Coordination Chemistry of Dimethylgold Halides with Bidentate Phosphorus and Arsenic Ligands – Revisited

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Dimethylgold(III) chloride and bromide, $(Me_2AuX)_2$, react with bis(diphenylphosphanyl)methane (dppm, molar ratio 1:2) to give the *P*-monohapto complexes *cis*-Me₂AuX(dppm) (**1a**, **b**) in quantitative yields. The products are readily oxidized by air to yield the *P*-hapto *P'*-monoxides **2a**, **b**. Treatment of **1a**, **b** with AgNO₃ affords an ionic nitrate $[Me_2Au(dppm)]_2$ $[NO_3^-]_2$ (**1c**), which contains a dinuclear cation. A mixed bromide/nitrate (from **1b** and half the equivalent amount of AgNO₃) is thermally unstable and undergoes elimination of ethane to give an ionic tetranuclear gold(I) complex $[(dppm)_4Au_4Br_2]^{2+}$ $[NO_3^-]_2$ (**3b**). – Treatment of (Me_2AuCl)₂ with CH₂(AsPh₂)₂ (dpam, molar ratio 1:2) gives *cis*-Me₂-

AuCl(dpam) (1d), the arsenic analog of 1a, which is not sensitive to oxygen. – The reaction of bis(diphenylphosphanyl)amine (dppa) yields 1:1 *P*-monohapto adducts Me₂. AuX(dppa), which are in equilibrium with ionic chelated systems Me₂Au(dppa)⁺ X⁻ (1e, f). Complex 1e is readily oxidized by air to the *P*-hapto *P'*-monoxide *cis* complex 2e. Treatment of 1e with AgNO₃ gives the ionic nitrate Me₂. Au(dppa)⁺ NO₃⁻ (1g). – All compounds were identified by standard analytical and spectroscopic techniques. The crystal structures of 2a, 3b, 1d, and 2e were determined by singlecrystal X-ray diffraction studies.

Dialkylgold(III) halides were among the first organogold compounds to be discovered by Gibson as early as $1907^{[1]}$. Their chemistry was developed further by Coates, Tobias, Kochi, and others^[2-4] as well as in our own laboratories^[5], but since about 1980 very little work has been done in this area of research. Originally, the interest in dialkylgold(III) complexes arose from the discovery that these compounds are surprisingly stable both thermally (e.g. as compared to silver compounds!), and also towards water and oxygen. They are colorless and diamagnetic and feature a characteristic square-planar *cis* geometry. There are analogies with the *cis*-diorganoplatinum(II) complexes, which are important reference systems for catalytically active platinum compounds^[6].

For diorganogold(III) compounds no catalyst properties could be found, however, and even the attempts to use them as model systems were of limited success. Furthermore, work with R_2AuX compounds was often discouraging since all available literature procedures gave yields no higher than 40% even in experienced hands.

The recent renewed attention is associated with the use of dialkylgold(III) compounds as volatile precursors for the deposition of gold metal on substrates^[7] and with potential medical applications (in the therapy of rheumatism, arthritis, and cancer)^[8]. There is also a significant progress to be noted in the synthesis of dimethylgold(III) halides by using tetramethyltin as a methylating reagent for HAu- $Cl_4(aq)^{[9]}$.

In the recent advances in diorganogold(III) chemistry the field of complexes with bidentate ligands proved to be most promising. We therefore reexamined some of the simple reactions in order to delineate further their course and their products. As ligands we used mainly bis(diphenylphosphanyl)methane (dppm), bis(diphenylphosphanyl)amine (dppa), and bis(diphenylarsanyl)methane (dpam), which had been studied also in some of our earlier studies^[10–12].

Bis(diphenylphosphanyl)methane as a Ligand of Dimethylgold(III) Halides and Nitrate

The dimers of cis-chloro- and cis-bromodimethylgold(III) react with two equivalents of dppm in diethyl ether at ambient temperature to give colorless, crystalline products of 1:1 stoichiometry (1a, b) (Scheme 1). The composition and the molecular mass follow from the analytical data and from the mass spectra. The ³¹P-NMR spectra of the products in chloroform at room temperature show two broadened doublet signals of an AX pattern in each case, which become sharp as the temperature is lowered to -60 °C. It therefore appears that the molecules are fluxional in solution at room temperature with the Me₂Au unit undergoing site exchange at a monohapto dppm ligand. This is confirmed by the variable-temperature ¹H- and ¹³C-NMR spectra.

