

S = 1.150
 1282 reflections
 166 parameters
 All H-atom parameters
 refined
 $w = 1/[\sigma^2(F_o^2) + (0.0208P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$

Extinction correction: none
 Atomic scattering factors
 from *International Tables
 for Crystallography* (1992,
 Vol. C, Tables 4.2.6.8 and
 6.1.1.4)

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Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i \cdot a_j$$

	x	y	z	U_{eq}
Cd1	0	0	0	0.0323 (3)
N1	0.1754 (11)	0.0787 (6)	0.1945 (7)	0.033 (2)
C1	0.3585 (17)	0.0771 (8)	0.2334 (10)	0.037 (3)
O1	0.4664 (10)	0.0489 (5)	0.1638 (7)	0.047 (2)
C2	0.4229 (16)	0.1103 (8)	0.3735 (9)	0.033 (3)
C3	0.5954 (16)	0.1146 (10)	0.4475 (12)	0.041 (3)
C4	0.6182 (19)	0.1448 (9)	0.5751 (12)	0.044 (4)
C5	0.4641 (20)	0.1731 (10)	0.6273 (10)	0.044 (3)
C6	0.2932 (18)	0.1696 (9)	0.5564 (11)	0.040 (3)
C7	0.2752 (15)	0.1384 (8)	0.4279 (9)	0.026 (3)
S1	0.0748 (4)	0.1177 (2)	0.3102 (2)	0.0361 (8)
O2	−0.0158 (11)	0.2137 (5)	0.2777 (7)	0.053 (2)
O3	−0.0354 (10)	0.0392 (5)	0.3493 (7)	0.052 (2)
N2	−0.1952 (16)	−0.0860 (9)	0.1122 (11)	0.050 (3)
N3	0.2147 (17)	−0.1313 (8)	0.0250 (12)	0.058 (3)

Table 2. Selected geometric parameters (Å, °)

Cd1—N2	2.324 (11)	Cd1—N1	2.423 (8)
Cd1—N3	2.338 (11)		
N2—Cd1—N3	93.6 (4)	N3—Cd1—N1	88.5 (4)
N2—Cd1—N1	94.6 (3)		

Overall quality of the sample was checked by rotation photography. Lattice parameters were checked by normal-beam oscillation photography and Lorentz–polarization and decay corrections were applied (Sheldrick, 1991)

Saccharinate H atoms were found in difference maps, ammine H atoms were found in a local slant Fourier. The ammine H atoms were constrained to have a common isotropic displacement parameter. Anisotropic displacement parameters were used for all non-H atoms. Refinement was by full-matrix least squares.

Data collection: *CAD-4 PC* (Enraf–Nonius, 1993). Cell refinement: *CAD-4 PC*. Data reduction: *SHELXTL-Plus* (Sheldrick, 1991). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus*. Software used to prepare material for publication: *SHELXL93*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NA1152). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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(Methyldiphenylphosphine)(trimethylsiloxy)gold(I)

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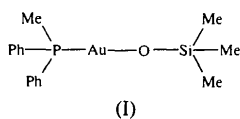
Abstract

Crystals of the title compound, [Au(C₃H₉O_{Si})(C₁₃H₁₃-P)], are composed of monomeric molecules with a nearly linear O—Au—P axis. The molecules are ordered in strings with these O—Au—P axes parallel. The steric bulk of the phosphine ligand and the Me₃SiO group prevent any intermolecular Au···Au contacts. The highly polar Au—O bond results in a short Au—P distance.

Comment

Silicate minerals of Cu and Ag are rare, and it was only with modern sophisticated synthetic methods that metal-rich silicates of the lighter coinage metals could be established (Jansen, 1987). For Au, however, no well defined silicates have been detected, neither for the standard oxidation states I or III, nor for the more unusual II or V (Schmidbaur & Dash, 1982). With the aid of phosphine donor ligands at gold(I) centres and with alkylsilanols as pseudo-silicate components, the first examples of complex molecules with a discrete

Au—O—Si bond system could be synthesized and characterized by analytical and spectroscopic data, as well as by a screening of the chemical reactivity (Schmidbaur & Shiotani, 1970). No structural data have been available to date; therefore, the present study of the title compound, (I), was undertaken to provide information on the molecular geometry of such species.



