

($2.2 \geq \Delta\rho \geq -2.0$). Calculations performed on the DEC-10 computer at the Edvard Kardelj University, Ljubljana, with *SHELX76* (Sheldrick, 1976). Interatomic distances and angles calculated using the *XRAY* system of crystallographic programs (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). Atomic scattering factors for neutral atoms from Cromer & Mann (1968) and values of f' and f'' for the anomalous-dispersion correction from Cromer & Liberman (1970).

Discussion. The positional and thermal parameters are listed in Table 1; * equivalent isotropic thermal parameters are given for Bi and I atoms and isotropic thermal parameters for N and C atoms. The projection of the structure along **b** is shown in Fig. 1. The interatomic distances and angles are given in Table 2.

The crystal structure consists of diethylammonium cations and binuclear $[\text{Bi}_2\text{I}_9]^{3-}$ anions with face-sharing octahedra. The Bi—I(terminal) distances are in the range 2.934 (4)–3.032 (3) Å, the Bi—I(bridging) distances in the range 3.169 (3)–3.277 (3) Å. The $[\text{Bi}_2\text{X}_9]^{3-}$ species ($X = \text{Cl}, \text{Br}, \text{I}$) seem to be very stable. They are present in many crystal structures with large

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43636 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

cations (Lazarini, 1985, and references cited therein). These compounds usually crystallize from solutions with a wide Bi:cation ratio.

The bond lengths and angles within the $[\text{NH}_2(\text{C}_2\text{H}_5)_2]^+$ cations are determined with lower accuracy, but they are in agreement with the values found in related compounds. Contacts between I atoms of different anions and between I and N atoms slightly shorter than the sum of van der Waals radii (4.30 and 3.65 Å respectively) are present (Table 2).

An isomorphous bromine compound also exists (Lazarini, 1985).

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The Structure of Tetrachlorobis- μ -[dimethylenediphenylphosphato(V)- C',C']-digold(III) Dihydrate, $[\text{Au}(\text{CH}_2)_2\text{P}(\text{C}_6\text{H}_5)_2]_2\text{Cl}_4 \cdot 2\text{H}_2\text{O}$, an Organometallic Dinuclear Gold(III) Ylide Complex Containing Chloride Ligands

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Abstract. $[\text{Au}_2\text{Cl}_4\{\text{P}(\text{CH}_2)_2(\text{C}_6\text{H}_5)_2\}_2] \cdot 2\text{H}_2\text{O}$, $M_r = 998.3$, triclinic, $P\bar{1}$, $a = 11.927$ (7), $b = 8.282$ (4), $c = 8.829$ (6) Å, $\alpha = 82.75$ (4), $\beta = 106.67$ (5), $\gamma = 100.24$ (4)°, $V = 819.5$ (8) Å³, $Z = 1$, $D_x = 2.02$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 9.61$ mm⁻¹, $F(000) = 472$, $T = 298$ K. Convergence to final conventional R values of $R = 0.0637$ and $wR = 0.0666$

was obtained using 139 variable parameters and 1651 reflections with $F_o^2 > 3\sigma(F_o^2)$. The structure consists of discrete dinuclear gold(III) ylide dimers containing four-coordinate gold centers with *trans* chloride ligands. The Au atoms have square-planar coordination geometries and are symmetrically bridged by the ylide anion ligands. The unit cell consists of one complete centrosymmetric dimer and two molecules of water. The eight-membered heterocyclic ring of the complex is in a chair conformation, with the metal centers separated by a distance of 3.087 (2) Å.

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Introduction. Our interest in the structures and reactivities of dinuclear gold ylide complexes has led to the preparation and characterization of several dinuclear gold complexes containing a variety of halide and alkyl halide ligands. While our interest has focused primarily on ylide complexes of gold, examples of organometallic complexes containing ylide ligands can be found for not only many of the transition-metal series of elements, but several main-group and lanthanide elements as well (Schmidbaur, 1975, 1983; Kaska, 1983).

The reaction of the dinuclear gold(I) ylide [Au(CH₂)₂P(C₆H₅)₂]₂ with various substrates has resulted in the generation of gold(II) complexes possessing discrete metal-metal bonds (Fackler & Basil, 1982), gold(III) species containing halide and alkyl-halide ligands (Murray, Porter & Fackler, 1987), as well as A-frame complexes containing bridging methylene ligands (Murray, Mazany & Fackler, 1985; Jandik, Schubert & Schmidbaur, 1982). In a limited number of instances, isomerization reactions have been observed (Dudis & Fackler, 1985), as well as cleavage reactions leading to mononuclear gold(I) products (Porter, Knachel & Fackler, 1986).