Complexes 1a, **b** undergo decomposition upon heating, predominantly with evolution of ethane (below). Solutions of 1a, **b** were also found to be surprisingly susceptible to oxidation by traces of oxygen at ambient temperature. Both species were converted rapidly and quantitatively into the *P*-monoxides 2a, **b**, which readily crystallized from the solutions. The molecular structures of 2a, **b** were established on the basis of analytical and spectroscopic data, and the crystal structure of 2a was determiend by a single-crystal X-ray Scheme 1



diffraction study (Figure 1). The gold atom is in a squareplanar environment with the two methyl groups in a *cis* position. As expected the dppmO ligand is *P*-bound, not *O*bound.

Figure 1. Molecular structure of the molecule $C_{27}H_{28}AuClOP_2$ (2a) (ORTEP, 50% probability ellipsoids, H atoms omitted for clarity). – Selected bond lengths [Å] and angles [°]: Au–Cl 2.053(9), Au–C2 2.081(8), Au–Cl1 2.370(2), Au–Pl 2.389(2), P2–O 1.511(7); Cl–Au–C2 85.9(5), Cl–Au–Pl 96.1(4), P1–Au–Cl1 89.00(8), Cl1–Au–C2 88.9(4)



According to the NMR data compounds 2a, b appear to be nonfluxional in solution: The two Au-bound methyl groups are nonequivalent, and their signals show no significant changes of chemical shifts or coupling constants at ambient temperature and at -60 °C (in CDCl₃).

Treatment of **1a** or **1b** with *silver nitrate* in methanol at low temperature affords the ionic compound $[Me_4Au_2(dppm)_2]^{2+} 2 NO_3^-$ (**1c**). The same product is obtained from the ligand and dimethylgold(III) nitrate, prepared in situ from $[Me_2AuCl]_2$ and AgNO₃. A structure with a doubly dppm-bridged dinuclear cation is suggested on the basis of the analytical and spectroscopic data. The compound is significantly less stable than the halide precursors and undergoes decomposition by reductive elimination of ethane quite rapidly both as a solid and in solution at ambient temperature.

Products of Reductive Elimination of Ethane from 1a-c

Upon heating of complexes 1a, b to +80 °C slow reductive elimination of ethane is observed, as detected by NMR spectroscopy and GLC/MS investigations. This decomposition pathway is typical of Me₂AuX(L) complexes and was studied in some detail in earlier work^[7,13-17]. The final product of the decomposition of 1a was fully characterized to be a dimer [(dppm)AuCl]₂ with an eight-membered ring structure and an *exo*-bound chlorine ligand at each of the two gold centers, which exhibit a T-shaped configuration^[18,19].

The products of the thermal elimination of ethane from complex 1c (in the solid or in pure solvents) may be written as $[(dppm)_2Au_2]^{2+}$ 2 NO₃⁻ (3a). All analytical data are in agreement with this proposal, and there is ample precedent for salts of the $[(dppm)_2Au_2]^{2+}$ dication, which is known to be a folded eight-membered ring with short transannular Au-Au contacts^[20-22].

$$1c \xrightarrow{\Delta I} [(dppm)_2Au]^{2+} 2 NO_3^- 3a$$

The thermal stability and the decomposition pathways of compounds 1a, e, and g (below) were also investigated by differential thermogravimetry followed by mass spectrometry (DTG/MS). On heating of the gold(III) compounds two distinct steps of decomposition are observed in the DTG curves as well as in the mass spectra of the volatile decomposition products. The first step indicates the loss of the two methyl groups attached to gold, which is in agreement with the observed weight decrease of the samples. At the same time the occurrance of ions with masses corresponding to CH_3^+ and $C_2H_6^+$ reaches a maximum in the

total ion count (TIC) of the mass spectra. This reductive elimination leads to new gold(I) species which decompose in the second step at higher temperatures to finally give metallic gold.

However, in the presence of bromide ions in the solutions of 1c undergoing reductive elimination of ethane, a novel product is obtained which is also an ionic species, but with a *tetranuclear* dication (3b). The same product is generated if two equivalents of 1b are treated with only one equivalent of AgNO₃ in methanol (Scheme 2). The crystal and molecular structure of 3b was determined by single-crystal X-ray diffraction analysis.

Scheme 2



The dication is composed of two dinuclear units $[(dppm)_2Au_2Br]^+$. In each unit the bromide ion is bridging two gold(I) centers, which show a short intramolecular Au-Au contact. External Au-Br contacts are responsible for the aggregation of these units into dimers (Figure 2).

