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[Au(^{n}BuPPh$_2$){$(Ph_2PS)_3C$}].CH_3CN: an Irregular Three-Coordinate Au^I Complex

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Abstract

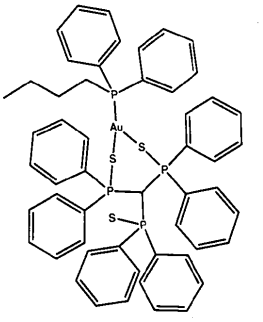
The molecule of [*n*-butyl(diphenyl)phosphine-*P*][tris-(diphenylthiophosphinoyl)methanido-*S*,*S*']gold(I) consists of an *n*-butyldiphenylphosphine ligand coordinated to the Au^I center with a normal Au—P distance [2.275 (4) Å], and a tris(diphenylthiophosphinoyl)methanide ligand coordinated to the Au^I center through two of the S atoms with two strikingly different Au—S distances [2.326 (4) and 2.894 (4) Å]. The Au^I center has T-shaped coordination geometry.

Comment

Our laboratories have been studying the coordination chemistry of gold(I) and silver(I) with phosphines and S ligands (Grim, Sangokoya, Rheingold, McFarlane, Colquhoun & Gilardi, 1991). These studies have provided a better understanding of ligand requirements needed to increase coordination around a gold(I) center.

The ability of gold(I) to sustain coordination numbers greater than two has been known for many years (Khan, Staples, King, Fackler & Winpenny, 1993) and increased coordination of the gold(I) monophosphine cation with S ligands has been observed in a few cases. Tungsten sulfides (Huffman, Roth & Siedle, 1976) and tetrasquarate complexes (Jones, Sheldrick, Fungnes, Gotzfried & Beck, 1981) have also been seen to form distorted T-shaped three-coordinate gold(I) phosphine complexes.

The use of tris(diphenythiophosphinoyl)methanide, $[(C_{12}H_{10}PS)_3C]^-$, (1), has shown it to be a good uninegative tridentate ligand. Reaction with the (^{n}Bu$_3$P)Ag^I cation results in the formation of a four-coordinate tetrahedral complex. Here we report the reaction of (1) with the title gold(I) phosphine cation [Au(^{n}BuPPh$_2$)]$^+$ and the crystal structure of the resulting product, (2). The formation of a four-coordinate tetrahedral complex was anticipated. The $^{31}P\{^1H\}$ NMR data showed the molecule to be fluxional in solution. In order to understand this behavior, a single crystal X-ray diffraction analysis was carried out. The molecular structure of the title compound is shown in Fig. 1.



(2)

The molecule consists of an *n*-butyldiphenylphosphine ligand coordinated to the Au^I center with a normal Au—P distance [Au—P(4) = 2.275 (5) Å], and a tris(diphenylthiophosphinoyl)methanide ligand coordinated to the metal center through atoms S(1) and S(3) with two strikingly different distances [2.326 (4) and 2.894 (4) Å, respectively]. As found in other three-coordinate Au^I complexes (Dávila, Elduque, Grant, Staples & Fackler, 1993), the metal atom has typical distorted T-shaped coordination [P(4)—Au(1)—S(1) = 161.4 (1), P(4)—Au(1)—S(3) = 90.0 (1) and S(1)—Au—S(3) = 104.6 (1)°]. The bonding in this complex is very similar to that in [Au(PPh_3)($SCNEt_2$)], (Wijnhoven, Bosman & Beurskens, 1972) in which a weak Au—S bond (3.01 Å) was also found. Tris(diphenylthiophosphinoyl)methanide is a tridentate ligand and a four-coordinate geometry was anticipated as in the analogous compounds [HgCl{$(Ph_2PS)(Me_2PS)_2C$}] (Grim *et al.*, 1985) and [Ag(*n*-Bu_3P){$(Ph_2PS)_3C$}] (Grim *et al.*, 1991). The title molecule is only three-coordinate. A combination of steric and electronic effects in the ligand may prevent the formation of a four-coordinate Au complex. To date, there are are no reports of four-coordinate Au^I complexes containing three Au—S bonds and one Au—P bond.