In this paper we report the preparation and crystal structure of the dinuclear gold(III) complex [Au(CH₂)₂P(C₆H₅)₂]₂Cl₄ obtained from the reaction of the Au^I ylide dimer with thionyl chloride.

Experimental. The dinuclear gold(I) ylide [Au(CH₂)₂P(C₆H₅)₂]₂ was prepared according to the literature procedure (Basil, Murray, Fackler, Tocher, Mazany, Trzcinska-Bancroft, Knachel, Dudis, Delord & Marler, 1985). The Au^{III} tetrachloride complex [Au(CH₂)₂P(C₆H₅)₂]₂Cl₄·2H₂O was obtained by the addition of excess thionyl chloride (Alfa Products, used as received) to a solution of the gold(I) dimer in benzene. Crystals suitable for X-ray analysis were obtained by recrystallization from a dichloromethane/diethyl ether solution.

Single multifaceted yellow crystal of approximate dimensions 0.25 × 0.20 × 0.25 mm mounted in a random orientation on a glass fiber. Triclinic symmetry suggested on the basis of interaxial angles and confirmed by a Delaunay reduction. Axial lengths checked by comparison with the interlayer spacings observed in axial photographs. Refined cell parameters obtained from the setting angles of 20 reflections with 30 < 2θ < 35°. Data collection carried out at room temperature using the ω-scanning technique in bisecting geometry. (Nicolet R3m/E diffractometer, graphite-monochromated Mo Kα radiation.) Intensities measured for 2212 unique reflections (*h* < 12, |*k*| < 8, |*l*| < 8) with 0 < 2θ < 45°, no symmetry-equivalent reflections were collected. Scan rate variable, 4–28° min⁻¹; scan range -1.0 in ω from Kα₁ to +1.0 from Kα₂. Backgrounds estimated from a 96-step peak profile. Three low-angle standards (010, 111, 011)

measured every 100 data. The data were corrected for standard decay (~23%) by scaling on the three standards' absorption, Lorentz and polarization effects, which decayed similarly. Corrections for absorption applied empirically on the basis of azimuthal scans of ten reflections spanning a range of 2θ values (min. and max. transmission 0.157 and 0.189, respectively). Structure solution and refinement carried out using the *SHELXTL* collection of crystallographic software (Sheldrick, 1981). Au-atom position determined from a sharpened Patterson map; all remaining non-H atoms located on difference Fourier maps. Phenyl rings refined as idealized polygons (C–C = 1.395 Å, C–C–C = 120°) using H atoms placed in calculated positions with fixed thermal parameters [*U*(H) = 0.08 Å²]. All non-H atoms refined anisotropically. Refinement based on *F* with weights of the form *w*⁻¹ = [σ²(*F*) + 0.0028(*F*²)]. The value of 0.0028, *g*, was refined by fitting (*F*_o - *F*_c)² to [σ²(*F*) + *gF*²]/*k* (*k* = scale factor) to put weights on an approximately absolute scale. Neutral scattering factors, including terms for anomalous dispersion, taken from *International Tables for X-ray Crystallography* (1974). Convergence to conventional *R* values of *R* = 0.0637 and *wR* = 0.0666 obtained using 139 variable parameters and 1651 reflections with *F*_o² > 3σ(*F*_o²). For final cycle max. shift/σ = 0.01 with a goodness-of-fit indicator of 1.000. Residual electron density on final difference Fourier map, using unique data, of +2.30 and -3.2 e Å⁻³ in the vicinity of Au(1).

Discussion. The product obtained from the reaction of thionyl chloride with the gold(I) ylide dimer consists of discrete dinuclear gold(III) ylide complexes with each gold center containing two chloride ligands bonded in a *trans* configuration. The unit cell consists of one centrosymmetric dimer and contains two molecules of water. A perspective view of the complex is shown in Fig. 1. A stereoview packing diagram of the cell contents projected down the *c* axis is shown in Fig. 2. Atomic positional and equivalent isotropic thermal parameters for all non-H atoms are presented in Table 1.* Bond angles and distances are summarized in Table 2.

The structure of the complex described here consists of an eight-membered heterocyclic ring system containing Au, P and C nuclei. The overall conformation of this complex is that of a centrosymmetric chair with an inversion center located midway between the two gold centers. Interaxial angles about Au(1) range from 88.3 (7) to 92.5 (5)°, with bonds to the two *trans* Cl(1) and Cl(2) ligands that measure 2.266 (6) and

* Lists of structure factors, anisotropic thermal parameters, and hydrogen-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43594 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

2.297 (7) Å, respectively. The Cl—Au—Cl atoms in this complex define an angle of 168.5°, and the C—Au—C atoms are collinear to within 3°. Bonds to the methylene C atoms show little variation and have an average length of 2.105 (25) Å [Au(1)—C(1) = 2.093 (24); Au(1)—C(2) = 2.116 (25) Å]. There are no unusually close intermolecular contacts between different molecules in the lattice, and Au(1) is separated from its symmetry-generated equivalent by a distance of 3.087 (2) Å. At this distance the two gold(III) centers are not strongly bonded.