 $[(dppm)_2Au_2]^{2+}$ complexes associated with (pseudo)halide anions were observed previously in various configurations, ranging from end-on at one gold atom (colinear or perpendicular with the Au-Au axis) to assymmetrical or symmetrical A-frame bridging $(A-D)^{[18-23]}$. The present case **3b** is the first example where type **D** is further aggregated. The dication has a crystallographic center of inversion in the middle of the intercationic Au-Au contact. The four gold atoms and the two bromine atoms are in a common plane and form two vertex-linked Au₂Br triangles. These triangles have slightly different Au-Br distances and are thus not isosceles triangles as might be expected for type **D**, which is fully symmetrical.

Bis(diphenylarsanyl)methane as a Ligand of Dimethylgold(III) Chloride

Dimeric chlorodimethylgold(III) reacts with two molequivalents of bis(diphenylarsanyl)methane (dpam) in



Figure 2. Molecular structure of the dication $[C_{50}H_{44}Au_2BrP_{4}]_2$ in its dinitrate salt **3b** (ORTEP, 50% probability ellipsoids, H atoms omitted for clarity). – Selected bond lengths [Å] and angles [°]: Au1–P1 2.307(4), Au1–P3 2.298(4), Au1–Br 3.058(2), Au1–Au2 3.0226(11), Au2–P2 2.396(4), Au2–P4 2.403(4), Au2–Br 3.013(2), Au2–Br' 3.063(2); Au2–Au1–Br 59.40(4), Au1–Au2–Br 60.88(4), Br-Au2–Br' 82.81(5), P1–Au1–P3 169.43(14), P2–Au2–P4 157.3(14)



dichloromethane to give a mononuclear product 1d in high yields (Scheme 3). The product decomposes at $129 \,^{\circ}$ C with evolution of ethane to leave a colorless solid, tentatively described as [(dpam)AuCl]₂. The NMR-spectroscopic data of chloroform solutions of 1d suggest a structure with a square-planar configuration at gold having the methyl groups retained in *cis* positions and the dpam ligand monohapto-coordinated. This assignment was confirmed by a crystallographic study (Figure 3). The NMR spectra show no significant temperature dependence, and the structure of 1d therefore appears to be non-fluxional in solution. In contrast to the observation with the phosphorus analog 1a, the second arsenic donor center in molecule 1d does not compete succesfully with the chloride ligand for the fourth coordination site at Au(III).

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Bis(diphenylphosphanyl)amine as a Ligand of Dimethylgold Chloride, Bromide, and Nitrate

The ligand (Ph₂P)₂NH (dppa) reacts with chloro- or bromodimethylgold(III) in diethyl ether to give the 1:1 complexes 1e and 1f, respectively (Scheme 4). The NMR spectra are temperature-dependent. They indicate an equilibrium between an ionic (Cl⁻, Br⁻), symmetrical component (a) and a mono (P)-hapto structure (b). At low temperature $(-60 \,^{\circ}\text{C}$ in chloroform) the symmetrical species (a) predominates (a/b \approx 20). The ³¹P-NMR spectrum shows only one singlet resonance for the two phosphorus atoms in (a), and in the ¹H- and ¹³C-NMR spectra the resonances of the hydrogen and carbon atoms of the methyl groups are identified as A₃XX'A₃ and AXX' spin systems, respectively. At ambient temperature (20 °C, $a/b \approx 0.5$) the monohapto form (b) is present as the main component. By analogy with the congeners 1a and 1b, a rapid ligand exchange becomes visible through line broadening and quenching of P,P-coupling in the ³¹P-NMR spectra.

Figure 3. Molecular structure of the molecule $C_{27}H_{28}AuAs_2Cl$ (1d) (ORTEP, 50% probability ellipsoids, H atoms omitted for clarity). – Selected bond lengths [A] and angles [°]: Au–Cl 2.050(7), Au–C2 2.061(6), Au–Cl1 2.383(2), Au–As1 2.4812(7); C1–Au–C2 86.9(3), C2–Au–Cl1 90.7(3), Cl1–Au–As1 87.03(5), As1–Au–Cl 95.3(2)



It was again observed that the complexes 1e, f are readily oxidized in solution by air, and the mono-oxidation product 2e was isolated. The spectroscopic data are indicative of a molecular structure with the two methyl groups in *cis* positions at square-planar gold and with the dppaO ligand *P*bound to the metal.

