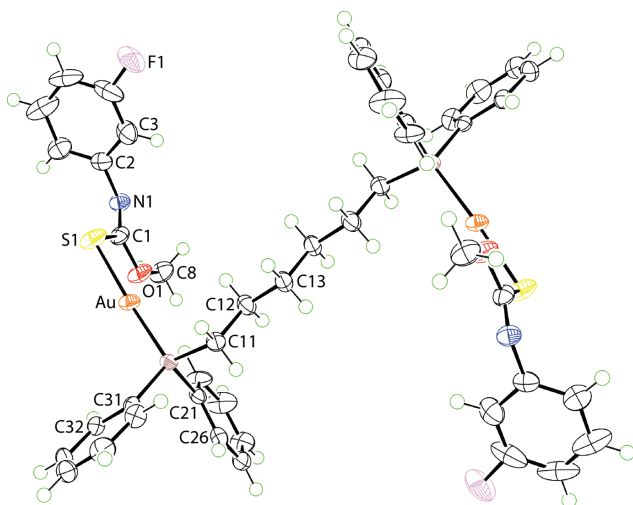


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Crystal structure of $(\mu_2\text{-}1,1'\text{-bis(diphenylphosphino)hexane-}\kappa^2P,P')\text{-bis}[(Z)\text{-}N\text{-(3-fluorophenyl)-}O\text{-methylthiocarbamate-}\kappa S]\text{digold(I)}$, $\text{C}_{46}\text{H}_{46}\text{Au}_2\text{F}_2\text{N}_2\text{O}_2\text{P}_2\text{S}_2$



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Abstract

$\text{C}_{46}\text{H}_{46}\text{Au}_2\text{F}_2\text{N}_2\text{O}_2\text{P}_2\text{S}_2$, triclinic, $P\bar{1}$ (no. 2), $a = 8.2496(3)$ Å, $b = 11.4366(4)$ Å, $c = 12.9504(4)$ Å, $\alpha = 109.171(3)^\circ$, $\beta = 92.496(3)^\circ$, $\gamma = 100.208(3)^\circ$, $V = 1128.98(7)$ Å³, $Z = 1$, $R_{\text{gt}}(F) = 0.0246$, $wR_{\text{ref}}(F^2) = 0.0560$, $T = 100(2)$ K.

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The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

NaOH (Merck; 0.020 g, 0.50 mmol) in water (5 mL) was added to a suspension of $(\text{Ph}_2\text{P}(\text{CH}_2)_6\text{PPh}_2)(\text{AuCl})_2$ (0.230 g,

Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.30 × 0.26 × 0.24 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	6.70 mm ^{−1}
Diffractometer, scan mode:	SuperNova, ω
θ_{max} , completeness:	27.5°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	26035, 5183, 0.063
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 4889
$N(\text{param})_{\text{refined}}$:	273
Programs:	CrysAlis ^{PRO} [1], SHELX [2, 3], WinGX/ORTEP [4]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Au	0.97896(2)	0.25052(2)	0.49788(2)	0.01946(5)
S1	0.98478(13)	0.09912(8)	0.33039(7)	0.0296(2)
P1	0.96417(10)	0.40673(8)	0.65548(6)	0.01542(17)
O1	0.7903(3)	−0.0164(2)	0.43519(17)	0.0279(6)
N1	0.7568(4)	−0.1193(3)	0.2504(2)	0.0218(6)
C1	0.8289(4)	−0.0256(3)	0.3333(2)	0.0209(7)
C2 ^a	0.7898(4)	−0.1212(3)	0.1432(2)	0.0225(7)
C3 ^a	0.7076(5)	−0.0561(3)	0.0922(3)	0.0305(8)
H3 ^a	0.630618	−0.008622	0.128836	0.037*
C4 ^a	0.7395(5)	−0.0614(4)	−0.0129(3)	0.0423(11)
F1 ^a	0.6603(4)	−0.0118(3)	−0.0698(3)	0.0435(11)
C5 ^a	0.8483(6)	−0.1289(4)	−0.0696(3)	0.0419(12)
H5 ^a	0.868862	−0.130630	−0.141690	0.050*
C6 ^a	0.9258(6)	−0.1935(4)	−0.0179(3)	0.0414(11)
H6 ^a	1.002071	−0.241244	−0.055287	0.050*
C7 ^a	0.8978(5)	−0.1922(3)	0.0866(3)	0.0294(8)
H7 ^a	0.952296	−0.239685	0.119604	0.035*
C2 ^b	0.7898(4)	−0.1212(3)	0.1432(2)	0.0225(7)
C3 ^b	0.7076(5)	−0.0561(3)	0.0922(3)	0.0305(8)
H3 ^b	0.630618	−0.008622	0.128836	0.037*
C4 ^b	0.7395(5)	−0.0614(4)	−0.0129(3)	0.0423(11)
H4 ^b	0.683218	−0.016148	−0.047355	0.051*
C5 ^b	0.8483(6)	−0.1289(4)	−0.0696(3)	0.0419(12)
H5 ^b	0.868862	−0.130630	−0.141690	0.050*
C6 ^b	0.9258(6)	−0.1935(4)	−0.0179(3)	0.0414(11)
F1 ^b	0.9943(9)	−0.2583(6)	−0.0855(5)	0.041(2)
C7 ^b	0.8978(5)	−0.1922(3)	0.0866(3)	0.0294(8)
H7 ^b	0.952296	−0.239685	0.119604	0.035*
C8	0.6606(5)	−0.1140(3)	0.4440(3)	0.0302(8)
H8A	0.559975	−0.118793	0.398340	0.045*

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Table 2 (continued)

Atom	x	y	z	U_{iso}^*/U_{eq}
H8B	0.637847	−0.094160	0.520806	0.045*
H8C	0.695654	−0.195324	0.418666	0.045*
C11	0.8457(4)	0.5171(3)	0.6317(2)	0.0196(7)
H11A	0.828846	0.577581	0.703209	0.024*
H11B	0.909014	0.565868	0.590703	0.024*
C12	0.6778(4)	0.4486(3)	0.5666(3)	0.0223(7)
H12A	0.694874	0.380724	0.499705	0.027*
H12B	0.610312	0.408126	0.611733	0.027*
C13	0.5824(4)	0.5348(3)	0.5328(3)	0.0230(7)
H13A	0.563610	0.601951	0.599610	0.028*
H13B	0.650151	0.576076	0.488300	0.028*
C21	0.8579(4)	0.3474(3)	0.7531(2)	0.0175(6)
C22	0.7765(5)	0.2221(3)	0.7213(3)	0.0275(8)
H22	0.780031	0.166404	0.648874	0.033*
C23	0.6897(5)	0.1776(4)	0.7949(3)	0.0359(9)
H23	0.633231	0.091884	0.772611	0.043*
C24	0.6856(5)	0.2579(3)	0.9001(3)	0.0302(8)
H24	0.625145	0.227530	0.950067	0.036*
C25	0.7687(4)	0.3821(3)	0.9335(3)	0.0241(8)
H25	0.767057	0.436433	1.006693	0.029*
C26	0.8551(4)	0.4283(3)	0.8601(2)	0.0192(7)
H26	0.911478	0.514142	0.882797	0.023*
C31	1.1635(4)	0.4955(3)	0.7282(2)	0.0156(6)
C32	1.2690(4)	0.4280(3)	0.7600(2)	0.0195(7)
H32	1.232752	0.339898	0.745266	0.023*
C33	1.4249(4)	0.4873(3)	0.8125(3)	0.0238(7)
H33	1.495443	0.440081	0.833949	0.029*
C34	1.4796(4)	0.6153(3)	0.8343(3)	0.0284(8)
H34	1.587132	0.656399	0.871050	0.034*
C35	1.3773(5)	0.6827(3)	0.8025(3)	0.0294(8)
H35	1.415204	0.770603	0.816973	0.035*
C36	1.2190(4)	0.6244(3)	0.7495(3)	0.0231(7)
H36	1.149321	0.672074	0.727893	0.028*

^aOccupancy: 0.670(6), ^bOccupancy: 0.330(6).

