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Structural Correlations between *trans*- and *cis*-Bis(diphenylphosphino)ethene, Bis(diphenylphosphino)methane and their Chlorogold(I) Complexes

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Abstract

The crystal structures of *trans*- and *cis*-bis(diphenylphosphino)ethene (**1**, **2**) have been determined by single crystal X-ray diffraction. The conformation of these free ligands is compared with structural data available in the literature for the corresponding 1:2 complexes with gold(I) chloride (**4**, **5**). In the *cis*-ligand **2** the conformation of the Ph_2P-groups is such, that the molecule approaches non-crystallographic C_s symmetry with the lone pairs at phosphorus pointing towards each other. Upon addition of AuCl, rotation of one Ph_2P group around the P–C bond by approximately 60° leads to a structure for **5** which allows an intramolecular Au···Au contact of 3.05(1) Å. The *trans*-ligand **1** undergoes little structural change upon adduct formation, but intermolecular Au···Au contacts of 3.043(1) Å are secured through aggregation. The synthesis, properties and ^{197}Au Mössbauer spectra of 1:1 and 1:2 complexes of **1** and **2** with AuCl are summarized with reference to a recent controversy in the literature.

The crystal structure of bis(diphenylphosphino)methane (**3**) has also been determined and the results compared with those published previously for the 1:2 complex with AuCl (**7**, crystallographic C_2 symmetry, Au···Au distance 3.351(2) Å). There is very little change of the ligand conformation upon coordination.

Introduction

The interest in the synthesis, structure and properties of gold(I) complexes with bidentate phosphines has increased rapidly since it was recently discovered that some of these adducts show chemotherapeutic potential in cancer treatment [1]. Complexes investigated previously mainly in connection with applications in the treatment of rheumatoid arthritis [2], in catalysis [3], or in thermal, reductive or photochemical deposition of metallic gold [4], are now reconsidered and tested in the light of the recent findings. Apart from these aspects, the structure and bonding in binuclear complexes of gold has also been of considerable significance from a theoretical point of view, when it became obvious that there are stereochemically important metal–metal interactions between the two closed-shell gold centers, which give rise to abnormally short intra- or intermolecular Au···Au distances [5]. These points are reflected by a growing number of publications from various laboratories.

In the course of these studies a minor controversy arose about the synthesis and properties of the title compounds [6, 7], which had been investigated at different stages of the development of the chemistry of systems containing gold(I) associated with bidentate phosphines [6–11]. Since we ourselves had also been engaged in that area [12–19], we are presenting here a few complementary data in an attempt to resolve the conflicting results and to add some of our ideas regarding the underlying structural and conformational principles.

Experimental

The ligands (**1**–**3**) were prepared as described in the literature [20, 21]. All gold complexes were synthesized following the same procedure as described for **5** below. The reactions were carried out under protection against light, at room temperature, and under an atmosphere of dry carbon monoxide.

Ethene-cis-bis[diphenylphosphinochlorogold(I)] (5)

To a solution of 1.26 g (4.8 mmol) of (carbonyl)-chlorogold(I) in 5 ml of benzene, 0.95 g (2.4 mmol) of ligand **2** in the same amount of solvent were added dropwise with stirring. CO gas was evolved and a white precipitate formed immediately. The product (**5**) was isolated by filtration, washed with pentane, and dried in a vacuum. It is air-stable and insoluble in many of the common organic solvents, but it can be crystallized from hot dichloromethane/diisopropylether. Yield 1.00 g (48%), melting point (m.p.) 202 °C with decomposition. *Anal.* Calc. for $C_{26}H_{22}Au_2Cl_2P_2$ (861.25): C, 36.26; H, 2.57. Found: C, 36.54; H, 2.66%.

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TABLE I. Crystallographic Data for 1 and 3

