Trichloro-μ3-[tris(diphenylphosphanyl)methane]-trigold(I): Auriophilicity in a Triangle of Gold Atoms

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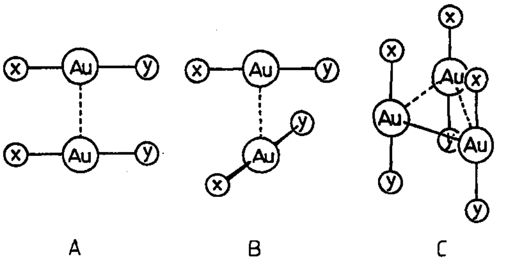
Trichloro-μ3-[tris(diphenylphosphanyl)methane]-trigold(I) (**1**) has been prepared by treating the tripod ligand tris(diphenylphosphanyl)methane with three equivalents of chloro(dimethyl sulfide)gold(I) in dichloromethane. **1** is converted into the tribromo (**2**), triiodo (**3**), and trimethyl derivatives (**4**) by treatment of suspensions of **1** in acetone with hydrogen bromide, potassium iodide, and methyllithium, respectively. Polycrystalline **1** has been studied by Mößbauer spectroscopy. From dichloromethane at room temperature cubic crystals of **1** are obtained, whereas at −30°C a monoclinic dichloromethane solvate of **1** crystallizes. X-Ray structure analyses have been performed for both forms. They contain essentially the same trinuclear complex with only marginal differences in the molecular dimensions. The striking structural feature of the complex is the triangular *all-cis* arrangement of the three gold atoms with rather short Au···Au contacts of 3.201(1) (cubic) and 3.281(1)−3.420(1) Å (monoclinic). This conformation is at variance with the structures of the free ligand (*all-trans*) and other adducts of the type $HC(PPh_2X)_3$ (*cis/cis/trans*) and is probably due to specific metal-metal interactions.

In a series of extensive experimental[1−5] and theoretical[6−8] studies it has been shown that linearly two-coordinate gold(I) complexes of the general formula L−Au−X (with L and X as a neutral or anionic ligand, respectively) show unexpected intermolecular interactions between the closed-shell (d^{10}) metal centers. The interactions cause an aggregation of the complexes in the solid state to dimers or polymers with short intermetallic contacts Au···Au of approximately 3.0 Å. The binding energy involved has been estimated[2d,e,9] and calculated[10] to be in the range of 6−9 kcal/mol. Other consequences of these forces are the induction of unusual molecular conformations[1,2e,h], and the accumulation of gold atoms around a central cluster nucleus leading to excessive coordination numbers[1,2a−c,f,g,4a] or nonclassical coordination geometries[5] of the central atom, typically carbon, nitrogen, phosphorus, and arsenic.

It is now generally believed that this phenomenon, termed "auriophilicity" because it appears to be most pronounced for the element gold[1], is largely based on relativistic effects which reach a local maximum for the atomic number 79 (gold) in the periodic table[6,8]. For the neighboring elements the effect is also observed, but less pronounced. The aggregation of mononuclear complex units L−Au−X is most common in the form of dimers, or of shorter or longer strings of gold atoms[3c,d,11,12]. In the examples known to date where more than two L−Au−X units are present, the metal atoms are found either in a parallel or perpendicular arrangement (**A**, **B**) and with a folding of the chains as they become extended[3c]. An arrangement in the form of rings is much less common, and the three-membered ring in particular (**C**) has been missing up to now with non-forcing ligands.



We now report on the synthesis and molecular structure of the 1:3 complex of *tris*(diphenylphosphanyl)methane[13] with gold(I) chloride. In this work we have been resuming and extending our studies on related complexes of *bis*(diphenylphosphanyl)methane and related ligands, where short Au(I)···Au(I) contacts as well as true short Au(II)−Au(II) bonds have first been noted[14].

Synthesis and Properties of the Title Complex and its Derivatives

Tris(diphenylphosphanyl)methane is available according to the method reported first by Issleib et al.[13], which has been improved both in yield and purity of the product[15]. The tripod ligand reacts with three equivalents of chloro(dimethyl sulfide)gold(I)[16] in dichloromethane at room temperature to give dimethyl sulfide and the colorless crystalline *trichloro complex* **1**. Precipitation is accomplished by addition of pentane (80% yield); the material is recrystallized from dichloromethane/diethyl ether (5:1).

The trichloro complex can be converted into the *tribromo complex* **2** by treatment of a suspension of **1** in acetone with concentrated aqueous hydrogen bromide (47 weight-%). On recrystallization the yellow-brown crude product yields colorless needles (88% yield).