The crystal structure of **2e** was elucidated on the basis of X-ray data. Its features are very similar to those of **2a**, the main difference being a trigonal-planar imino group bridging the two phosphorus atoms instead of the tetrahedral methylene group in **2a**. The P-N-P angle in **2e** of $127.9(2)^{\circ}$ is larger than the P-C-P angle in **2a** [113.0(4)°]. The imino group is not hydrogen-bonded, but its hydrogen atom is orientated towards the chlorine atom (Figure 4).

Figure 4. Molecular structure of the molecule $C_{26}H_{27}AuCINOP_2$ (2e) (ORTEP, 50% probability ellipsoids, H atoms omitted for clarity). – Selected bond lengths [Å] and angles [°]: Au-C1 2.070(5), Au-C2 2.042(5), Au-C1 2.391(1), Au-P1 2.382(1), P2-O 1.467(3); C1-Au-C2 85.7(2), C2-Au-P1 92.6(2), P1-Au-Cl 90.74(4), C1-Au-C1 90.9(2)



Compound 2e melts with decomposition at $136 \,^{\circ}$ C. The residue of the ethane evolution contains elemental gold and is thus not a well-defined Au(I) complex, owing to the poorer donor properties of the P=O function for Au(I).

Treatment of dimethylgold(III) *nitrate* (generated in situ from Me₂AuBr and AgNO₃ in methanol) with dppa gives the ionic complex 1g. As derived from the NMR data and by analogy with 1e, f (above) the cation is symmetrical and gives rise to a single P resonance and an A₃XX'A'₃ spin system for the methyl hydrogen atoms. The FAB mass spectrum shows the mononuclear cation and fragmentation products. No ions of higher oligomers are present.

All dppa complexes decompose with reductive elimination of ethane. The gold(I) complexes generated as solid residues were not characterized further since their composition and structure are straightforward in standard cases. There are prototypes reported in the literature which can be used as guidelines^[24].



Discussion

The present work has shown that the reaction of 1,3-difunctional phosphorus and arsenic ligands with dialkylgold(III) chloride and bromide leads to mononuclear square-planar gold(III) complexes, in which the methyl groups remain in the *cis* position and the incoming ligands show monohapticity. It is only upon replacement of the halogen atoms by a more efficient leaving group like the nitrate anion that chelation becomes the favoured mode of complexation. It should be noted that the analogous reactions with 1,4-difunctional phosphorus ligands (like dppe) give chelated complexes with ligand dihapticity^[5]. It thus appears that it is the strain of the four-membered rings which makes monohapticity the preferred alternative to the systems under investigation.

The dppm- or dppa-chelated dimethylgold(III) cations are less stable in their nitrates than in the acyclic halide complexes and undergo rapid elimination of ethane to yield cyclic dinuclear gold(I) complexes already at ambient temperature. Ethane elimination is generally the preferred and remarkably selective decomposition pathway for $Me_2AuX(L)$ complexes, but it requires external heating to occur with the non-chelated complexes.

The cyclic dinuclear gold(I) complexes obtained as the decomposition products were obtained previously from gold(I) precursors, and their structures are known from these earlier investigations $(A-D)^{[18-23]}$. It was now found for the first time, however, that these rings can be associated to give more extended aggregates, as observed for the cationic species [(dppm)₄Au₄Br₂]²⁺ in its dinitrate (3b).

It was surprising to discover that the complexes $Me_2AuX(L)$ with L = dppm or dppa (1) are readily oxi-

dized in solution by air at ambient temperature to give the corresponding dppmO or dppaO complexes (2). The oxidation of the *complexed* ligand is clearly more rapid than that of the *free* ligand. This implies that this oxidation is a metal-assisted process, the mechanism of which still needs to be elucidated. The diarsenic ligand dpam is less susceptible to oxidation, and no complexes with an arsenic oxide ligand were detected. This probably reflects the higher oxidation potential of arsenic as compared to phosphorus. The arsenic oxidation is not favored even in the case of metal-assistance.

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Experimental

All experiments were carried out under pure, dry nitrogen. Solvents were purified, dried, and stored over molecular sieves under nitrogen. – NMR: TMS as internal standard for ¹H and ¹³C{¹H} and H₃PO₄ (85% in H₂O) as external standard for ³¹P{¹H}; Jeol-GX 400 and Jeol-GX 270. – MS: Finnigan MAT90. – DTG/MS: Perkin Elmer TGA7 coupled with a Balzers QMG 420 spectrometer; the samples were heated from 50 to 400 °C within 35 min. dppm^[25], dpam^[27], [Me₂AuCI]₂, and [Me₂AuBr]₂^[9] were prepared according to literature methods.

