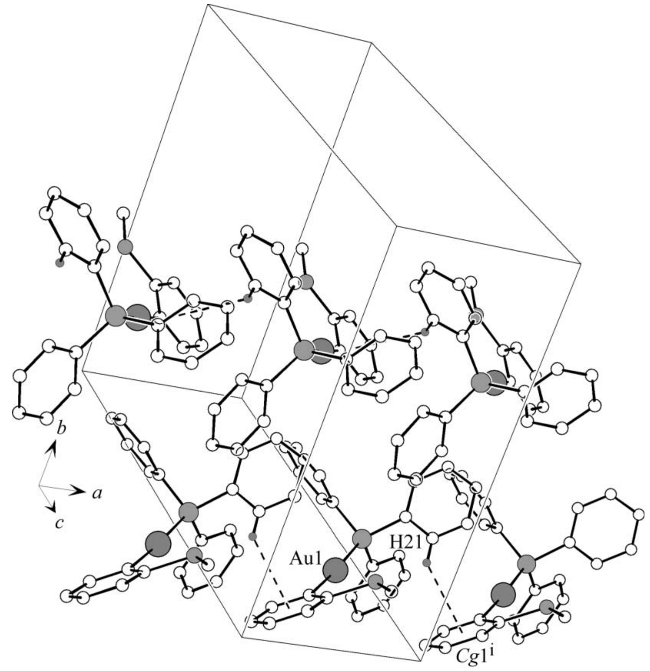

Figure 2
Chain formation in (I), mediated by a weak C—H$\cdots\pi$ contact. $Cg1$ is the centroid of the C1–C6 ring. [Symmetry code: (i) $1 + x, y, z$.]

product is in all likelihood a racemic conglomerate. The chiral space group $P2_12_12_1$ is that which is most frequently observed for enantiopure crystals, according to Jacques *et al.* (1981).

Each mononuclear Au^{I} centre has a linear ligand coordination with geometric parameters inside the remarkably narrow range found in this family of compounds. There are 17 examples in the Cambridge Structural Database (CSD, Version 5.30; Allen, 2002) of gold(I) linearly bonded to a phosphine and to the C atom of an *ortho*-substituted phenyl group, including one with an Au—C π bond; 15 of these report three-dimensional coordinates (Table 1). Their Au—P and Au—C distances are similar to those of the title compound and they also show angular interactions involving phenyl rings (C—H$\cdots\pi$ interactions). 14 are nonchiral and in fact crystallize in centrosymmetric space groups. There is one chiral compound, the dimer [μ_2-1,2-bis(diphenylphosphino)ethane]-[μ_2-2,2′-bis(phenylene)methane]digold(I) (Baukanova *et al.*, 1994), which crystallizes in the space group $P2_1$.

In spite of the presence of four phenyl rings in (I), there are no π–π stacking interactions, but there are angular interactions between C-bound H atoms and the phenyl rings of neighbouring molecules. There is one C—H$\cdots\pi$ contact of note, from C21—H21 to the centroid $Cg1$ of the C1–C6 ring of a neighbouring molecule, with H21$\cdots Cg1^{i}$ = 2.83 Å, C21$\cdots Cg1^{i}$ = 3.584 (9) Å and C21—H21$\cdots Cg1^{i}$ = 137° [symmetry code: (i) $1 + x, y, z$]. The molecules involved in these contacts form a chain parallel to the *a* axis (Fig. 2).

Experimental

To a suspension of (methylthiophenyl)boronic acid, $CH_3SC_6H_4$-$B(OH)_2$ (0.336 g, 0.2 mmol), in propan-2-ol (10 ml), solid $CsCO_3$ (0.0386 g, 0.2 mmol) was added. After a few minutes of stirring, $AuPPh_3Cl$ (0.05 g, 0.1 mmol) was added and a condenser was attached to the reaction flask. The white suspension was refluxed at 333 K for 10 h, after which time the liquid looked clear. Clumps of white solid slowly formed. The propan-2-ol solution was then reduced to dryness under vacuum. The dry residue was rinsed with hexane and extracted with benzene (5 ml). Upon layering the benzene solution with hexane, shiny crystals of (I) grew within a week, with a yield of 90%. The sample used in data collection was mounted on a loop using Paratone oil. ^{1}H NMR ($CDCl_3$): δ 7.70–7.45 [*m*, $P(C_6H_5)_3$], 7.13–7.07 (*m*, C_6H_4), 2.5 (*s*, S—CH_3).