0.25 mmol) in acetonitrile (20 mL), followed by the addition of MeOC(=S)N(H)C₆H₄F-3 [5] (0.093 g, 0.50 mmol) in acetonitrile (20 mL) and stirred for 3 h. The resulting mixture was left for slow evaporation at room temperature, yielding crystals after 3 weeks. Yield: 0.243 g (80%). **M. pt** (Biobase automatic melting point apparatus MP450): 413–414 K. Elemental Analysis for C₄₆H₄₆Au₂F₂N₂O₂P₂S₂ (Leco TruSpec Micro CHN Elemental Analyser): C, 45.40; H, 3.81; N, 2.30%. Found: C, 45.68; H, 3.83; N, 2.15%. **IR** (Bruker Vertex 70v FTIR Spectrophotometer; cm^{−1}): 1578 (s) ν(C=N), 1123 (s) ν(C–O), 1105 (s) ν(C–S). **¹H NMR** (Bruker Ascend 400 MHz NMR spectrometer with chemical shifts relative to tetramethylsilane in CDCl₃ solution at 298 K, ppm): δ 7.60–7.45 (m, br, 20H, Ph₂P), 6.99 (dt, 2H, aryl-H5, ⁴J_{HF} = 7.09 Hz, ³J_{HH} = 7.49 Hz), 6.62–6.57 (m, br, 4H, aryl-H2,6), 6.47–6.43 (m, br, 2H, aryl-H4), 3.88 (s, 6H, OCH₃), 2.33–2.27 (m, br, 4H, PCH₂), 1.51 (s, br, 4H, PCH₂CH₂), 1.42 (s, br, 4H, PCH₂CH₂CH₂). **¹³C{¹H} NMR** (as for ¹H NMR): δ 165.5 (Cq), 163.1 (d, aryl-C3, ¹J_{CF} = 244.43 Hz), 152.8 (d, aryl-C1, ³J_{CF} = 9.69 Hz), 133.2 (d, m-PC₆H₅, ³J_{CP} = 13.20 Hz),

131.7 (d, p-PC₆H₅, ⁴J_{CP} = 1.73 Hz), 130.0 (d, i-PC₆H₅, ¹J_{CP} = 55.77 Hz), 129.8 (d, aryl-C5, ³J_{CF} = 9.17 Hz), 129.2 (d, o-PC₆H₅, ²J_{CP} = 11.21 Hz), 117.9 (d, aryl-C6, ⁴J_{CF} = 2.43 Hz), 109.2 (d, aryl-C2, ²J_{CF} = 22.10 Hz), 109.1 (d, aryl-C4, ²J_{CF} = 21.16 Hz), 55.5 (OCH₃), 30.2 (d, PCH₂CH₂CH₂, ³J_{CP} = 16.31 Hz), 27.9 (d, PCH₂, ¹J_{CP} = 34.92 Hz), 25.4 (d, PCH₂CH₂, ²J_{CP} = 4.19 Hz). **³¹P{¹H} NMR** (as for ¹H NMR but with chemical shift referenced to 85% aqueous H₃PO₄ as the external reference): δ 34.6.

Experimental details

The C-bound H atoms were geometrically placed (C–H = 0.95–0.99 Å) and refined as riding with $U_{iso}(H) = 1.2–1.5U_{eq}(C)$. The maximum and minimum residual electron density peaks of 1.12 and 1.05 eÅ^{−3}, respectively, were located 0.85 and 0.70 Å from the Au atom. The 3-fluorophenyl ring was disordered over two co-planar orientations so the carbon atoms were exactly coincident but, two positions were apparent for the F atom; the latter sites were refined independently. At the conclusion of the refinement, the major component of the disorder had a site occupancy factor of 0.670(6).