The coordination of four S atoms around a gold(I) center, or of three S atoms and a phosphine, has not yet been observed. The ligand (1) has the ability to form tetrahedral complexes, as the silver(I) complex of Grim *et al.* (1991) shows, but this was not observed with the [Au(^{n}BuPPh$_2$)]$^+$ cation. The $^{31}P\{^1H\}$ NMR spectrum of this complex, in $CDCl_3$, shows a broad singlet for the [$(Ph_2PS)_3C$] ligand (δ =

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43.5 p.p.m.) and a signal for (^{n}BuPPh$_2$) (δ = 33.4 p.p.m.) (even at 193 K), suggesting that fluxionality exists.

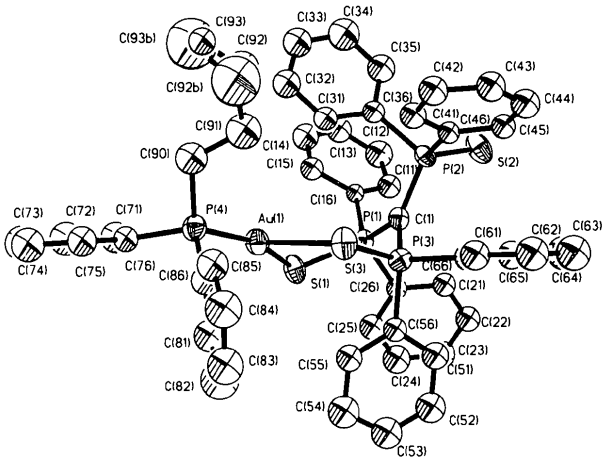

Fig. 1. A diagram of the molecular structure showing 50% probability ellipsoids.

Experimental

Crystal data

[Au{($C_{12}H_{10}PS)_3C$}-($C_{16}H_{19}P$)].CH_3CN	Mo $K\alpha$ radiation
M_r = 1144	λ = 0.71073 Å
Orthorhombic	Cell parameters from 25 reflections
$P2_12_12_1$	θ = 22–29°
a = 14.934 (2) Å	μ = 3.23 mm^{-1}
b = 27.355 (5) Å	T = 293 K
c = 12.147 (3) Å	Block
V = 4962 (2) Å^3	0.5 × 0.4 × 0.4 mm
Z = 4	Colorless
D_x = 1.53 Mg m^{-3}	Crystal source: recrystallized from CH_3CN–MeOH

Data collection

Nicolet *R3m/E* diffractometer	R_{int} = 0.038
ω scans	θ_{max} = 22.5°
Absorption correction: empirical	h = 0 → 17
T_{min} = 0.340, T_{max} = 0.663	k = 0 → 30
3670 measured reflections	l = 0 → 14
3345 independent reflections	3 standard reflections monitored every 97 reflections
2656 observed reflections [$F_o^2 > 3\sigma(F_o^2)$]	intensity variation: <1%

Refinement

Refinement on F	$(\Delta/\sigma)_{max}$ = 0.012
R = 0.0418	$\Delta\rho_{max}$ = 0.56 e Å^{-3}
wR = 0.0440	$\Delta\rho_{min}$ = −0.54 e Å^{-3}
S = 1.008	Extinction correction: none
2656 reflections	Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)
310 parameters	
H-atom parameters not refined	
$w = 1/[\sigma^2(F_o) + 0.00150(F_o)^2]$	

Table 1. *Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters* (Å^2)

U_{iso} for phenyl and solvent atoms; $U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$ for Au, P, S and C(1).