Crystal data

$[Au(C_7H_7S)(C_{18}H_{15}P)]$
$M_r = 582.42$
Orthorhombic, $P2_12_12_1$
$a = 6.986\ (4)$ Å
$b = 15.553\ (9)$ Å
$c = 20.060\ (12)$ Å
$V = 2180\ (2)$ Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 6.93$ mm^{-1}
$T = 110$ K
0.17 × 0.10 × 0.10 mm

Data collection

Bruker APEXII diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2006)
$T_{\min} = 0.391$, $T_{\max} = 0.544$ (expected range = 0.359–0.500)
24159 measured reflections
4680 independent reflections
4396 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.135$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.099$
$S = 1.05$
4680 reflections
254 parameters
9 restraints
H-atom parameters constrained
$\Delta\rho_{\max} = 2.96$ e Å^{-3}
$\Delta\rho_{\min} = -1.35$ e Å^{-3}
Absolute structure: (Flack, 1983), with 2016 Friedel pairs
Flack parameter: −0.003 (11)

Table 1
Main structural features of linear (phosphine)(*ortho*-substituted phenyl)-gold(I) compounds.

Compound	Space group	Au—P	Au—C	P—Au—C
$C_{38}H_{32}Au_2P^{a}$	$P2_1/a$	2.295, 2.297	2.011, 2.062	176.8, 175.9
$C_{30}H_{24}AuOP^{b}$	$P\overline{1}$	2.288	2.040	179.5
$C_{48}H_{38}Au_2OP_2{}^{b}$	$P2_1/c$	2.269, 2.280	2.052, 2.059	174.8, 174.7
$C_{27}H_{35}AuP^{+}\cdot SbF_6{}^{-c}$	$P2_1/n$	2.2643 (10)	2.299 (5), 2.423 (5)†	157.2, 164.9
$C_{30}H_{42}AuP^{d}$	$P\overline{1}$	2.291	2.051	174.5
$C_{24}H_{20}AuP^{e}$	$P\overline{1}$	2.296 (2), 2.295	2.045 (6), 2.054	175.5 (2), 177.6
$C_{37}H_{32}Au_2P_2{}^{e}$	$C2/c$	2.300 (2)	2.07 (2)	175.8 (4)
$C_{50}H_{42}Au_2P_2\cdot CH_2Cl_2{}^{f}$	$P2_1/c$	2.279 (8)	2.05 (2)	174.5 (5)
$C_{30}H_{24}AuP^{g}$	$P\overline{1}$	2.285	2.055	177.1
$C_{53}H_{77}Au_2NP_2{}^{h}$	$C2/c$	2.302 (9), 2.302 (13)	2.053 (9), 2.059 (13)	175.82 (19), 177.93 (22)
$C_{18}H_{32}AuP^{i}$	$P2_1/n$	2.305 (1)	2.055 (6)	177.9 (2)
$C_{44}H_{38}Au_2P_2{}^{i}$	$P\overline{1}$	2.284 (1)	2.044 (4)	174.8 (2)
$C_{39}H_{34}Au_2P_2\cdot 2C_6H_6{}^{f}$	$P2_1$	2.296 (5), 2.296 (4)	2.04 (2), 2.05 (2)	179.0 (5), 168.6 (4)
$C_{13}H_{20}AuN_3P^{+}\cdot C_{24}H_{20}B^{-j}$	$P2_1/n$	2.274 (3)	2.04 (1)	176.5 (5)
$C_{12}H_{17}AuN_3P^{j}$	$P2_1/n$	2.289 (5)	2.040 (2)	170.1 (5)
This work	$P2_12_12_1$	2.293 (2)	2.042 (8)	175.9 (2)

† π side-on gold–phenyl-ring bond. References: (*a*) Bennett *et al.* (2004); (*b*) Baukanova *et al.* (1994); (*c*) Herrero-Gomez *et al.* (2006); (*d*) Partyka *et al.* (2006); (*e*) Hong *et al.* (1994); (*f*) Baukanova *et al.* (1997); (*g*) Osawa *et al.* (2007); (*h*) Kui *et al.* (2006); (*i*) Sladek *et al.* (1995); (*j*) Forward *et al.* (1995).

The difference peak of 2.96 e Å^{-3} is 0.81 Å from the Au1 atom. Rigid-bond restraints on the displacement parameters of atoms C23, C24 and C25 (three restraints), and isotropic behaviour restraints at C24 (six restraints), were applied during refinement. All aromatic H atoms were placed in calculated positions and refined using a riding model [C—H = 0.95 Å and $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C)]. The H atoms on methyl atom C7 were located in a local difference Fourier calculation and refined as riding with a variable torsion angle about the C7—S1 bond [C—H = 0.98 Å and $U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(C7)].

Data collection: *APEX2* (Bruker–Nonius, 2008); cell refinement: *APEX2*; data reduction: *APEX2*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *X-SEED* (Barbour, 2001); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA3184). Services for accessing these data are described at the back of the journal.

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