[Bis(diphenylphosphanyl)methane-P]chloro-cis-dimethylgold(III) (1a): A solution of $[Me_2AuCl]_2$ (0.115 g, 0.220 mmol) in 3 ml of diethyl ether was added to a suspension of dppm (0.169 g, 0.440 mmol) in 3 ml of the same solvent. Within 1 min a voluminous, colorless precipitate formed. After stirring for 2 h the product was filtered off, washed with little diethyl ether, and dried in vacuo. Yield 0.270 g (95%), m.p. 188 °C (dec.). - ¹H NMR (CDCl₃,

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-60 °C): δ = 0.94 [d, ³*J*(HP) = 8.3 Hz, CH₃ (*cis*-P)], 1.15 [d, ³*J*(HP) = 9.0 Hz, CH₃ (*trans*-P)], 3.58 (m, N = 11.0 Hz, CH₂), 7.1–7.7 (m, Ph). $-^{31}P\{^{1}H\}$ NMR (CDCl₃, -60 °C): δ = -26.9 [d, ²*J*(PP) = 58 Hz, P], 26.3 [d, ²*J*(PP) = 58 Hz, P-Au]. $-^{13}C\{^{1}H\}$ NMR (CDCl₃, -60 °C): δ = 9.8 [d, ²*J*(CP) = 5.0 Hz, CH₃ (*cis*-P)], 18.8 [d, ²*J*(CP) = 114.6 Hz, CH₃ (*trans*-P)], 24.1 [dd, ¹*J*(CP) = 23.1, 30.3 Hz, CH₂], 126–137 (m, Ph). - DTG/MS (*T* = 188 °C): weight decrease: calcd. 4.6%, found 4.8%; obs. masses: *m/z* 15, 30; (*T* = 318 °C): weight decrease: calcd. 64.9%, found 65%; obs. masses: *m/z* 183, 200.

Bromo[bis(diphenylphosphanyl)methane-P]-cis-dimethylgold(III) (1b): According to the procedure described for 1a, with 0.130 g (0.212 mmol) of [Me₂AuBr]₂ and 0.163 g (0.424 mmol) of dppm. Yield 0.281 g (96%) of 1b, m.p. 148 °C (dec.). – ¹H NMR (CDCl₃, -60 °C): $\delta = 1.02$ [d, ³J(HP) = 8.3 Hz, CH₃ (cis-P)], 1.22 [d, ³J(HP) = 9.0 Hz, CH₃ (trans-P)], 3.69 [d, ¹J(HP) = 10.7 Hz, CH₂], 7.1–7.8 (m, Ph). – ³¹P{¹H} NMR (CDCl₃, -60 °C): $\delta =$ -27.0 [d, ²J(PP) = 71 Hz, P], 24.2 [d, ²J(PP) = 71 Hz, P-Au]. – ¹³C{¹H} NMR (CDCl₃, -60 °C): $\delta =$ 13.8 [d, ²J(CP) = 4.4 Hz, CH₃ (cis-P)], 17.5 [d, ²J(CP) = 115 Hz, CH₃ (trans-P)], 25.6 [dd, ¹J(CP) = 22.5, 29.5 Hz, CH₂], 126–137 (Ph)]. – C₂₇H₂₈AuBrP₂ (691.3): calcd. C 46.91, H 4.08, Br 11.56; found C 46.03, H 4.02, Br 11.84. – MS (FAB), m/z: 611.4 [Me₂Au(dppm)]⁺, 581.4 [Au(dppm)]⁺ (100%).