Many gold(I) complexes show very unusual supra-molecular structural chemistry in the solid state, based on non-classical intermolecular $\text{Au}^I \cdots \text{Au}^I$ interactions with short contacts of *ca* 3.0 Å (Schmidbaur, 1990, 1992, 1993). The stabilization of systems with this type of bonding is particularly strong in main group element-centered polynuclear species with intramolecular $\text{Au}^I \cdots \text{Au}^I$ contacts (Scherbaum, Grohmann, Müller & Schmidbaur, 1989; Grohmann, Riede & Schmidbaur, 1990; Zeller, Beruda, Kolb, Bissinger, Riede & Schmidbaur, 1991), but is also observed for mononuclear compounds. Through intermolecular $\text{Au}^I \cdots \text{Au}^I$ contacts, dimers or chains are formed in the crystal (Schmidbaur & Aly, 1979; Dyson, Parish, McAuliffe, Pritchard, Fields & Beagley, 1989; Schmidbaur, Aly, Weidenhiller, Steigelmann & Müller, 1989; Schmidbaur, Weidenhiller, Steigelmann & Müller, 1990; Stützer, Bissinger & Schmidbaur, 1992). The formation and the strength of the $\text{Au} \cdots \text{Au}$ interactions is influenced by the electronic effects of the substituents *L* and *X* at the Au atom on one hand, and by steric effects on the other. From their reactivity pattern, the gold silyloxides are known to have a highly polar Au—O bond, which should enhance $\text{Au} \cdots \text{Au}$ interaction.

The title compound, (I), is obtained from the reaction of $(\text{MePh}_2\text{P})\text{AuCl}$ with Me_3SiONa in dichloromethane (72% yield, colourless rod-like crystals, which decompose upon heating and when exposed to daylight to produce a gold mirror). Single crystals from *n*-hexane are composed of monomeric molecules $\text{MePh}_2\text{P—Au—OSiMe}_3$ (Fig. 1), which are aligned in a parallel fashion (Fig. 2).

The O—Au—P axis deviates only slightly from linearity [angle $177.9(2)^\circ$]. The highly polar Au—O bond is long [$1.986(4)$ Å], but the Au—P bond of only $2.202(1)$ Å is very short. Other compounds of the type $\text{R}_3\text{P—Au—X}$ have Au—P distances between 2.235 and 2.290 Å (Jones, 1981). The Si—O—Au angle [$128.0(3)^\circ$] is significantly smaller than the reference angle in hexamethyldisiloxane (148° ; Elschenbroich & Salzer, 1989) and that in many heterosiloxanes (metal silyloxides). As this angle is obviously very flexible, the molecular structure appears to be largely determined by packing forces.

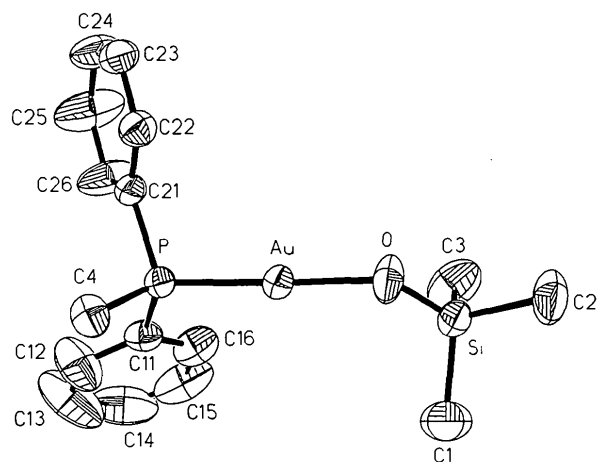


Fig. 1. An ORTEP (Johnson, 1976) view of the molecule showing the numbering scheme. Atoms are shown with displacement ellipsoids drawn at the 50% probability level. For clarity, H atoms have been omitted.

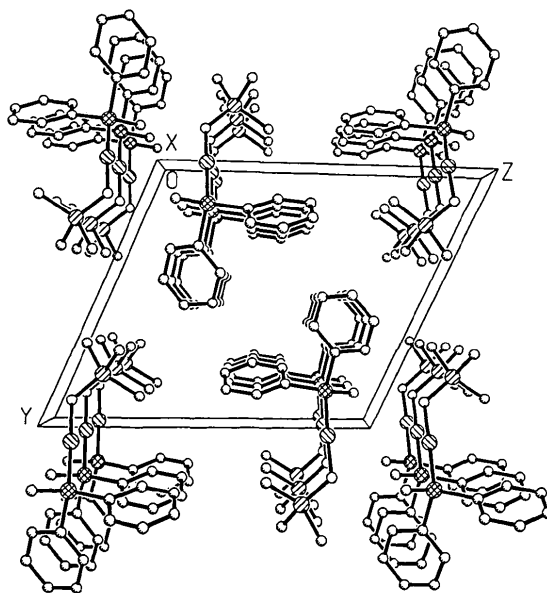


Fig. 2. Parallel arrangement of the molecules in the unit cell.

There are no short intermolecular $\text{Au} \cdots \text{Au}$ contacts between molecules of the same or neighbouring strings as a result of steric repulsion between the bulky substituents. The Au atoms are separated by 4.059 (1) and 6.190 (1) Å. This is perhaps not unexpected, as most tertiary phosphine gold halides with larger PR_3 groups and branched anions are monomeric in the crystal state (Puddephatt, 1978). Chain formation or dimerization *via* $\text{Au} \cdots \text{Au}$ contacts is observed, however, for sterically less demanding tertiary and particularly secondary and primary phosphine complexes.