Addition of an excess of potassium iodide suspended in acetone to a slurry of the trichloro complex **1** in the same solvent affords the *triiodo complex* **3** in 70% yield after recrystallization from dichloromethane/diethyl ether.

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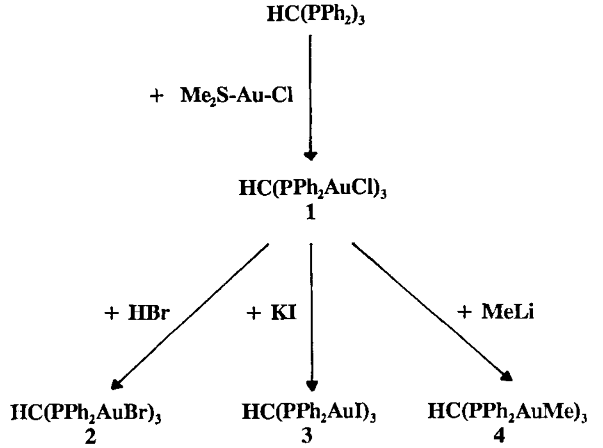
The *trimethyl* derivative **4** can be obtained by reaction of complex **1** with an excess of methyllithium in diethyl ether at 0°C. Compound **4** can be precipitated from the solution in 70% yield by addition of pentane.

Scheme 1



Compounds **1**–**4** are air-stable, light-sensitive complexes, insoluble in non-polar solvents, but slightly soluble in DMSO. Their thermal decomposition is induced on melting (273°C **1**, 282°C **2**, 320°C **3** and 165°C **4**).

The complexes **1**–**4** have been characterized by means of $\{^1H\}^{31}P$-, $\{^1H\}^{13}C$-, and ^1H-NMR spectroscopy and mass spectrometry and elemental analysis. The spectroscopic data are summarized in the experimental section.

In the $\{^1H\}^{31}P$-NMR spectra at room temperature compounds **1**–**4** show one sharp singlet in each case, which is indicative of full equivalence of the three phosphorus atoms in solutions of all four complexes at ambient temperature. The same situation is encountered with the related tris(boranatodiphenylphosphonio)methane, $HC[PPh_2(BH_3)]_3$, for which the $\{^1H\}^{31}P$-NMR spectrum also shows a singlet at 24°C. However, this resonance is split into two signals at −50°C, which finally appears resharpened at −91°C. This result suggests an unsymmetrical low-temperature conformation for this tris-adduct in solution owing to restricted P–C bond rotation[15]. Based on the spectroscopic data the barrier to rotation about the phosphorus-methyne carbon bond has been calculated to be 7.5 kcal/mol. This value is in good agreement with that of other molecules of the type $HC(PPh_2O)_n(PPh_2S)_{3-n}$ [$n = 3$ (9.2)[17], $n = 1$ (9.5)[17], $n = 0$ (11.7)[18]], for which an unsymmetrical conformation has also been confirmed both in solution (at −90°C) and for the crystal. By contrast, an X-ray structure analysis of the free tripod ligand, $HC(PPh_2)_3$, reveals a symmetrical *all-trans* orientation of the three phosphorus lone pairs, while in solution free intramolecular motions of the molecule are observed in the temperature range from +35 to −90°C[15].

Unfortunately – due to the poor solubility in all conventional solvents – the NMR measurements with compounds **1**–**4** have been restricted to room temperature. In order to find out, whether the sterically favored *all-trans* conformation is retained in the gold complexes or – assuming sufficiently strong intermetallic attraction of the three gold atoms – is changed to the symmetrical *all-cis* orientation with the gold atoms arranged in a three-membered ring, an X-ray structure analysis has been carried out for the trichloro compound **1**. In addition, the polycrystalline powder of compound **1** has also been studied by ^{197}Au Mößbauer spectroscopy. The spectrum shows a doublet with an isomer shift of 2.47 mm s^{-1} and a quadrupole coupling constant of 7.29 mm s^{-1}, indicating the equivalence of the three gold(I) units in the polycrystalline solid.

Molecular Structure of Complex 1 in two Crystalline Forms

Compound **1** crystallizes from dichloromethane at room temperature in a cubic, solvent-free form (**1a**), and at −30°C as a monoclinic dichloromethane solvate (**1b**). X-Ray structure analyses of these two forms (Tables 1, 2) have shown that they both contain essentially the same trinuclear complex with only marginal differences in the molecular dimensions. Standard plots are almost indistinguishable (Figure 1 and its caption). This is important evidence that the molecular configuration and – in particular – the molecular *conformation* of the complex are not induced by crystal packing forces.