	1	3
Formula	$C_{26}H_{22}P_2$	$C_{25}H_{22}P_2$
M_r	396.41	384.4
Crystal system	monoclinic	orthorhombic
Space group	$P2_1/c$ (No. 14)	*Pbca* (No. 61)
a (Å)	8.854(3)	9.820(2)
b (Å)	21.605(5)	10.231(2)
c (Å)	11.566(3)	40.541(7)
β (°)	102.46(2)	90.0
V (Å^3)	2160.4	4073.1
Z	4	8
D_{calc} (g cm^{-3})	1.219	1.254
μ (Mo Kα) (cm^{-1})	2.0	2.1
F(000) (e)	832	1616
T (°C)	21	−40
Radiation	Mo Kα, graphite monochromator	
λ (Å)	0.71069	0.71069
Diffractometer	Enraf-Nonius CAD 4	Syntex $P2_1$
Scan	$\vartheta-2\vartheta$	ω
Scan width in ω (°)	$0.5 + 0.35 \tan\vartheta$	1.2
Scan speed (° min^{-1})	1–10	0.9–29.3
$(\sin\lambda)_{max}$ (Å^{-1})	0.648	0.572
hkl range	±11, +28, +15	+11, +11, +46
Reflections measured	5261	3564
Reflections unique	4894	3185
R_{int}	0.014	
Solution (direct methods)	MULTAN-80	SHELXS-86
Refinement	anisotropic H(ethylene) isotr./H(phenyl) fixed	anisotropic H fixed
Parameters refined	261	244
R^a	0.047	0.067
$R_w{}^b$	0.054	0.060
w	$1/[\sigma^2(F_o) + kF^2]$ $k = 0.000094$	$1/\sigma^2(F_o)$
(Shift/error)$_{max}$	0.002	0.001
$\Delta\rho_{fin}$ (max/min) (e Å^{-3})	+0.24/−0.30	+0.42/−0.32

$^aR = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. $^bR_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o{}^2]^{1/2}$.

Ethene-trans-bis[diphenylphosphinochlorogold(I)] (4)

From 0.71 g (2.72 mmol) of (CO)AuCl and 0.54 g (1.36 mmol) of ligand 1 a yield of 1.10 g (93%) of complex 4 was obtained similarly, which crystallizes from hot dichloromethane/ethanol, m.p. 270 °C with decomposition (lit. [7]: 262–264 °C with decomposition). *Anal.* Calc. for $C_{26}H_{22}Au_2Cl_2P_2$ (861.25): C, 36.26; H, 2.57. Found: C, 35.90; H, 2.67%.

[Ethene-trans-bis(diphenylphosphine)] chlorogold(I) (6)

0.72 g (2.76 mmol) of (CO)AuCl and 1.09 g (2.75 mmol) of ligand 1 gave 1.63 g (93%) of product 6, m.p. 263 °C with decomposition. *Anal.* Calc. for $C_{26}H_{22}AuClP_2$ (628.83): C, 49.66; H, 3.21. Found: C, 50.43; H, 3.53%.

Experiments with ligand 2 in a molar ratio 1:1 gave black precipitates which could not be fully characterized. The products contained metallic gold.

X-ray Structure Determination of 1–3

Crystal data and numbers pertinent to data collection, reduction and structure refinement of 1 and 3 are summarized in Table I. Tables II–V contain the atomic coordinates and prominent bond lengths and angles. See also 'Supplementary Material'.

The structure of the *cis*-ligand 2 (monoclinic, space group *Pn*(*P*2/*n*) with $a = 12.732(3)$, $b = 5.627(1)$, $c = 15.796(4)$ Å, $\beta = 106.59(2)°$, $V = 1084.6$ Å^3, $D_{calc} = 1.214$ g cm^{-3} for $Z = 2$) could be solved in the non-centrosymmetric space group *Pn*, but refinement did not proceed satisfactorily, presumably due to poor crystal quality. (The molecules do not possess twofold symmetry but rather approximate mirror symmetry, which excludes the centrosym-

TABLE II. Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters for 1[a]

Atom	*x/a*	*y/b*	*z/c*	U_{eq}
P1	0.5551(1)	0.2260(1)	0.7475(1)	0.047
P2	0.8690(1)	0.0886(1)	0.6154(1)	0.048
C1	0.6446(3)	0.1596(1)	0.6947(3)	0.048
C2	0.7787(3)	0.1568(1)	0.6606(3)	0.047
C10	0.3654(3)	0.2286(1)	0.6469(2)	0.044
C11	0.3202(4)	0.1930(2)	0.5463(3)	0.064
C12	0.1693(4)	0.1972(2)	0.4792(3)	0.073
C13	0.0671(4)	0.2378(2)	0.5105(4)	0.068
C14	0.1111(4)	0.2736(2)	0.6101(4)	0.070
C15	0.2578(3)	0.2684(1)	0.6786(3)	0.057
C20	0.6552(3)	0.2918(1)	0.6988(2)	0.042
C21	0.6541(3)	0.3052(1)	0.5813(2)	0.048
C22	0.7313(4)	0.3561(1)	0.5518(3)	0.058
C23	0.8125(4)	0.3943(1)	0.6390(4)	0.065
C24	0.8142(4)	0.3817(2)	0.7557(3)	0.067
C25	0.7364(4)	0.3311(1)	0.7860(3)	0.055
C30	1.0631(3)	0.0922(1)	0.7100(2)	0.043
C31	1.1090(3)	0.1318(1)	0.8057(3)	0.054
C32	1.2566(4)	0.1298(2)	0.8746(3)	0.064
C33	1.3603(3)	0.0873(2)	0.8502(3)	0.063
C34	1.3177(4)	0.0474(2)	0.7554(4)	0.065
C35	1.1714(3)	0.0505(1)	0.6846(3)	0.057
C40	0.7830(3)	0.0265(1)	0.6890(3)	0.046
C41	0.8128(4)	0.0194(1)	0.8105(3)	0.064
C42	0.7428(4)	−0.0265(2)	0.8632(3)	0.074
C43	0.6446(5)	−0.0676(2)	0.7956(5)	0.075
C44	0.6117(4)	−0.0616(2)	0.6748(4)	0.073
C45	0.6820(4)	−0.0145(2)	0.6201(3)	0.067