	x	y	z	U_{iso}/U_{eq}
Au(1)	0.5085 (1)	0.6974 (1)	0.9455 (1)	0.043 (1)
P(1)	0.3946 (2)	0.6101 (1)	0.7682 (3)	0.030 (1)
P(2)	0.5350 (2)	0.6104 (1)	0.5864 (3)	0.031 (1)
P(3)	0.5831 (2)	0.5793 (1)	0.8258 (3)	0.033 (1)
P(4)	0.6040 (2)	0.7513 (1)	1.0263 (3)	0.038 (1)
S(1)	0.3808 (2)	0.6517 (2)	0.9075 (3)	0.043 (1)
S(2)	0.4792 (3)	0.5681 (2)	0.4731 (3)	0.055 (2)
S(3)	0.6558 (3)	0.6329 (2)	0.8918 (4)	0.045 (1)
C(1)	0.5038 (9)	0.5976 (4)	0.7236 (10)	0.031 (4)
C(11)	0.2825 (9)	0.6150 (5)	0.5846 (12)	0.044 (4)
C(12)	0.2250 (11)	0.6411 (6)	0.5089 (15)	0.064 (5)
C(13)	0.2182 (10)	0.6907 (5)	0.5137 (13)	0.053 (4)
C(14)	0.2625 (11)	0.7163 (6)	0.5942 (14)	0.058 (5)
C(15)	0.3159 (9)	0.6923 (5)	0.6704 (13)	0.043 (4)
C(16)	0.3271 (8)	0.6417 (4)	0.6640 (11)	0.026 (3)
C(21)	0.3408 (10)	0.5161 (5)	0.7241 (12)	0.042 (4)
C(22)	0.2918 (10)	0.4734 (6)	0.7403 (13)	0.048 (4)
C(23)	0.2283 (11)	0.4721 (6)	0.8231 (14)	0.057 (5)
C(24)	0.2199 (11)	0.5087 (6)	0.8931 (15)	0.064 (5)
C(25)	0.2704 (10)	0.5511 (5)	0.8795 (13)	0.048 (4)
C(26)	0.3315 (9)	0.5542 (5)	0.7923 (12)	0.033 (3)
C(31)	0.5250 (9)	0.7097 (5)	0.6411 (12)	0.040 (4)
C(32)	0.5148 (11)	0.7593 (5)	0.6222 (13)	0.054 (4)
C(33)	0.4906 (11)	0.7740 (6)	0.5195 (13)	0.060 (4)
C(34)	0.4804 (11)	0.7412 (6)	0.4367 (16)	0.075 (5)
C(35)	0.4885 (9)	0.6922 (5)	0.4553 (13)	0.056 (4)
C(36)	0.5132 (8)	0.6749 (4)	0.5604 (11)	0.036 (3)
C(41)	0.7100 (10)	0.6461 (5)	0.6092 (13)	0.045 (4)
C(42)	0.8039 (10)	0.6460 (6)	0.5879 (13)	0.049 (4)
C(43)	0.8397 (10)	0.6075 (5)	0.5301 (13)	0.050 (4)
C(44)	0.7870 (10)	0.5714 (6)	0.4899 (14)	0.051 (4)
C(45)	0.6959 (9)	0.5718 (5)	0.5096 (12)	0.038 (4)
C(46)	0.6553 (8)	0.6087 (5)	0.5695 (12)	0.031 (3)
C(51)	0.4937 (10)	0.4983 (5)	0.9202 (12)	0.049 (4)
C(52)	0.4531 (11)	0.4727 (6)	1.0068 (14)	0.062 (5)
C(53)	0.4441 (12)	0.4948 (6)	1.1040 (16)	0.066 (5)
C(54)	0.4736 (11)	0.5417 (6)	1.1273 (16)	0.067 (5)
C(55)	0.5173 (9)	0.5668 (5)	1.0378 (12)	0.045 (4)
C(56)	0.5251 (8)	0.5455 (5)	0.9343 (12)	0.037 (3)
C(61)	0.7475 (10)	0.5351 (6)	0.7915 (13)	0.051 (4)
C(62)	0.8034 (12)	0.4981 (6)	0.7455 (15)	0.062 (5)
C(63)	0.7663 (12)	0.4644 (7)	0.6790 (16)	0.071 (5)
C(64)	0.6805 (12)	0.4628 (7)	0.6515 (16)	0.070 (5)
C(65)	0.6245 (11)	0.4976 (5)	0.6955 (13)	0.050 (4)
C(66)	0.6558 (10)	0.5327 (5)	0.7653 (13)	0.046 (4)
C(71)	0.4614 (11)	0.8095 (6)	1.0985 (15)	0.061 (5)
C(72)	0.4243 (13)	0.8485 (7)	1.1530 (16)	0.074 (6)
C(73)	0.4751 (13)	0.8761 (7)	1.2248 (17)	0.079 (6)
C(74)	0.5623 (12)	0.8655 (7)	1.2383 (16)	0.069 (5)
C(75)	0.6008 (11)	0.8265 (6)	1.1785 (14)	0.052 (4)
C(76)	0.5516 (9)	0.7977 (5)	1.1119 (12)	0.039 (4)
C(81)	0.6379 (11)	0.6869 (6)	1.1954 (14)	0.058 (5)
C(82)	0.6937 (14)	0.6592 (7)	1.2660 (18)	0.085 (6)
C(83)	0.7843 (12)	0.6636 (6)	1.2571 (16)	0.069 (5)
C(84)	0.8218 (12)	0.6909 (6)	1.1823 (15)	0.071 (5)
C(85)	0.7686 (11)	0.7184 (6)	1.1121 (15)	0.055 (5)
C(86)	0.6769 (10)	0.7170 (5)	1.1209 (13)	0.045 (4)
C(90)	0.6748 (11)	0.7871 (6)	0.9351 (15)	0.061 (5)
C(91)	0.7228 (12)	0.7621 (6)	0.8452 (15)	0.074 (6)
C(92)	0.7587 (23)	0.7937 (12)	0.7559 (32)	0.071 (11)
C(92*b*)	0.8171 (35)	0.7898 (17)	0.8080 (48)	0.136 (21)
C(93)	0.8330 (18)	0.8311 (10)	0.7887 (25)	0.039 (8)