In the cubic crystals **1a** the complex has crystallographic C_3 symmetry with the central C–H bond on the threefold axis rendering the three PPh_2AuCl units equivalent in the non-centrosymmetric space group $I\bar{4}3d$ (No. 220, International Tables), there is only one of the two chiral enantiomers (the left-handed propeller) present. (The mirror image was checked and discarded due to worse *R* values.)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters for **1a**; $U(eq.) = (U_1 \cdot U_2 \cdot U_3)^{1/3}$, where U_1, U_2, U_3 are the eigenvalues of the U_{ij} matrix; e.s.d.'s in parentheses

ATOM	X/A	Y/B	Z/C	U(eq.)
AU	-0.40082(2)	-0.64444(2)	-0.03830(2)	0.022
P	-0.4934(1)	-0.4756(1)	-0.3984(2)	0.019
CL	-0.4403(2)	-0.3195(2)	-0.3142(2)	0.033
C	-0.2219(6)	-0.2219(6)	-0.2219(6)	0.024
C11	-0.7103(5)	-0.2808(6)	-0.1215(6)	0.023
C12	-0.4369(7)	-0.5399(7)	-0.3238(6)	0.026
C13	-0.4207(6)	-0.5878(6)	-0.3025(6)	0.030
C14	-0.4366(8)	-0.6361(8)	-0.3259(7)	0.035
C15	-0.4678(7)	-0.6386(7)	-0.3699(7)	0.034
C16	-0.4869(6)	-0.5887(6)	-0.3929(6)	0.028
C21	-0.4326(6)	-0.0186(6)	-0.3971(6)	0.022
C22	-0.5961(6)	-0.5134(5)	-0.4315(6)	0.025
C23	-0.6521(7)	-0.5163(6)	-0.4268(6)	0.031
C24	-0.6791(6)	-0.4894(7)	-0.3859(7)	0.032
C25	-0.6507(7)	-0.4567(6)	-0.3507(7)	0.038
C26	-0.5929(6)	-0.4521(5)	-0.3562(6)	0.024

In the monoclinic crystals the complex **1b** has no crystallographically imposed symmetry, but deviations from threefold symmetry as in **1a** are small. Owing to a center of symmetry in the crystal (space group $P2_1/c$) equal portions of both enantiomers of the molecular propeller are present, however.

In both crystalline forms the three gold atoms form an equilateral or almost equilateral triangle, with three Au···Au distances of 3.201(1) Å in **1a** and 3.281(1), 3.329(1), and 3.420(1) Å in **1b**. These rather short contacts are possible

Table 2. Fractional atomic coordinates and equivalent isotropic displacement parameters for **1b**