[a] $U_{eq} = (U_1 U_2 U_3)^{1/3}$, where U_{eq} are the eigenvalues of the U_{ij} matrix.

symmetric alternative). The plot of the molecular structure in Fig. 1 is based on these approximate coordinates. Since for the scope of the present discussion the knowledge of the overall conformation is sufficient, the structure analysis was not pursued any further.

TABLE IV. Important Bond Lengths (Å) and Angles (°) for 1[a]

P1–C1	1.807(3)	C1–P1–C10	102.7(1)
P1–C10	1.827(3)	C1–P1–C20	103.7(1)
P1–C20	1.828(3)	C10–P1–C20	102.7(1)
P2–C2	1.808(3)	C2–P2–C30	102.1(1)
P2–C30	1.829(3)	C2–P2–C40	102.0(1)
P2–C40	1.838(3)	C30–P2–C40	100.6(1)
C1–C2	1.331(4)	P1–C1–C2	128.3(2)
C1–H1	1.00(3)	P1–C1–H1	114(2)
C2–H2	0.96(3)	C2–C1–H1	118(2)
		P2–C2–C1	126.9(3)
		P2–C2–H2	114(2)
		C1–C2–H2	119(2)

[a] e.s.d.s in units of the last significant figure given in parentheses.

TABLE III. Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters for 3

Atom	*x/a*	*y/b*	*z/c*	U_{eq}
P1	0.0336(2)	0.6058(1)	0.1092(1)	0.036
P2	0.2666(2)	0.6522(1)	0.1544(1)	0.036
C1	0.1998(6)	0.5388(5)	0.1221(1)	0.036
C11	0.0802(6)	0.7306(5)	0.0789(1)	0.031
C12	0.2069(6)	0.7413(6)	0.0635(1)	0.050
C13	0.2292(6)	0.8415(6)	0.0409(1)	0.054
C14	0.1298(10)	0.9273(6)	0.0330(2)	0.057
C15	0.0038(9)	0.9189(6)	0.0480(2)	0.053
C16	−0.0194(6)	0.8210(6)	0.0707(1)	0.048
C21	−0.0303(6)	0.4736(5)	0.0825(1)	0.035
C22	−0.0630(6)	0.4888(5)	0.0495(1)	0.042
C23	−0.1164(6)	0.3837(6)	0.0317(1)	0.044
C24	−0.1345(6)	0.2634(6)	0.0464(1)	0.051
C25	−0.1034(6)	0.2485(6)	0.0793(1)	0.053
C26	−0.0517(6)	0.3516(5)	0.0971(1)	0.041
C31	0.4438(6)	0.5978(6)	0.1596(1)	0.037
C32	0.5316(6)	0.6816(5)	0.1761(1)	0.041
C33	0.6679(6)	0.6487(6)	0.1807(1)	0.050
C34	0.7169(6)	0.5331(6)	0.1683(1)	0.051
C35	0.6324(6)	0.4497(6)	0.1525(1)	0.051
C36	0.4963(6)	0.4803(5)	0.1479(1)	0.044
C41	0.1869(5)	0.5801(5)	0.1913(1)	0.032
C42	0.0711(6)	0.6390(5)	0.2042(1)	0.048
C43	0.0080(6)	0.5876(6)	0.2319(1)	0.059
C44	0.0599(6)	0.4792(6)	0.2473(1)	0.045
C45	0.1744(6)	0.4200(6)	0.2346(1)	0.048
C46	0.2364(6)	0.4701(5)	0.2068(1)	0.039

TABLE V. Important Bond Lengths (Å) and Angles (°) for 3

P1–C1	1.848(5)	C1–P1–C11	103.2(2)
P1–C11	1.828(5)	C1–P1–C21	101.3(2)
P1–C21	1.842(5)	C11–P1–C21	101.8(2)
P2–C1	1.868(5)	C1–P2–C31	102.9(2)
P2–C31	1.839(6)	C1–P2–C41	99.9(2)
P2–C41	1.842(5)	C31–P2–C41	100.9(2)
		P1–C1–P2	106.2(3)