C(93*b*)	0.7778 (33)	0.8403 (19)	0.7817 (46)	0.146 (22)
N(1)	0.9722 (19)	0.1192 (10)	0.2453 (25)	0.203 (12)
C(2*s*)	0.9691 (20)	0.1040 (10)	0.3385 (27)	0.146 (11)
C(1*s*)	0.9681 (27)	0.0814 (12)	0.4504 (29)	0.261 (21)

Table 2. *Selected geometric parameters* (Å, °)

Au(1)—P(4)	2.275 (4)	P(1)—S(1)	2.051 (6)
Au(1)—S(3)	2.894 (4)	P(1)—C(16)	1.835 (13)
P(1)—C(1)	1.753 (14)	P(2)—S(2)	1.982 (5)
P(1)—C(26)	1.818 (13)	P(2)—C(36)	1.823 (13)
P(2)—C(1)	1.765 (13)	P(3)—S(3)	1.993 (5)
P(2)—C(46)	1.809 (12)	P(3)—C(56)	1.829 (14)
P(3)—C(1)	1.787 (13)	P(4)—C(76)	1.818 (15)
P(3)—C(66)	1.830 (16)	P(4)—C(90)	1.818 (17)
P(4)—C(86)	1.840 (16)	C(2*s*)—C(1*s*)	1.494 (47)
Au(1)—S(1)	2.326 (4)	N(1)—C(2*s*)	1.206 (44)
P(4)—Au(1)—S(1)	161.4 (1)	C(1)—P(3)—C(56)	109.2 (6)
S(1)—Au(1)—S(3)	104.6 (1)	C(1)—P(3)—C(66)	108.0 (7)
S(1)—P(1)—C(16)	104.6 (4)	Au(1)—P(4)—C(76)	115.4 (5)
S(1)—P(1)—C(26)	106.3 (5)	C(76)—P(4)—C(86)	104.7 (7)
C(16)—P(1)—C(26)	102.9 (6)	C(76)—P(4)—C(90)	102.9 (7)
S(2)—P(2)—C(36)	111.7 (5)	Au(1)—S(1)—P(1)	112.3 (2)
S(2)—P(2)—C(46)	108.9 (5)	P(1)—C(1)—P(2)	119.9 (7)
C(36)—P(2)—C(46)	100.5 (6)	P(2)—C(1)—P(3)	122.4 (8)
S(3)—P(3)—C(56)	109.9 (5)	P(1)—C(16)—C(11)	119.8 (10)
S(3)—P(3)—C(66)	110.6 (5)	P(1)—C(26)—C(25)	120.7 (10)
C(56)—P(3)—C(66)	102.6 (7)	P(2)—C(36)—C(35)	121.9 (10)
Au(1)—P(4)—C(86)	108.0 (5)	P(2)—C(46)—C(45)	120.9 (10)
Au(1)—P(4)—C(90)	116.8 (6)	P(3)—C(56)—C(55)	118.6 (10)
C(76)—P(4)—C(90)	108.1 (7)	P(3)—C(66)—C(65)	122.4 (12)
Au(1)—S(3)—P(3)	97.2 (2)	P(4)—C(76)—C(75)	121.1 (11)
P(1)—C(1)—P(3)	117.2 (7)	P(4)—C(86)—C(85)	121.8 (12)
P(1)—C(16)—C(15)	119.7 (10)	P(4)—C(90)—C(91)	119.0 (12)
P(4)—Au(1)—S(3)	90.9 (1)	P(1)—C(26)—C(21)	120.0 (11)
S(1)—P(1)—C(1)	117.2 (4)	P(2)—C(36)—C(31)	121.5 (10)
C(1)—P(1)—C(16)	113.0 (6)	P(2)—C(46)—C(41)	121.6 (10)
C(1)—P(1)—C(26)	111.6 (6)	P(3)—C(56)—C(51)	122.9 (11)
S(2)—P(2)—C(1)	115.4 (5)	P(3)—C(66)—C(61)	117.0 (12)
C(1)—P(2)—C(36)	107.9 (6)	P(4)—C(76)—C(71)	120.7 (12)
C(1)—P(2)—C(46)	111.4 (7)	P(4)—C(86)—C(81)	118.2 (12)
S(3)—P(3)—C(1)	115.8 (4)	N(1)—C(2*s*)—C(1*s*)	175.4 (31)