Comment

Phosphanegold(I) thiolate molecules/complexes of the basic formula R₃PAu[SC(OR')=NAr] continue to attract attention owing to their biological potential against Gram-positive bacteria [6] and cancer [7]. Further, their ready crystallisation lend these molecules to systematic crystallographic studies [8, 9] and investigations of their solid-state photoluminescence properties [10]. While binuclear analogues are well-known [9, 10], no structure has yet been reported with the biphosphane Ph₂P(CH₂)₆PPh₂ (dpph), featuring a hexyl bridge between the phosphorus donor atoms. In recognition of this, herein, the crystal and molecular structures of (dpph){Au[SC(OMe)=N(C₆H₄F-3)]₂}, (I), are described.

The molecular structure of the binuclear species in (I) is shown in the figure (70% displacement ellipsoids; the minor components of the disordered fluorophenyl rings are omitted; unlabelled atoms are related by the symmetry operation (i) 1 − x, 1 − y, 1 − z) and is disposed about a centre of inversion. The Au atom is coordinated by thiolate-S1 [2.2972(8) Å] and phosphane-P1 [2.2531(8) Å] atoms which define a linear geometry with P1–Au1–S1 = 175.77(3)°. As is usually observed in these molecules [8–10], the thiolate ligand is orientated to place the methoxy-O in close proximity to the gold atom; Au⋯O1 = 2.996(2) Å. The other orientation sometimes observed in R₃PAu[SC(OR')=NAr] results in the formation of an intramolecular Au⋯π interaction [8], for which DFT calculations indicate are slightly more stable, by about 6 kcal/mol, than Au⋯O interactions [11, 12]. The hexyl

bridge adopts an open, all-*trans*, conformation as seen in the values of the P1–C11–C12–C13 and C11–C12–C13–C13ⁱ torsion angles of $-173.2(2)$ and $179.3(3)^\circ$, respectively.

The disorder in the 3-fluorophenyl rings precludes a detailed analysis of the molecular packing of (I). Weak non-covalent interactions are evident in the crystal such as fluorophenyl-C–H...S(thiolate) [C5–H5...S1ⁱⁱ: H5...S1ⁱⁱ = 2.87 Å, C5...S1ⁱⁱ = 3.796(4) Å with angle at H = 165° for (ii) 2–x, –y, –z], phosphane-phenyl-C–H...N(imine) [C32–H32...N1ⁱⁱⁱ: H32...N1ⁱⁱⁱ = 2.56 Å, C32...N1ⁱⁱⁱ = 3.456(5) Å with angle at H32 = 158° for (iii) 2–x, –y, 1–z] along with a number of C–H...π interactions [e.g. C7–H7...Cg2ⁱⁱⁱ: H7...Cg2ⁱⁱⁱ = 2.63 Å with angle at H7 = 149°] which combine to assemble molecules into a three-dimensional architecture.