Results and Discussion

Synthesis and Composition of the AuCl Complexes of trans- and cis-Bis(diphenylphosphino)ethene

1:2 complexes of the two ligands *trans*- and *cis*-bis(diphenylphosphino)ethene are readily obtained from the reactions of the phosphines with two equivalents of (CO)AuCl in benzene as a solvent. The products **4** and **5** appear as colourless precipitates of correct analytical composition and in good yields. The product prepared from the *trans* ligand and $HAuCl_4$ in the presence of a reducing agent [6]

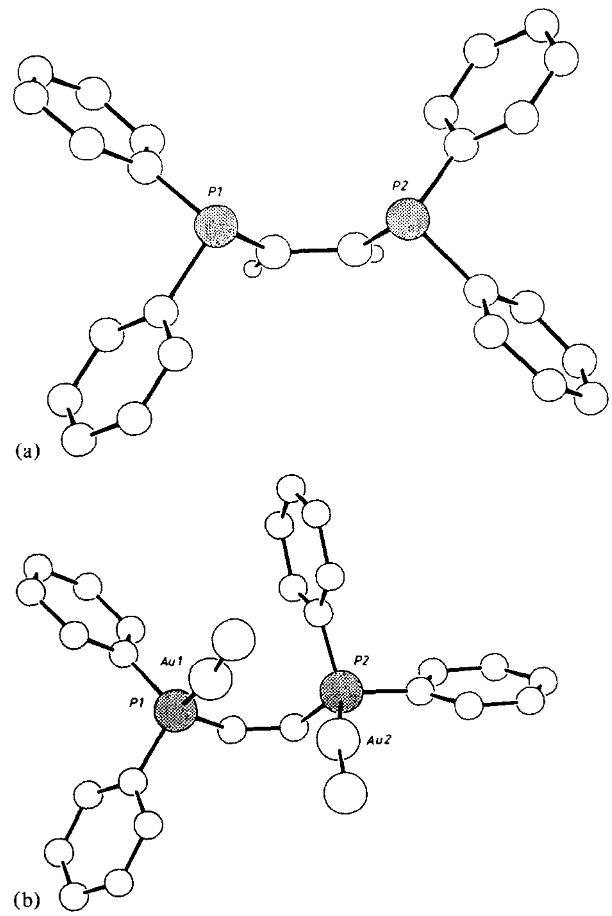


Fig. 1. Comparison of the *cis*-ligand **2** (a) and its 1:2 AuCl complex **5** [8] (b).

has similar properties. In the absence of a reducing agent, when the ligand itself functions as the electron acceptor, only the 1:1 adduct is formed [7, see also below].

Compounds **4** and **5** have also been characterized by ^{197}Au Mössbauer spectroscopy. The values obtained (in mm s^{-1}) for the isomeric shifts (*IS*) and quadrupole coupling constants (*QS*) show significant differences, but are in each case within the limits established empirically for gold(I) complexes with phosphine donors [22] (Fig. 2):

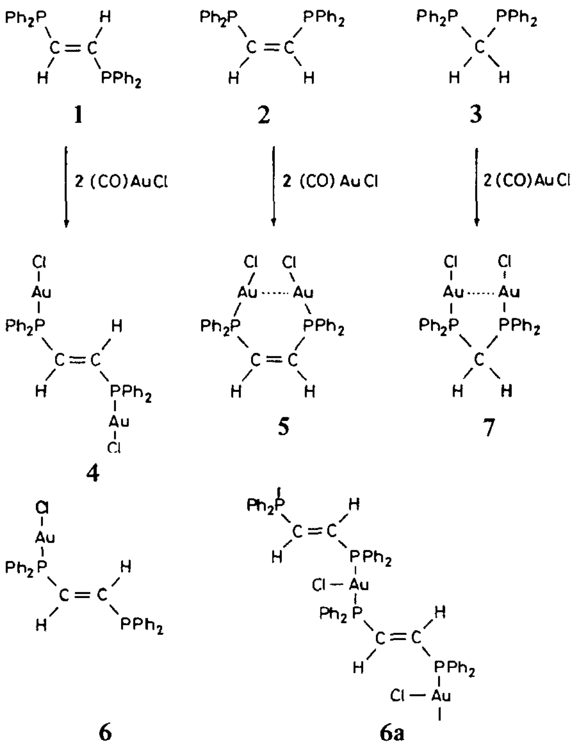
	IS	*QS*
trans-$ClAuPh_2PCH{=}CHPPh_2AuCl$ (**4**)	2.721	7.932
cis-$ClAuPh_2PCH{=}CHPPh_2AuCl$ (**5**)	2.542	7.196

Data quoted in the secondary literature [22] of a compound of unspecified stereochemistry (*cis*/*trans*) could not be found in the primary literature [23] and could not be confirmed.