ATOM	X/A	Y/B	Z/C	U(eq.)
AU1	0.32575(9)	0.10286(4)	0.34004(5)	0.027
AU2	0.16314(8)	0.24239(4)	0.33179(4)	0.025
AU3	0.45593(9)	0.24767(4)	0.42455(4)	0.029
P1	0.4378(6)	0.1471(3)	0.2699(3)	0.024
P2	0.2089(6)	0.2359(3)	0.2255(3)	0.024
P3	0.4485(6)	0.2946(3)	0.3174(3)	0.025
CL1	0.1969(7)	0.0486(3)	0.3976(3)	0.040
CL2	0.1121(6)	0.2604(3)	0.4381(3)	0.040
CL3	0.4821(7)	0.2094(3)	0.5395(3)	0.043
C	0.380(2)	0.233(1)	0.243(1)	0.023
C111	0.423(2)	0.101(1)	0.187(1)	0.026
C112	0.452(2)	0.129(1)	0.126(1)	0.026
C113	0.447(2)	0.092(1)	0.066(1)	0.042
C114	0.409(2)	0.024(1)	0.064(1)	0.045
C115	0.378(2)	-0.004(1)	0.122(1)	0.040
C116	0.386(2)	0.033(1)	0.185(1)	0.030
C121	0.600(2)	0.151(1)	0.311(1)	0.021
C122	0.688(2)	0.167(1)	0.271(1)	0.029
C123	0.809(3)	0.162(1)	0.305(2)	0.043
C124	0.849(3)	0.141(1)	0.375(2)	0.040
C125	0.765(3)	0.121(1)	0.415(2)	0.060
C126	0.640(2)	0.127(1)	0.381(1)	0.035
C211	0.160(2)	0.3094(9)	0.169(1)	0.018
C212	0.206(2)	0.322(1)	0.109(1)	0.029
C213	0.157(3)	0.378(1)	0.067(1)	0.045
C214	0.068(3)	0.423(1)	0.083(2)	0.052
C215	0.023(2)	0.407(1)	0.140(1)	0.037
C216	0.068(2)	0.349(1)	0.185(1)	0.033
C221	0.148(2)	0.161(1)	0.173(1)	0.022
C222	0.094(2)	0.111(1)	0.203(1)	0.028
C223	0.048(2)	0.052(1)	0.165(1)	0.039
C224	0.053(2)	0.045(1)	0.097(1)	0.041
C225	0.106(2)	0.093(1)	0.064(1)	0.036
C226	0.151(2)	0.155(1)	0.099(1)	0.032
C311	0.366(2)	0.3748(9)	0.306(1)	0.019
C312	0.310(2)	0.393(1)	0.361(1)	0.024
C313	0.253(2)	0.457(1)	0.357(1)	0.031
C314	0.250(3)	0.498(1)	0.302(1)	0.042
C315	0.302(2)	0.480(1)	0.246(1)	0.035
C316	0.360(2)	0.418(1)	0.251(1)	0.030
C321	0.596(2)	0.318(1)	0.302(1)	0.029
C322	0.695(2)	0.315(1)	0.365(1)	0.038
C323	0.811(3)	0.338(1)	0.356(2)	0.050
C324	0.829(3)	0.364(2)	0.294(2)	0.046
C325	0.728(3)	0.362(1)	0.233(2)	0.048
C326	0.613(3)	0.337(1)	0.236(2)	0.053
C/CL	0.50370	0.04030	0.52380	0.100
CL/C	0.50370	0.04030	0.52380	0.100
CL	0.46830	0.03040	0.60040	0.100
CL41	0.75690	0.12820	0.04560	0.100
CL42	0.82510	0.23790	0.14010	0.100
C4	0.80960	0.20680	0.06170	0.100

after a rotation of the three PPh_2 groups about the $HC-PPh_2$ bonds out of the positions in the free ligand. In uncomplexed $HC(PPh_2)_3$ the phosphorus lone pairs, calculated as the missing corners of the pseudo-tetrahedra[15] (Figure 2a), are oriented in the plane of the three phosphorus atoms, as evidenced by the dihedral angles HCPE of ca. 90° (E = lone pair of electrons). In the complexes **1a** and **1b** the mean value of the dihedral angles HCPAu is 158.9°, as a consequence of a conrotatory twist of ca. 70° of the PPh_2 groups relative to the position in the free ligand. In Figure 2 the orientation of one of the PPh_2E/PPh_2AuCl groups is drawn bold-print for comparison, with the rest of the molecules drawn in thin lines.

The conformation encountered in **1** is at variance with the structures for other adducts of the type $HC(PPh_2X)_3$, where X = O, S, Se or BH_3[15,17,18]. These molecules adopt structures with at least one of the PPh_2X groups oriented in a different direction than the other two, as also shown by 2:1 NMR non-equivalency of the phosphorus atoms. Such a *cis/cis/trans* structure obviously represents the electrostatic and steric energy minimum for this stoichiometry. Since the steric requirements of the (linear!) P–Au–Cl groups are certainly not very different from that of P–X groups, we have to conclude that the *all-cis* conformation with close proximity of the gold atoms in a triangle (**1a,b**) is caused by specific metal-metal interactions. The barriers to rotation about the P–C single bonds in the $HC(PPh_2X)_3$ molecules have been calculated on the basis of variable-temperature NMR spectra to be between 7 and 10 kcal/mol. Owing to the NMR equivalence of the phosphorus nuclei in both $HC(PPh_2)_3$ and **1**, the analogous barrier cannot be determined for these symmetrical molecules. On steric grounds it appears likely that the energy barrier in **1** should