Chloro [(diphenylphosphanyl) (diphenylphosphinyl) methane-P Jcis-dimethylgold (III) (2a): A solution of 1a (0.160 g, 0.247 mmol) in 20 ml of CH₂Cl₂ was exposed to air. After the solvent had evaporated, 2a was isolated by crystallization of the residue from CH₂Cl₂/Et₂O; colorless crystals, yield 0.134 g (82%), m.p. 156°C (dec.). – ¹H NMR (CDCl₃, 20°C): $\delta = 0.73$ [d, ³J(HP) = 8.9 Hz, CH₃ (*cis*-P)], 1.12 [d, ³J(HP) = 9.2 Hz, CH₃ (*trans*-P)], 4.03 [t, ²J(HP) = 12 Hz, CH₂], 7.3–7.45 (m, Ph). – ³¹P{¹H} NMR (CDCl₃, 20°C): $\delta = 25.2$ [d, ²J(PP) = 14 Hz], 25.4 [d, ²J(PP) = 14 Hz]. – ¹³C{¹H} NMR (CDCl₃, 20°C): $\delta = 9.8$ [d, ²J(CP) = 4.8 Hz, CH₃ (*cis*-P)], 18.3 [d, ²J(CP) = 109 Hz, CH₃ (*trans*-P)], 27.2 [dd, ¹J(CP) = 15, ¹J(CP=O) = 60 Hz, CH₂], 128.5–134.5 (Ph). – C₂₇H₂₈AuClOP₂ (662.9): calcd. C 48.92, H 4.26, Cl 5.35; found C 47.89, H 4.11, Cl 5.48. – MS (FAB), *m*/z: 627 [Me₂Au(dppmO)]⁺, 612 [MeAu(dppmO)]⁺, 597 [Au(dppmO)]⁺ (100%), 400 [dppmO]⁺.

Bromo [(diphenylphosphanyl) (diphenylphosphinyl) methane-P]cis-dimethylgold(III) (2b) was prepared from 1b (0.138 g, 0.200 mmol) as described for 2a. Yield 0.131 g (93%), m.p. 139 °C (dec.). - ¹H NMR (CDCl₃, 20 °C): δ = 0.88 [d, ³J(HP) = 8.3 Hz, CH₃ (cis-P)], 1.15 [d, ³J(HP) = 9.3 Hz, CH₃ (trans-P)], 4.11 [t, ²J(HP) = 12 Hz, CH₂], 7.3-7.45 (m, Ph). - ³¹P{¹H} NMR (CDCl₃, 20 °C): δ = 22.8 [d, ²J(PP) = 14.3 Hz], 26.1 [d, ²J(PP) = 14.3 Hz]. - MS (FAB), *m*/z: 627 [Me₂Au(dppmO)]⁺, 612 [MeAu(dppmO)]⁺, 597 [Au(dppmO)]⁺ (100%).

Bis- μ -[bis(diphenylphosphanyl)methane-P,P']-cis,cis-tetramethyldigold(III) Dinitrate (1c): To a solution of [Me₂AuBr]₂ (0.144 g, 0.235 mmol) in 10 ml of methanol AgNO₃ (0.080 g, 0.471 mmol) was added, and the reaction mixture was stirred for 2 h. The AgBr precipitate was filtered off and the clear and colorless filtrate added to a suspension of dppm (0.181 g, 0.471 mmol) in 10 ml of Et₂O/THF. After stirring for 2 h all volatile compounds were evaporated in vacuo. Recrystallization of the residue from CH₂Cl₂/ Et₂O afforded 1c as a colorless solid, yield 0.166 g (86%), m.p. 171 °C (dec.). – ¹H NMR (CDCl₃, –60 °C): $\delta = 1.14$ (broad s, CH₃). 4.50 (broad s, CH₂), 7.1–7.7 (m, Ph). – ³¹P{¹H} NMR (CDCl₃, –60 °C): $\delta = 35.3$ s. – ¹³C{¹H} NMR (CDCl₃, –60 °C): $\delta = 26.5$ (m, CH₂), 27.6 (m, CH₃), 125–134 (m, Ph). – MS (CI), m/z: 1223 [M + 1]⁺ (100%). Bis[μ -bromo-bis- μ -[bis(diphenylphosphanyl)methane]digold(I)] Dinitrate (**3b**): To a solution of **1b** (0.150 g, 0.217 mmol) in 20 ml of CH₂Cl₂ was added a solution of AgNO₃ (0.0184 mg, 0.108 mmol) in 20 ml of methanol. After stirring for 20 min the solvents were removed in vacuo, and the residue was extracted with CH₂Cl₂. The clear filtrate was allowed to stand at ambient temp. for 2 d, after which reductive elimination was complete. Compound **3b** was isolated as colorless crystals by slow evaporation of the solvent, yield 105 mg (82%), m.p. 271 °C (dec.). – MS (FAB), m/z: 1241.8/ 1243.8 [M⁺], 1162.8 [Au₂(dppm)₂]⁺ (100%), 857.4/859.4 [Au₂(dppm)Br]⁺.