Of the *trans* ligand **1**, a 1:1 complex **6** could also be obtained. This product again appears to be identical with materials generated from the ligand and $HAuCl_4$ in the absence [7] or in the presence of a reducing agent [6]. The ^{197}Au Mössbauer spectrum of this complex (**6**) is different from the spectrum of the 1:2 complex (**4**), with values *IS* = 1.660 and *QS* = 7.742 mm s^{-1}. Differences in the infrared spectra of **4** and **6** have been pointed out previously [6].

A 1:1 complex of the *cis* ligand **2** and AuCl could not be prepared using (CO)AuCl under standard reaction conditions. This result is in agreement with previous studies, where this complex is also missing in the list of materials investigated [7]. It has been mentioned, however, that several products are formed in the reaction of **2** with (CO)AuCl, but only one has been identified (**5**) [8]. It is concluded therefore, that the 1:1 complex of AuCl and **2** readily undergoes secondary reactions.

The crystal structures of the 1:2 complexes (**4, 5**) have been determined [6, 8] and are revisited below where the conformations are compared with those of the free ligands. The structure of the 1:1 adduct **6**, however, is as yet unknown. On the basis of the ^{197}Au Mössbauer spectrum it is concluded that the gold atoms in this structure have the same environment. From the data it may also be tentatively derived [22] that the gold atoms have a coordination number in excess of two with loose contacts to chloride anions in addition to two phosphorus donors (**6a**). Very weak and slightly shifted infrared absorptions in the ν(AuCl) region are in agreement with this proposal [6, 7].