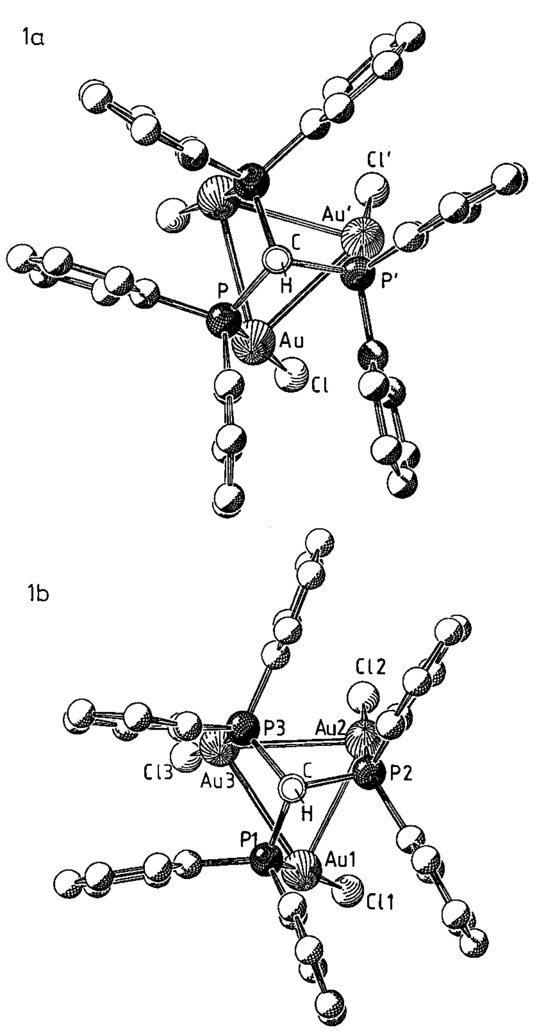


Figure 1. Molecular structure of the cubic (**1a**) and monoclinic (**1b**) form of compound **1**. View along the H–C bond (threefold axis in the case of **1a**, SCHAKAL, phenyl hydrogen atoms omitted). – Selected bond distances [Å] and angles [°]: **1a**: Au–Au′ 3.201(1), Au–P 2.253(3), Au–Cl 2.299(4), C–P 1.88(2); P–Au–Cl 172.5(1), P–C–P′ 107.5(7), H–C–P–Au 158.88(1); **1b**: Au1–Au2 3.281(1), Au1–Au3 3.420(1), Au2–Au3 3.329(1), Au1–P1 2.240(6), Au2–P2 2.231(5), Au3–P3 2.238(6), Au1–Cl1 2.296(6), Au2–Cl2 2.283(5), Au3–Cl3 2.281(5), C–P1 1.84(2), C–P2 1.87(2), C–P3 1.88(2); P1–Au1–Cl1 171.7(2), P2–Au2–Cl2 174.2(2), P3–Au3–Cl3 172.9(2), P1–C–P2 111(1), P1–C–P3 109(1), P2–C–P3 109(1), H–C–P1–Au1 156.16(1), H–C–P2–Au2 160.37(1), H–C–P3–Au3 161.38(1)

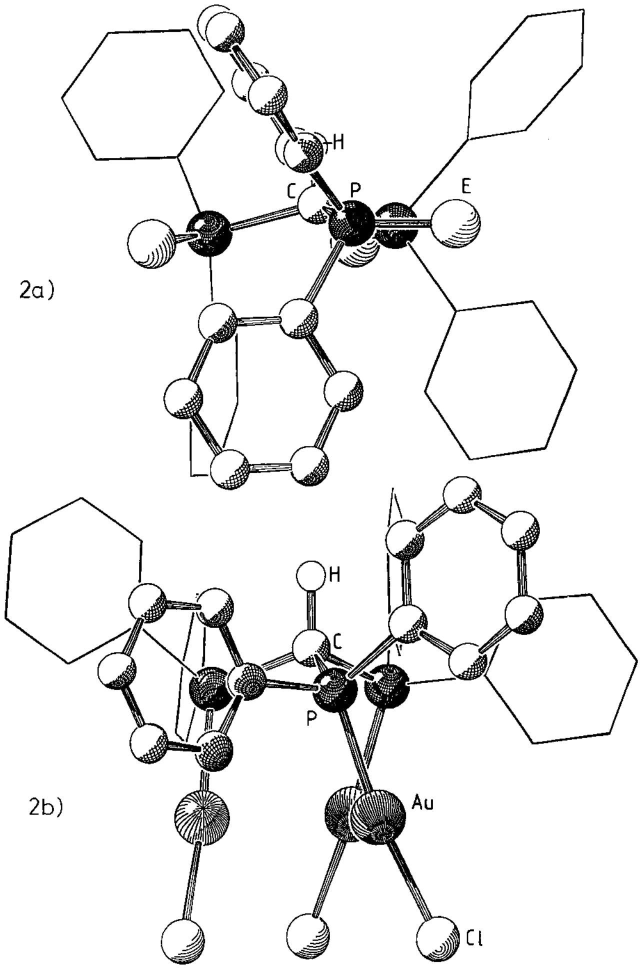


Figure 2. *all-trans* Orientation of the phosphorus lone pairs (E) in the free ligand, calculated as the missing corners of the pseudo-tetrahedra (dihedral angle H – C – P – E ca. 90°, 2a), compared with the *all-cis* orientation of the Au – Cl units in **1a** (dihedral angle H – C – P – Au 158.88(1)°, 2b)

be of the same order of magnitude, which would confirm previous estimates for dinuclear complexes[2d,9,10].