[Bis(diphenylarsanyl)methane-As]chloro-cis-dimethylgold(III) (1d): According to the procedure described for 1a, with 0.204 g (0.389 mmol) of $[Me_2AuCl]_2$ and 0.368 g (0.779 mmol) of dpam. Colorless crystals from CH₂Cl₂. Yield 0.520 g (91%), m.p. 129°C (dec.). – ¹H NMR (CDCl₃, 20°C): δ = 0.88 [s, CH₃ (*cis*-As)], 1.33 [s, CH₃ (*trans*-As)], 3.21 (s, CH₂), 7.17–7.63 (m, Ph). – ¹³C{¹H} NMR (CDCl₃, 20°C): δ = 6.80 (s, CH₃), 19.9 (s, CH₃), 22.0 (s, CH₂), 128–134 (Ph). – MS (FAB), *m/z*: 734 [M⁺], 719 [MeAu-(dpam)Cl]⁺, 699 [Me₂Au(dpam)]⁺, 669 [Au(dpam)]⁺ (100%), 472 [dpam]⁺.

[Bis(diphenylphosphanyl)amine-P]chloro-cis-dimethylgold(III) (1e): dppa (0.367 g, 0.952 mmol) was added to a solution of [Me₂AuCl]₂ (0.250 g, 0.476 mmol) in 10 ml of diethyl ether. After stirring for 5 h at 20 °C a minor amount of a solid was filtered off. Evaporation of the solvent from the filtrate and recrystallization of the residue from CH₂Cl₂/pentane afforded 1e as a colorless solid. Yield 0.574 mg (93%), m.p. 171°C (dec.). - ¹H NMR (CDCl₃, -60 °C): $\delta = 1.27$ (broad s, A₃XX'A₃, CH₃), 7.41-7.84 (m, Ph). $- {}^{13}C$ NMR (CDCl₃, $-60 \circ C$): $\delta = 11.5$ [dd, AXX', ${}^{2}J(CP)_{cis} =$ 7.4, ²J(CP)_{trans} = 112 Hz, CH₃], 129.4–132.7 (m, Ph). – ³¹P NMR $(CDCl_3, -60 \circ C)$: $\delta = 30.3$ [d, ${}^2J(PP) = 10$ Hz], 35.3 (s, P cyclic isomer), 64.0 [d, ${}^{2}J(PP) = 10$ Hz]. $- {}^{1}H$ NMR (CDCl₃, -20 °C): $\delta = 0.88$ [d, ³J(HP) = 9.3 Hz, CH₃ (*cis*-P)], 1.17 [d, ³J(HP) = 9.8 Hz, CH₃ (trans-P)], 1.30 (broad s, A₃XX'A₃, CH₃ cyclic isomer), 7.3-7.9 (m, Ph). $-^{31}$ P NMR (CDCl₃, -20° C): $\delta = 30.8$ [d, ${}^{2}J(PP) = 10$ Hz], 34.9 (s, P cyclic isomer), 64.2 [d, ${}^{2}J(PP) = 10$ Hz]. $- {}^{1}$ H NMR (CDCl₃, 20 °C): $\delta = 0.88$ [d, ${}^{2}J$ (HP) = 9.3 Hz, CH₃ (cis-P)], 1.17 [d, ${}^{2}J(HP) = 9.8$ Hz, CH₃ (trans-P)], 1.30 (broad s, $A_3XX'A_3'$, CH₃ cyclic isomer), 7.3-7.9 (m, Ph). - ³¹P NMR $(CDCl_3, 20^{\circ}C)$: $\delta = 31.0 \text{ [d, } {}^2J(PP) = 10 \text{ Hz}$], 34.7 (s, cyclic isomer), 64.4 [d, ${}^{2}J(PP) = 10$ Hz]. – DTG/MS ($T = 171 \,^{\circ}C$): weight decrease: calcd. 4.6%, found 4.7%; obs. masses: m/z 15, 30; (T = 335°C): weight decrease: calcd. 64.9%, found 65%; obs. mass: m/z 152.