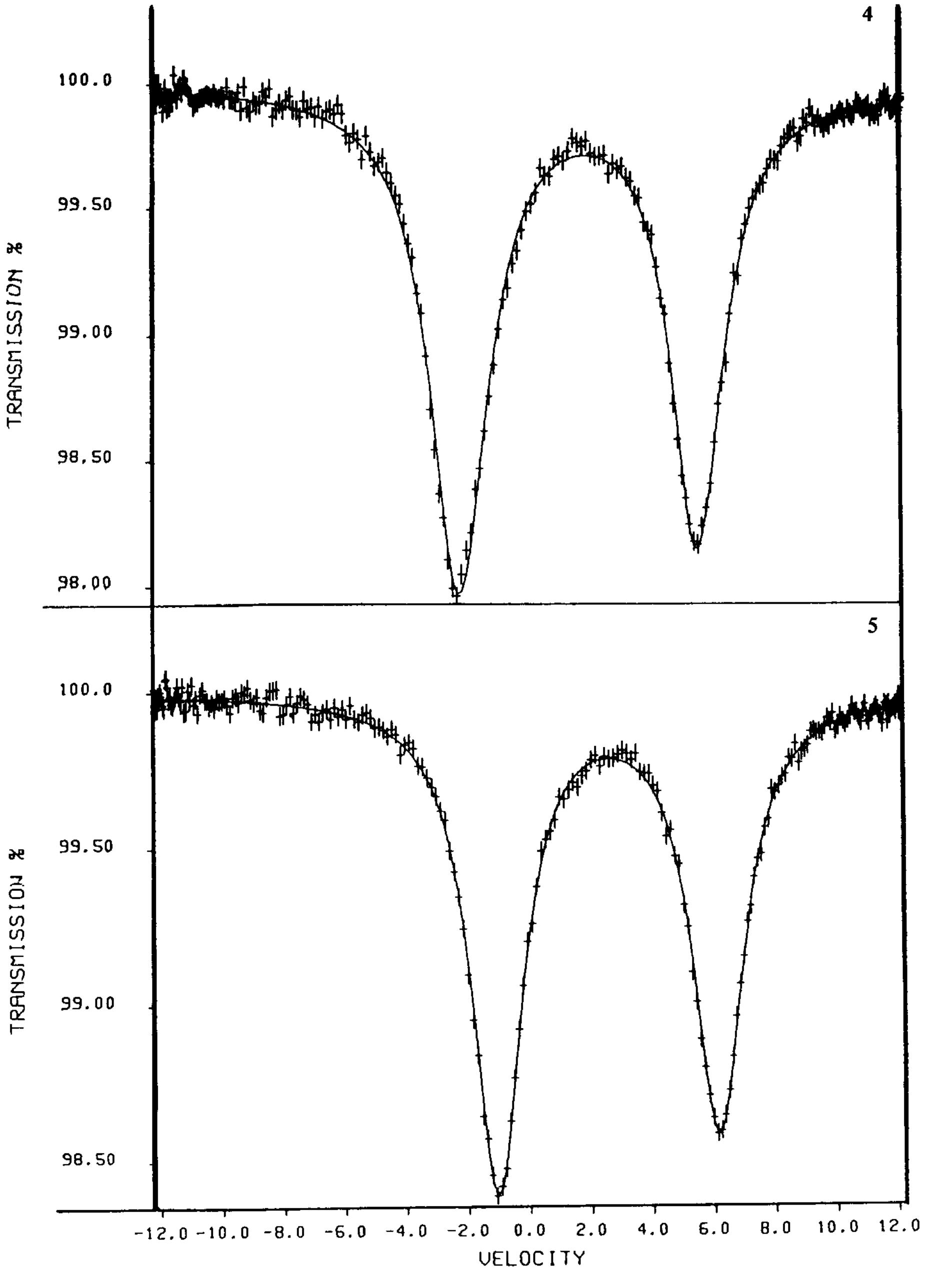


Fig. 2. ^{197}Au Mössbauer spectra of the complexes 4 and 5.

The Molecular Structures of the Ligands 1–3

Ethene-trans-bis(diphenylphosphine) (**1**) has the approximately centrosymmetrical structure shown in Fig. 3. The bond distances and angles listed in Table IV show no anomalies and are in good agreement with data for related compounds. It is notable that the P–C and C=C bond lengths do not indicate any appreciable delocalization of the olefinic double bond across the P–C bonds. The phosphorus atoms have the pyramidal geometry expected for triorganophosphines. The vacant coordination sites are oriented in opposite directions, *i.e.* the lone pairs of electrons are pointing away from each other at both ends of the molecule. Their orientation with respect to the olefinic double bond is roughly orthogonal, as expected for the minimization of their repulsive interactions. Coordination of two equivalents of AuCl without a change of ligand conformation is therefore expected to afford a complex with the two metal atoms very far apart at opposite sides of the plane of the olefinic skeleton.

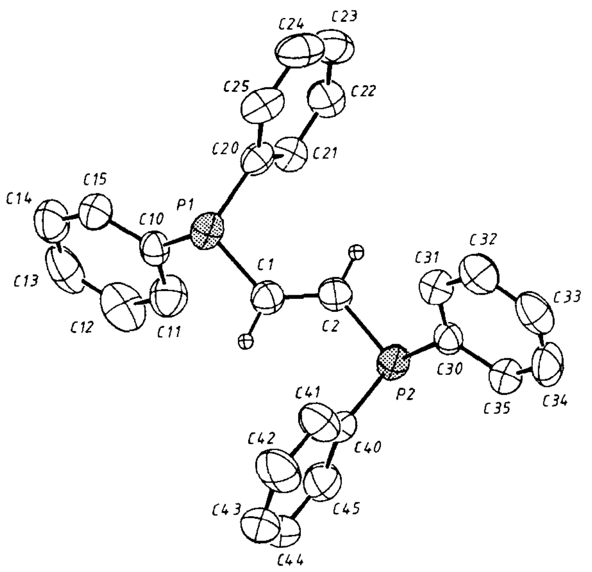


Fig. 3. Molecular structure of **1** without phenyl hydrogen atoms (ORTEP, displacement parameters at the 50% probability level, H atoms with arbitrary radii).

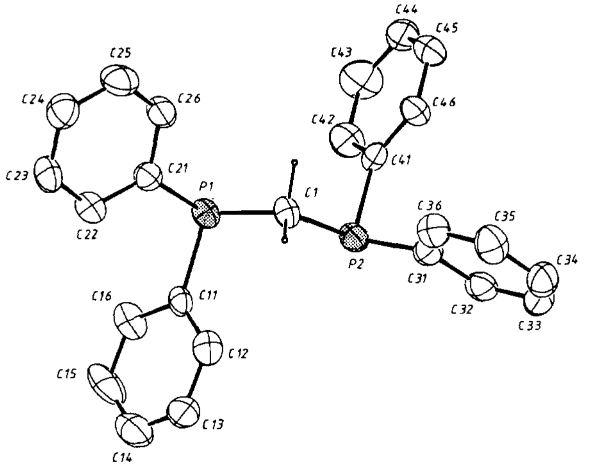


Fig. 4. Molecular structure of **3** (without phenyl H atoms).