This result clearly demonstates that the Au···Au attraction between the closed shell (d^{10}) metal centers is operative as a weak, but conformation-determining force not only in pairs or extended chains of gold atoms, but also for triangular units. However, in a given trinuclear complex the intramolecular triangular gold clustering may not necessarily be the energetically most favorable constitution in the crystal: The structure of the more flexible molecule $HC(CH_2PPh_2AuCl)_3$ shows intra- and intermolecular pairing of gold atoms instead of the internal triangular coordination observed in **1**[2h], a caveat for all future structure predictions.

Further structural details of compounds **1a** and **1b** are listed in the Figure captions, in Tables 1, 2, and in the depository material.

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Experimental

All experiments were carried out under dry and purified nitrogen. Solvents and glassware were dried and saturated/filled with nitrogen. – NMR: [D_2]dichloromethane and [D_6]dimethyl sulfoxide as solvents, tetramethylsilane and phosphoric acid as reference compounds, Jeol JNM GX 270 and GX 400 spectrometers. – MS: Varian MAT 311 (FD). – Tris(diphenylphosphanyl)methane and chloro(dimethyl sulfide)gold(I) were prepared as described[15,16], all other reagents were obtained commercially.

Trichloro-μ_3-[tris(diphenylphosphanyl)methane]-trigold(I) (**1**): To a solution of chloro(dimethyl sulfide)gold(I) (1.34 g, 4.55 mmol) in 100 ml of dichloromethane a solution of tris(diphenylphosphanyl)methane (0.85 g, 1.50 mmol) in 70 ml of the same solvent was added dropwise at room temp. Upon stirring for 1 h, **1** precipitated as a white solid. The reaction mixture was concentrated in vacuo to 50 ml, and the precipitation of **1** was completed by the addition of 150 ml of pentane. The solid was filtered, washed with 30 ml of pentane, and dried in vacuo. Recrystallisation from dichloromethane/diethyl ether yielded 1.52 g of white needles of **1** (80%), m.p. 273°C (dec.). – ^1H NMR ([D_6]DMSO): $\delta = 6.47$ [q, $^2J(PH) = 10.07$ Hz, 1H, HCP_3], 7.11 [t, $^3J(HH) = 7.33$ Hz, 12H, *m*-H], 7.28 [t, $^3J(HH) = 7.33$ Hz, 6H, *p*-H], 7.87 [s, br. ($A_2A'_2X$), $N = 19.5$ Hz, 12H, *o*-H]. – $\{^1H\}^{13}C$ NMR ([D_6]DMSO): $\delta = 32.05$ [q, $^1J(CP) = 18.30$ Hz, HCP_3], 126.03 [m (AXX'_2), $N = 54.0$ Hz, C-1], 128.60 [m (AXX'_2), $N = 47.3$ Hz, C-3,5], 132.40 (s, C-4), 135.09 [s, br. (AXX'_2), $N = 27.5$ Hz, C-2,6]. – ^{13}C NMR: $^1J(CH) = 162.80$ Hz. – $\{^1H\}^{31}P$ NMR ([D_6]DMSO): $\delta = 39.61$ [s]. – MS (FD, CH_2Cl_2): *m/z* (%) = 1066 (1.78) [M^+ – Au – H], 834 (100) [M^+ – Au – H – AuCl], 798 (4.05) [834 – Cl]. – ^{197}Au-Mößbauer ($T = 4$ K), IS (mm/s) = 2.47, QS (mm/s) = 7.29.

$C_{37}H_{31}Au_3Cl_3P_3$ (1265.8)

Calcd.	C 35.11	H 2.47	Au 46.68	Cl 8.40	P 7.34
Found	C 35.03	H 2.64	Au 47.60	Cl 8.12	P 7.55