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References

1. Agilent Technologies. CrysAlis^{PRO}. Agilent Technologies, Santa Clara, CA, USA (2014).
2. Sheldrick, G. M.: A short history of SHELX. *Acta Crystallogr.* **A64** (2008) 112–122.
3. Sheldrick, G. M.: Crystal structure refinement with SHELXL. *Acta Crystallogr.* **C71** (2015) 3–8.
4. Farrugia, L. J.: WinGX and ORTEP for Windows: an update. *J. Appl. Cryst.* **45** (2012) 849–854.
5. Yeo, C. I.; Tan, S. L.; Kwong, H. C.; Tiekink, E. R. T.: [(Z)-N-(3-Fluorophenyl)-O-methylthiocarbamate-κS]-(triphenylphosphane-κP)gold(I): crystal structure, Hirshfeld surface analysis and computational study. *Acta Crystallogr.* **E76** (2020) 1284–1290.
6. Yeo, C. I.; Sim, J.-H.; Khoo, C.-H.; Goh, Z.-J.; Ang, K.-P.; Cheah, Y.-K.; Fairuz, Z. A.; Halim, S. N. B. A.; Ng, S. W.; Seng, H.-L.; Tiekink, E. R. T.: Pathogenic Gram-positive bacteria are highly sensitive to triphenylphosphane-gold(O-alkylthiocarbamates), Ph₃PAu[SC(OR)=N(p-tolyl)] (R = Me, Et and iPr). *Gold Bull.* **46** (2013) 145–152.
7. Ooi, K. K.; Yeo, C. I.; Mahandaran, T.; Ang, K. P.; Akim, A. M.; Cheah, Y.-K.; Seng, H.-L.; Tiekink, E. R. T.: G₂/M cell cycle arrest on HT-29 cancer cells and toxicity assessment of triphenylphosphane-gold(I) carbonimidothioates, Ph₃PAu[SC(OR)=NPh], R = Me, Et, and iPr, during zebrafish development. *J. Inorg. Biochem.* **166** (2017) 173–181.
8. Kuan, F. S.; Ho, S. Y.; Tadbuppa, P. P.; Tiekink, E. R. T.: Electronic and steric control over Au...Au, C–H...O and C–H...π interactions in the crystal structures of mononuclear triarylphosphine-gold(I) carbonimidothioates: R₃PAu[SC(OMe)=NR'] for R = Ph, *o*-tol, *m*-tol or *p*-tol, and R' = Ph, *o*-tol, *m*-tol, *p*-tol or C₆H₄NO₂-4. *CrystEngComm* **10** (2008) 548–564.
9. Ho, S. Y.; Tiekink, E. R. T.: Supramolecular aggregation patterns in the crystal structures of the dinuclear phosphine-gold(I) thiolates, [(Ph₂P(CH₂)₄PPh₂){AuSC(OR)=NC₆H₄Y-4}]₂ for R = Me, Et or iPr and Y = H, NO₂ or Me: the influence on intermolecular interactions exerted by R and Y. *CrystEngComm* **9** (2007) 368–378.
10. Ho, S. Y.; Cheng, E. C.-C.; Tiekink, E. R. T.; Yam, V. W.-W.: Luminescent phosphine-gold(I) thiolates: correlation between crystal structure and photoluminescent properties in [R₃PAu{SC(OMe)=NC₆H₄NO₂-4}] (R = Et, Cy, Ph) and [(Ph₂P-R-PPh₂){AuSC(OMe)=NC₆H₄NO₂-4}]₂ (R = CH₂, (CH₂)₂, (CH₂)₃, (CH₂)₄, Fc). *Inorg. Chem.* **45** (2006) 8165–8174.
11. Yeo, C. I.; Tan, S. L.; Otero-de-la-Roza, A.; Tiekink, E. R. T.: A conformational polymorph of Ph₃PAu[SC(OEt)=NPh] featuring an intramolecular Au...π interaction. *Z. Kristallogr. CM* **231** (2016) 653–661.
12. Yeo, C. I.; Khoo, C.-H.; Chu, W.-C.; Chen, B.-J.; Chu, P.-L.; Sim, J.-H.; Cheah, Y.-K.; Ahmad, J.; Halim, S. N. A.; Seng, H.-L.; Ng, S. W.; Otero-de-la-Roza, A.; Tiekink, E. R. T.: The importance of Au...π(aryl) interactions in the formation of spherical aggregates in binuclear phosphane-gold(I) complexes of a bipodal thiocarbamate dianion: a combined crystallographic and computational study, and anti-microbial activity. *RSC Adv.* **5** (2015) 41401–41411.