Experimental

The title compound was prepared by the reaction of (MePh₂P)AuCl with Me₃SiONa. Crystals were obtained by recrystallization from *n*-hexane.

Crystal data

[Au(C₃H₉OSi)(C₁₃H₁₃P)]

$M_r = 486.38$

Triclinic

$P\bar{1}$

$a = 6.190(1) \text{ \AA}$

$b = 12.278(1) \text{ \AA}$

$c = 14.110(1) \text{ \AA}$

$\alpha = 110.79(1)^\circ$

$\beta = 99.18(1)^\circ$

$\gamma = 103.87(1)^\circ$

$V = 937.3 \text{ \AA}^3$

$Z = 2$

$D_x = 1.723 \text{ Mg m}^{-3}$

Data collection

Enraf-Nonius CAD-4 diffractometer

θ - θ scans

Absorption correction: ψ scan

$T_{\min} = 0.477$, $T_{\max} = 0.999$

4056 measured reflections

3741 independent reflections

3202 observed reflections

$[F > 4\sigma(F)]$

Refinement

Refinement on F

$R = 0.0277$

$wR = 0.0303$

$S = 1.24$

3202 reflections

181 parameters

$w = 1/\sigma^2(F)$

$(\Delta/\sigma)_{\max} = 0.001$

Mo $K\alpha$ radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 15 reflections

$\theta = 13\text{--}17^\circ$

$\mu = 7.97 \text{ mm}^{-1}$

$T = 296 \text{ K}$

Needle

$0.50 \times 0.22 \times 0.10 \text{ mm}$

Colourless

$R_{\text{int}} = 0.042$

$\theta_{\max} = 27^\circ$

$h = -7 \rightarrow 7$

$k = -15 \rightarrow 15$

$l = 0 \rightarrow 17$

3 standard reflections monitored every 100 reflections

intensity decay: 25.9%

$\Delta\rho_{\max} = 1.08 \text{ e \AA}^{-3}$

$\Delta\rho_{\min} = -1.12 \text{ e \AA}^{-3}$

Extinction correction: none

Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

$$U_{\text{eq}} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^* \cdot \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Au	0.09328 (4)	0.00800 (2)	0.14749 (2)	0.048 (1)
P	0.4171 (2)	0.1634 (1)	0.2086 (1)	0.042 (1)
O	-0.2037 (8)	-0.1293 (4)	0.0892 (4)	0.02 (1)
Si	-0.3086 (3)	-0.2212 (2)	0.1406 (1)	0.048 (1)
C1	-0.124 (2)	-0.3112 (8)	0.1606 (8)	0.086 (7)
C2	-0.588 (1)	-0.3312 (7)	0.0475 (7)	0.079 (5)
C3	-0.356 (2)	-0.1401 (9)	0.2687 (7)	0.102 (8)
C4	0.596 (1)	0.1526 (6)	0.1189 (5)	0.055 (4)
C11	0.598 (1)	0.1840 (6)	0.3313 (5)	0.051 (4)
C12	0.834 (1)	0.238 (1)	0.3590 (7)	0.095 (5)
C13	0.967 (2)	0.254 (1)	0.4541 (9)	0.142 (8)
C14	0.869 (3)	0.216 (1)	0.5199 (9)	0.123 (8)
C15	0.640 (3)	0.1599 (9)	0.4950 (7)	0.103 (8)
C16	0.503 (2)	0.1444 (7)	0.3999 (6)	0.073 (6)
C21	0.3623 (9)	0.3098 (5)	0.2354 (5)	0.043 (3)

C22	0.222 (1)	0.3213 (6)	0.1562 (5)	0.050 (4)
C23	0.167 (1)	0.4295 (6)	0.1738 (6)	0.059 (4)
C24	0.252 (1)	0.5234 (6)	0.2692 (6)	0.075 (5)
C25	0.390 (2)	0.5139 (8)	0.3481 (7)	0.121 (8)
C26	0.446 (2)	0.4065 (7)	0.3325 (7)	0.093 (7)

Table 2. Selected geometric parameters (\AA , $^\circ$)

Au—P	2.202 (1)	Si—O	1.613 (6)
Au—O	1.986 (4)		
O—Au—P	177.9 (2)	Au—O—Si	128.0 (3)

H atoms were calculated and allowed to ride on the corresponding C atoms with fixed isotropic displacement parameters ($U_{\text{iso}} = 0.10 \text{ \AA}^2$).

Data collection: *CAD-4 Software* (Enraf-Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *SDP* (Enraf-Nonius, 1988). Program(s) used to solve structure: *SHELXTL-Plus* (Sheldrick, 1989). Program(s) used to refine structure: *SHELXTL-Plus*. Molecular graphics: *ORTEPII* (Johnson, 1976).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: JZ1043). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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