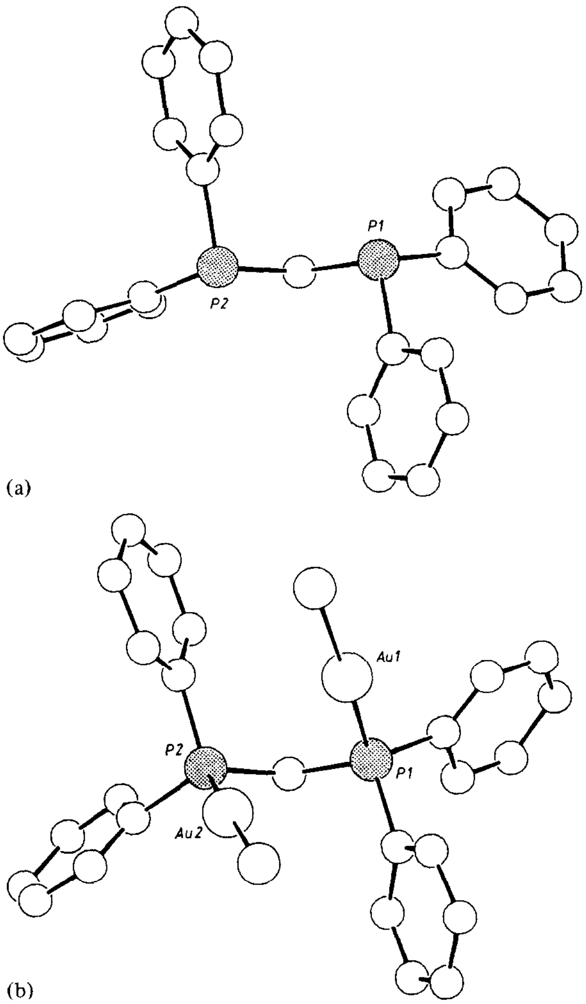


Fig. 5. Comparison of the molecular structures of **3** (a) and **7** [15] (b).

Ethene-cis-bis(diphenylphosphine) (**2**) has the molecular structure shown in Fig. 1a. The molecule has no crystallographic symmetry, but the overall geometry approaches the point group C_s. The orientation of the two phosphino groups is such that the lone pairs of electrons at the phosphorus atoms are directed towards each other in the plane of the olefinic skeleton. While this conformation is ideal for a chelating coordination with only one metal atom, it is clearly unfavourable for the complexation of two metal atoms. A change of conformation is therefore to be expected upon formation of 1:2 complexes with AuCl.

Bis(diphenylphosphino)methane (**3**) (Table V, Fig. 4) again has no crystallographic symmetry. The relative orientation of the two phosphino groups at the common methylene moiety is such that staggered conformations result for the lone pairs and phenyl groups at the two phosphorus atoms and the hydrogen atoms at the CH_2 bridge. Disregarding the relative orientations of the phenyl rings, the C_2PCPC_2 skeleton thus approaches C_2 symmetry. The lone pairs at the phosphorus atoms are on different sides of the plane through the phosphorus atoms and the methylene carbon atom, with approximately the same inclination relative to this plane, as can for example be recognized from the relative orientations of the phenyl groups in Fig. 5. Coordination of two equivalents of AuCl should therefore be possible without major changes in ligand conformation, provided that secondary forces induce no reorientation.

It should be pointed out, that the AuCl components with their linear geometry at the gold atoms in complexes of the form LAuCl (L = Ligand) are