The phosphorus center in the bridging ylide ligand in this complex is tetrahedral and forms bonds to both phenyl and methylene C atoms. The deviation from ideal tetrahedral geometry is minimal; the average C—P—C angle measures 111.3 (11)° with a maximum variation of less than 8°. Bonds to methylene C(1) and C(2) atoms are not significantly different from those to C(16) and C(26) of the phenyl rings, although in other ylides, both free and stabilized, some shortening of the methylene—P bond has been observed (Bart, 1968, 1969).

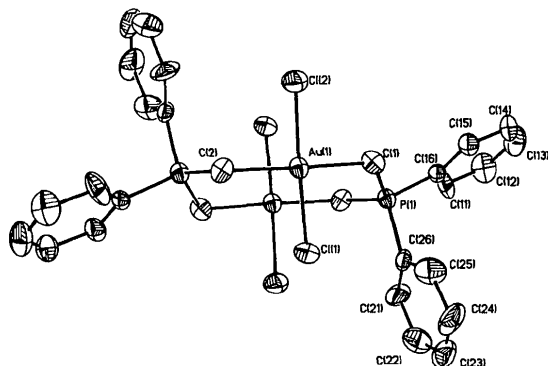


Fig. 1. A perspective view of the $[\text{Au}(\text{CH}_2)_2\text{P}(\text{C}_6\text{H}_5)_2]_2\text{Cl}_4$ structure. Thermal ellipsoids have been drawn at the 50% probability level. H atoms have not been included.

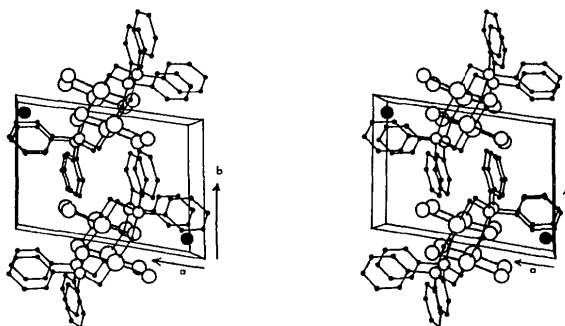


Fig. 2. A stereoview packing diagram viewed down the *c* axis. Au, Cl and P atoms are shown as open circles. O atoms belonging to water molecules are shown as filled circles. H atoms have not been included.

The Au—Cl bond lengths in the structure described here are in good agreement with the 2.296 (3) to 2.331 (3) Å range of bond lengths observed in a related *trans, trans* gold(III) complex containing three chloride ligands and a coordinated trichloromethyl group (Murray, Fackler, Porter & Mazany, 1986). The *cis, trans* isomer of the title complex has been previously reported (Dudis & Fackler, 1985). In that structure, Au—Cl bond distances at the *trans* gold center measure 2.295 (9) and 2.272 (9) Å, compared with 2.338 (9) and 2.360 (7) Å at the *cis* gold center. With the rigorous exclusion of water, the complex described here crystallizes in space group $P2_1/c$ with $Z = 2$ and is isostructural with a gold(III) complex containing bromide ligands (Murray, Porter & Fackler, 1985). The structure of the tetraiodide derivative, however, is unknown, as this complex has yet to be prepared.

Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\text{Å}^2 \times 10^3$) for $[\text{Au}(\text{CH}_2)_2\text{P}(\text{C}_6\text{H}_5)_2]_2\text{Cl}_4$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}^*
Au(1)	4698 (1)	1259 (1)	916 (1)	27 (1)
Cl(1)	6488 (6)	920 (9)	2622 (8)	47 (3)
Cl(2)	2871 (6)	1951 (9)	-452 (8)	48 (3)
P(1)	6513 (6)	2616 (7)	-1443 (7)	28 (2)
O(1)	449 (26)	8909 (34)	4274 (23)	89 (14)
C(1)	5454 (23)	3156 (32)	-509 (28)	34 (10)
C(2)	3883 (22)	-626 (30)	2243 (27)	32 (9)
C(11)	6292 (15)	5680 (18)	-3071 (17)	37 (9)
C(12)	6453	6918	-4261	57 (13)
C(13)	6939	6617	-5445	57 (13)
C(14)	7264	5079	-5439	56 (13)
C(15)	7103	3841	-4249	54 (12)
C(16)	6617	4142	-3065	27 (8)
C(21)	8810 (16)	1841 (22)	-276 (24)	67 (15)
C(22)	9986	2129	633	85 (19)
C(23)	10337	3313	1738	64 (14)
C(24)	9510	4210	1936	69 (15)
C(25)	8334	3922	1027	58 (13)
C(26)	7983	2738	-79	32 (9)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 2. Bond lengths (Å) and angles (°) for $[\text{Au}(\text{CH}_2)_2(\text{PC}_6\text{H}_5)_2]_2\text{Cl}_4$