Tribromo-μ_3-[tris(diphenylphosphanyl)methane]-trigold(I) (**2**): A suspension of **1** (0.20 g, 0.16 mmol) in 90 ml of acetone was heated under reflux and treated with 3 ml of concentrated aqueous hydrogen bromide (47%, 26.14 mmol). After 90 min of stirring under reflux and 3 h at room temp. the orange-yellow suspension was filtered, and the orange-brown solid was recrystallized from dichloromethane/diethyl ether to yield 0.195 g of colorless needles (88%), m.p. 282°C (dec.). – ^1H NMR ([D_6]DMSO): $\delta = 6.64$ [q, $^2J(PH) = 9.77$ Hz, 1H, HCP_3], 7.11 [t, $^3J(HH) = 7.33$ Hz, 12H, *m*-H], 7.28 [t, $^3J(HH) = 7.33$ Hz, 6H, *p*-H], 7.88 [s, br. ($A_2A'_2X$), $N = 19.5$ Hz, 12H, *o*-H]. – $\{^1H\}^{13}C$ NMR ([D_6]DMSO): $\delta = 32.78$ [q, $^1J(CP) = 17.30$ Hz, HCP_3], 126.44 [m (AXX'_2), $N = 66.0$ Hz, C-1], 128.52 ["q" (AXX'_2), $N = 12.2$ Hz, C-3,5], 132.34 (s, C-4), 134.89 ["q" (AXX'_2), $N = 28.9$ Hz, C-2,6]. – $\{^1H\}^{31}P$ NMR ([D_6]DMSO): $\delta = 38.85$ (s). – MS (FD, CH_2Cl_2): *m/z* (%) = 1202 (31.04) [M^+ – Au], 1120 (5.72) [M^+ – Au – HBr], 924 (100) [1120 – Au], 740 (95.47) [924 – $P(C_6H_5)_2$], 660 (52.68) [740 – Br].

$C_{37}H_{31}Au_3Br_3P_3$ (1399.2)

Calcd.	C 31.76	H 2.23	Br 17.13	P 6.64
Found	C 30.04	H 2.27	Br 15.25	P 6.57

Triiodo-μ_3-[tris(diphenylphosphanyl)methane]-trigold(I) (**3**): A suspension of KI (0.56 g, 3.77 mmol) was slowly added to a suspension of **1** (0.43 g, 0.34 mmol) in 300 ml of acetone under reflux. The resulting mixture was stirred for 1 h at this temp. and for 20 h at room temp., then concentrated to 20 ml. Treatment with 150 ml of pentane afforded a white precipitate, which was collected and recrystallized from dichloromethane/diethyl ether to yield colorless needles (0.36 g, 70%), m.p. 319–323°C (dec.). – ^{1}H NMR ([D$_6$]DMSO): $\delta = 6.53$ (s, 1H, HCP$_3$), 7.09 [t, ^3J(HH) = 7.00 Hz, 12H, *m*-H], 7.28 [t, ^3J(HH) = 7.00 Hz, 6H, *p*-H], 7.97 [s, br. ($A_2A'_2X$), $N = 20.9$ Hz, 12H, *o*-H]. – $\{^1H\}^{13}$C NMR ([D$_6$]DMSO): $\delta = 30.70$ (s, HCP$_3$), 126.88 [s, br. (AXX'_2), C-1], 128.40 [s, br. (AXX'_2), $N = 10.7$ Hz, C-3,5], 132.27 (s, C-4), 134.79 [s, br. (AXX'_2), $N = 15.3$ Hz, C-2,4]. – $\{^1H\}^{13}$P NMR ([D$_6$]DMSO): $\delta = 37.16$ (s).

$C_{37}H_{31}Au_3I_3P_3$ (1540.2) Calcd. C 28.85 H 2.03
Found C 28.79 H 2.29

Trimethyl-μ_3-[tris(diphenylphosphanyl)methane]-trigold(I) (**4**): **1** (0.48 g, 0.38 mmol) was suspended in 50 ml of diethyl ether and treated dropwise with 2 ml of a solution of methyllithium (1.6 M in diethyl ether, 3.2 mmol), then diluted with 10 ml of diethyl ether, at 0°C. The reaction mixture was allowed to warm to room temp. and stirred for 6 h. Then it was cooled to 0°C, treated with 50 ml of dichloromethane and filtered. Addition of 150 ml of pentane led to the formation of a colorless precipitate of **4** (0.32 g, 70%), which was separated, washed with 50 ml of pentane, and dried in vacuo, m.p. 165°C (dec.). – ^{1}H NMR (CD$_2$Cl$_2$): $\delta = 0.88$ ["t" ($A_3X)_3$, $N = 7.9$ Hz, 9H, PAuCH$_3$], 5.72 [q, ^2J(PH) = 8.75 Hz, 1H, HCP$_3$], 7.02 [t, ^3J(HH) = 7.33 Hz, 12H, *m*-H], 7.14 [t, ^3J(HH) = 7.33 Hz, 6H, *p*-H], 7.79 [s, br. ($A_2A'_2X$), 12H, *o*-H]. – $\{^1H\}^{13}$C NMR (CD$_2$Cl$_2$): $\delta = 9.25$ ["dt" (AXX'_2), $N' = 96.0$ Hz, PAuCH$_3$], 33.32 [q, ^1J(CP) = 5.60 Hz, HCP$_3$], 128.46 ["q" (AXX'_2), $N = 11.5$ Hz, C-3,5], 130.30 [m (AXX'_2), $N = 51.1$ Hz, C-1], 131.30 (s, C-4), 135.63 ["q" (AXX'_2), $N = 15.3$ Hz, C-2,6]. – $\{^1H\}^{31}$P NMR (CD$_2$Cl$_2$): $\delta = 41.19$ (s). – MS (FD, CH$_2$Cl$_2$): m/z (%) = 1204 (5.03) [M$^+$], 1189 (3.31) [M$^+$ – CH$_3$], 992 (100) [M$^+$ – CH$_3$ – Au], 780 (18.8) [M$^+$ – 2 CH$_3$ – 2 Au].