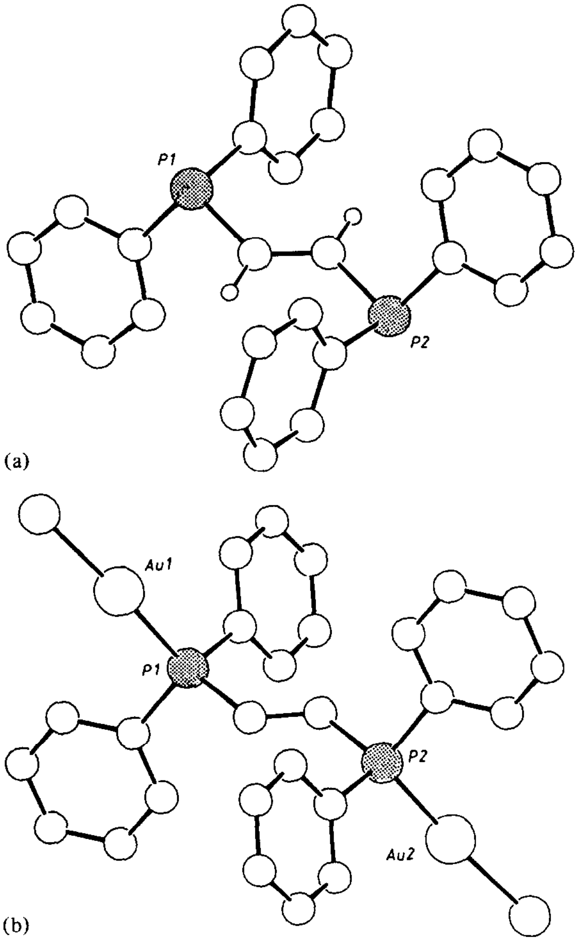


Fig. 6. Comparison of the molecular structures of the *trans*-ligand **1** (a) and its 1:2 AuCl complex **4** [6] (b) shown in approximately equal orientations (ORTEP, arbitrary radii).

exceptional among all metal coordination sites due to the absence of any sterical or conformational requirements based on the residual coordination sphere as compared to, say, trigonal planar, pyramidal, tetrahedral, octahedral, or other complex geometries. This unusual geometrical situation allows the assignment of any structural changes occurring upon coordination to metal–metal interactions and to the subtle distortions expected directly at the donor sites. The following discussion of the goemetry of the complexes is based on this reasoning.

The Molecular Structure of the Complexes 4, 5 and 6 [6, 8, 15]

Ethene-trans-bis[diphenylphosphinechlorogold(I)] (**4**) [6] has a centrosymmetrical structure very similar in dimensional and conformational details to the structure of the free ligand **1**. Inspection of Fig. 6 clearly shows that only very minor changes occur upon coordination of the two AuCl groups at the phosphorus atoms. Even the orientation of the phenyl rings is largely the same in **4** and **1**. It therefore appears that coordination of gold to the Ph_2P–CH= groups indeed brings about very little structural change owing to the minimum sterical requirements of the two-coordinate metals. With the metals far apart from each other at different ends of the ligand, any intramolecular interactions between the two groups are also negligible.

Given this geometrical situation it is the more striking that in the crystal the complex molecules are oriented in a way which allows intermolecular Au···Au interactions as suggested by the intriguingly short Au···Au contacts of only 3.043(1) Å [6]. This phenomenon is very similar to the packing observed for ethane-1,2-bis[diphenylphosphinechlorogold(I)] [9] and other polynuclear gold(I) complexes. The new results are therefore further important support for the assumption of a structure-determining interaction between low-coordinate gold(I) centers. Recent studies of related mercury analogues [24] indicate that a similar interaction is operative with complexes of this neighbouring element in the Periodic Table.

Ethene-cis-bis[diphenylphosphinechlorogold(I)] (**5**) [8] has a structure with no crystallographic symmetry. Inspection of Fig. 1 shows that upon AuCl coordination one Ph_2P group has kept its orientation relative to the olefinic skeleton (P1), while the other has been rotated in such a way that one of the phenyl groups is now eclipsed with the neighbouring ethene hydrogen (P2). Due to this conformational change, one gold atom to a good approximation is situated in the plane of the olefine, while the other is out of this plane (Fig. 1).

The most important result of the comparison of the structures of **2** and **5** is to be seen in the finding that the intramolecular Au···Au contact established by the conformational changes is again 3.05(1) Å, a value not only in agreement with the intermolecular contacts in **4**, but also with those in many other polynuclear gold(I) species [5]. Because there is no obvious other reason for the specific conformation detected in **5**, this structure is suggested to be mainly due to attractive forces between the closed-shell Au(I) centers.

Bis[chlorogold(I)diphenylphosphino]methane (**7**) [15] has a structure with crystallographic C_2 symmetry as shown in Fig. 5. There are only very small changes in the ligand geometry (**3**) on addition of the two AuCl units (**7**). Deviations in the conformation of the Ph_2P groups and even the relative phenyl rotations are only barely noticeable. Nevertheless, the subtle changes are in the direction which brings the gold atoms slightly closer than in the original conformation of the ligand. The resulting Au···Au distance is quite large, however, at 3.351(2) Å. In the case of 7, the Au···Au attraction appears to be too weak to fully overcome the steric pressure in a relatively crowded molecule as compared to the more relaxed situation in **4** or **5**. This is in agreement with observations made with other overcrowded binuclear complexes recently, where conformations with Au···Au contacts proved unacceptable altogether [25].

Supplementary Material

Complete tables of atomic and displacement parameters as well as lists of observed and calculated structure factors have been deposited at the Fachinformationszentrum Energie, Physik, Mathematik GmbH., D-7514 Eggenstein-Leopoldshafen 2, F.R.G. Enquiries should be accompanied by the depository number CSD 52762, the names of the authors, and the literature citation.

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