Au(1)—Cl(1)	2.266 (6)	Au(1)—Cl(2)	2.297 (7)
Au(1)—C(1)	2.116 (25)	Au(1)—C(2)	2.093 (24)
Au(1)—Au(1a)	3.087 (2)	P(1)—C(1)	1.834 (32)
P(1)—C(16)	1.794 (16)	P(1)—C(26)	1.809 (18)
P(1)—C(2a)	1.807 (26)	C(2)—P(1a)	1.807 (26)
Cl(1)—Au(1)—Cl(2)	168.5 (3)	Cl(1)—Au(1)—C(1)	92.5 (7)
Cl(2)—Au(1)—C(1)	88.3 (7)	Cl(1)—Au(1)—C(2)	89.9 (7)
Cl(2)—Au(1)—C(2)	89.5 (7)	C(1)—Au(1)—C(2)	177.5 (9)
Cl(1)—Au(1)—Au(1a)	82.8 (2)	Cl(2)—Au(1)—Au(1a)	108.7 (2)
C(1)—Au(1)—Au(1a)	88.2 (8)	C(2)—Au(1)—Au(1a)	91.4 (8)
C(1)—P(1)—C(16)	107.4 (10)	C(1)—P(1)—C(26)	111.3 (11)
C(1)—P(1)—C(2a)	115.2 (12)	Au(1)—C(1)—P(1)	116.9 (14)
Au(1)—C(2)—P(1a)	115.9 (14)	P(1)—C(16)—C(11)	119.5 (6)
P(1)—C(16)—C(15)	120.3 (7)	P(1)—C(26)—C(21)	120.7 (7)
P(1)—C(26)—C(25)	118.6 (7)		

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The Geometry of Bis(η^5 -cyclopentadienyl) Metal Diligand Complexes: Structure of Mo(Cp)₂(benzoate)₂

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Abstract. Dibenzoatobis(η^5 -cyclopentadienyl)-molybdenum(IV), [Mo(C₅H₅)₂(C₇H₅O₂)₂], $M_r = 468.34$, monoclinic, $P2_1/n$, $a = 22.530(6)$, $b = 7.648(1)$, $c = 12.307(3)$ Å, $\beta = 103.76(2)^\circ$, $V = 2059.8(8)$ Å³, $Z = 4$, $D_x = 1.51$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 5.82$ cm⁻¹, $F(000) = 952$, $T = 293$ K. Final $R(F) = 0.0353$, $wR = 0.044$ for 2049 observed diffractometer reflexions. The Mo atom has the usual distorted tetrahedral geometry comprising the Mo–Cp (Cp = η^5 -C₅H₅) ring normals [Mo⋯Cp = 1.970, 1.975(8) Å] and two Mo–O bonds [Mo–O 2.102, 2.113(4) Å] to the monodentate benzoates. The Cp/Cp conformation is staggered and the Cp–Mo–Cp and O–Mo–O angles are 133.3(4) and 72.3(2)° respectively. The geometry of this molecule is compared with that of the corresponding Ti complex, and the importance of steric factors in both molecules is assessed.

Introduction. The structure determination of the title complex has been completed as part of a continuing study of structural and thermodynamic properties of

molybdenum dicyclopentadienyl complexes (Calhorda, Carrondo, Dias, Domingos, Martinho Simões & Teixeira, 1986).

Experimental. Crystals prepared at the Centro de Química Estrutural (Teixeira, 1986). Laue symmetry and systematic absences consistent with $P2_1/n$; 2862 independent hkl intensities were measured (range of hkl : h 0→24, k 0→8, l -13→13), 813 unobserved with $F_o < 3\sigma(F_o)$, θ - 2θ scans, $\theta_{\text{max}} = 23^\circ$. CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$ radiation. Unit-cell parameters refined from 25 reflexions, $9 < \theta < 15^\circ$. 414, 307, 707 used as standards, intensities showed no decay throughout data collection. Mo position from sharpened Patterson synthesis map, O and C positions from subsequent difference Fourier synthesis. Full-matrix least-squares refinement with *SHELX* (Sheldrick, 1976), isotropic temperature factors, gave $R = 0.10$. Anisotropic refinement reduced R to 0.048. H atoms included at calculated positions, C–H distance 1.08 Å, refined isotropically. Final