A single crystal was mounted in a random orientation on a glass fiber with epoxy. The initial unit cell and orientation matrix were obtained from a rotation photograph. Orthorhombic symmetry was suggested on the basis of interaxial angles and confirmed by a Delaunay reduction and axial photographs. Backgrounds were estimated from a 96-step peak profile. All data processing, crystal solution and refinement were performed on a Data General Eclipse S140 mini computer using *SHELXTL* crystallographic software (Sheldrick, 1985). The space group was uniquely determined by the systematic absences. The position of the Au atom was determined by direct methods. All remaining non-H atoms were obtained by subsequent difference Fourier synthesis maps. The positions of H atoms on the phenyl rings were calculated with fixed C—H distances of 0.96 Å and refined with fixed temperature factors of 0.08 $Å^2$; their contributions were included in the structure-factor calculations. Au, P and S atoms, and one C atom were refined anisotropically, while the remaining atoms were refined isotropically. The butyl group was found to be disordered in the last two C atoms. These atoms were refined at 50% occupancy. A molecule of CH_3CN was found in the lattice.

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Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: ST1090). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Dávila, R. M., Elduque, A. E., Grant, T., Staples, R. J. & Fackler, J. P. Jr (1993). *Inorg. Chem.* **43**, 1749–1755.

Grim, S. O., Sangokoya, S. A., Rheingold, A. L., McFarlane, W., Colquhoun, I. J. & Gilardi, R. D. (1991). *Inorg. Chem.* **30**, 2519–2522.

Grim, S. O., Smith, P. H., Nittolo, S., Ammon, H. L., Satek, L. C., Sangokoya, S. A., Khanna, R. K., Colquhoun, I. J., McFarlane, W. & Holden, J. R. (1985). *Inorg. Chem.* **24**, 2889–2895.

Huffman, J. C., Roth, R. S. & Siedle, A. R. (1976). *J. Am. Chem. Soc.* **98**, 4340–4341.

Jones, P. G., Sheldrick, G. M., Fungnes, A., Gotzfried, F. & Beck, W. (1981). *Chem. Ber.* **114**, 1413–1417.

Khan, M. N. I., Staples, R. J., King, C., Fackler, J. P. Jr & Winpenny, R. E. P. (1993). *Inorg. Chem.* **32**, 5800–5807.

Sheldrick, G. M. (1985). *SHELXTL User's Manual.* Revision 5.1. Nicolet XRD Corporation, Madison, Wisconsin, USA.

Wijnhoven, J. G., Bosman, J. H. & Beurskens, P. T. (1972). *J. Cryst. Mol. Struct.* **2**, 7–9.

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Co-Crystallized Bis(μ-*tert*-butylphosphido)-bis(di-*tert*-butylgallium) and Tetra-*tert*-butylcyclotetraphosphane

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Abstract

Crystals of the title compound $[Ga_2(C_4H_9)_4(C_4H_{10}P)_2].(C_{16}H_{36}P_4)$ (1) consist of the two independent neutral molecules $[Ga\{\mu\text{-}PH(^tBu)\}^tBu_2]_2$ (1*a*) and $[(P^tBu)_4]$ (1*b*). Both molecules are situated on a crystallographically imposed mirror plane and their idealized molecular point group symmetries are 2/*m* (1*a*) and $\bar{4}2m$ (1*b*). (1*a*) is the *anti* isomer of a phosphido-bridged Ga dimer. It contains an almost planar Ga_2P_2 ring [P(1)—Ga—P(2)—Ga^i 0.90 (7)°] with Ga—P bond lengths of 2.466 (1) and 2.472 (1) Å. The coordination about both the Ga and P atoms is distorted tetrahedral, with much stronger distortion about P than Ga. (1*b*) posseses a non-planar P_4 ring [$P(4^i)$—P(3)—P(4)—P(5)

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