$C_{40}H_{40}Au_3P_3$ (1204.6) Calcd. C 39.89 H 3.35 P 7.71
Found C 39.47 H 3.40 P 7.10

Crystal Structure Determination of Complex **1**, *HC[P(C$_6$H$_5$)$_2$-AuCl]$_3$*: Enraf-Nonius CAD4 diffractometer, Mo-K_α radiation, $\lambda = 0.71069$ Å, graphite monochromator, $T = -50$°C.

Crystal Data (**1a**): $C_{37}H_{31}Au_3Cl_3P_3$, $M_{rel} = 1265.84$, cubic space group $I\bar{4}3d$ (No. 220) with $a = 24.539(2)$ Å, $V = 14704.3$ Å^3, $Z = 16$, $d_{calcd.} = 2.276$ g/cm^3, μ(Mo-K_α) = 122.2 cm^{-1}, 3988 reflections, 2670 unique, and 2148 "observed" with $F_o \geqslant 4\sigma(F_o)$ [*hkl* range: ±31, +31, +31, with $k > l > h$, $(\sin\theta/\lambda)_{max} = 0.5779$ Å], data corrected for absorption effects (empirical). The structure was solved with direct methods (SHELXS 86[19]) and refined with anisotropic displacement parameters for all non-hydrogen atoms (SHELX 76[20]). The hydrogen atom at C-1 was found, phenyl hydrogen atoms were calculated and fixed in idealized geometry with $U_{iso(fix)} = 0.05$. R (R_w) = 0.046 (0.047), $w = 1.5029/(\sigma^2(F_o) + 0.000537\, F_o^2)$ for 140 refined parameters; residual electron density: +7.39/–2.07 e/Å^3, located on the threefold axis. R (R_w) of the enantiomorphic structure: 0.0634 (0.0794).

Crystal Data (**1b**): $C_{37}H_{31}Au_3Cl_3P_3 \cdot 2\,CH_2Cl_2$, $M_{rel} = 1435.71$, monoclinic space group $P2_1/c$ (No. 14) with $a = 11.239(2)$, $b = 19.687(5)$, $c = 19.224(4)$ Å, $\beta = 104.74(2)$°, $V = 4125.9$ Å^3, $Z = 4$, $d_{calcd.} = 2.311$ g/cm^3, μ(Mo-K_α) = 112.1 cm^{-1}, 9568 reflections, 8850 unique, and 5831 "observed" with $F_o \geq 4\sigma(F_o)$ [*hkl* range: ±14, +25, +24, $(\sin\theta/\lambda)_{max} = 0.638$ Å^{-1}], measurement data corrected for absorption (empirical). The structure was solved with direct methods (SHELXS 86[19]) and refined with anisotropic displacement parameters for all non-hydrogen atoms (SHELX 76[20]) except for C and Cl atoms of the disordered solvent molecules, which were refined with $U_{iso(fix)} = 0.10$. All hydrogen atoms were calculated and fixed in idealized geometry with $U_{iso(fix)} = 0.05$. R (R_w) = 0.065 (0.068), $w = 2.3547/\sigma^2(F_o)$ for 415 refined parameters, residual electron density: +6.10/–7.12 e/Å^3, located at one of the solvent molecules.

Further information on the X-ray structure determinations may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, W-7514 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD-55662, the names of the authors, and the journal citation.

CAS Registry Numbers

1: 137845-40-0 / **1** · 2 CH$_2$Cl$_2$: 137845-41-1 / **2**: 137845-42-2 / **3**: 137868-37-2 / **4**: 137845-43-3 / chloro(dimethyl sulfide)gold(I): 29892-37-3

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