[Bis(diphenylphosphanyl)amine-P]bromo-cis-dimethylgold(III) (1f): According to the same procedure as described for 1a, with 0.173 g (0.282 mmol) of [Me₂AuBr]₂ and 0.217 g (0.563 mmol) of dppa. Yield 0.355 mg (91%), m.p. 140 °C (dec.). – ¹H NMR (CDCl₃, -60 °C): $\delta = 1.28$ (broad s, A₃XX'A'₃, CH₃), 5.8 (broad s, NH), 7.2–7.9 (m, Ph). – ¹³C{¹H} NMR (CDCl₃, -60 °C): $\delta =$ 11.57 [dd, ²J(CP)_{cis} = 7.2, ²J(CP)_{trans} = 111 Hz, CH₃], 128–133 (m, Ph). – ³¹P{¹H} NMR (CDCl₃, -60 °C): $\delta =$ 30.9 [d, ²J(PP) = 10 Hz], 37.0 (s, cyclic isomer), 63.5 [d, ²J(PP) = 10 Hz]. – ³¹P{¹H} NMR (CDCl₃, 20 °C): $\delta =$ 32.1 (s), 36.6 (s), 63.7 (s), all broad.

Chloro[(diphenylphosphanyl)(diphenylphosphinyl)amine-P]-cisdimethylgold(III) (2e): According to the procedure described for 2a, with 0.200 g (0.309 mmol) of 1e. Yield 0.179 g (87%), m.p. 136°C (dec.). – ¹H NMR (CDCl₃, 20°C): $\delta = 0.93$ [d, ³J(HP) = 9.5 Hz, CH₃ (cis-P)], 1.21 [d, ³J(HP) = 9.8 Hz, CH₃ (trans-P)], 3.8–4.3 (broad s, NH), 7.2–7.8 (m, Ph). – ³¹P{¹H} NMR (CDCl₃, 20°C): $\delta = 25.0$ [d, ²J(PP) = 39 Hz, P(O)], 60.6 [d, ²J(PP) = 39

Table 1. X-ray structural analyses, details of solution and refinement

	2a	bl	2e	36
empirical formula	C27H28AuClOP2	C27H28AuAs2Cl	C26H27AuCINOP2	C ₅₀ H ₄₄ Au ₂ BrNO ₃ P ₄
formula weight	662.85	734.75	663.84	1304.64
crystal system	orthorhombic	orthorhombic	monoclinic	monoclinic
space group (No.)	$P2_12_12_1$ (19)	$P2_12_12_1$ (19)	P21/c (14)	P21/n (14)
a [Å]	10.536 (2)	10.635(1)	12.885 (1)	15.210 (2)
b [Å]	11.910 (2)	12.050(1)	11.836 (1)	15.104 (2)
c [Å]	20.690 (4)	20.476(4)	17.863 (2)	22.137 (3)
β [°]	90	90	110.80(1)	107,46 (1)
V [Å']	2596.3	2624.0	2546.7	4851.3
pente [gcm ⁻³]	1.70	1.86	1.73	1.44
z	4	4	4	4
F(000) [e]	1296	1408	1296	2100
$\mu(Mo-K_{\alpha})$ [cm ⁻¹]	59.1	82.2	60.3	39.6
cryst. dim. [mm]	0.20, 0.25, 0.50	0.10, 0.25, 0.40	0.35, 0.30, 0.35	0.35, 0.30, 0.15
T [°C]	20	-71	-72	-62
scan	θ-θ	۵	۵	θ- θ
hkl-range	+13/±15/+26	+13/±15/+26	±15/±15/+22	+19/-19/±26
measured reflections	6097	6152	11286	10443
unique reflections	5653	5709	5531	10415
observed reflections	5653	5709	5530	10415
Rint	0.0198	0.0245	0.0458	0.0000
$F_o^2 \ge$	-3 σ(F _o ²)	-3 σ(F _e ²)	-3 σ(F _o ²)	-3 σ(F₀²)
refined parameters	291	282	295	527
H-atoms (found/calc.)	-/28	-/28	-/27	-/44
absorption corr.:	DIFABS	DIFABS	DIFABS	DIFABS
Tmis/Tmax	0.559/1.000	0.634/1.000	0.520/1.000	0,240/1.000
R ^[a] based on F (OMIT 4)	0.035	0.030	0.029	0.086
R _w ^(b)	0.089	0.060	0.072	0.259
weighting par. ^[c] (a,b)	0.0429, 4.73	0.0265, 1.22	0.0329, 1.44	0.0929, 191.02
o. (max/min) ^[d] [eÅ-3]	2.14/-1.18	0.91/ -0.63	1.54/ -1.27	2.78/ -4.94

[a]
$$R = \frac{\sum ||F_o| - ||F_o||}{\sum ||F_o||}$$
; [b] $wR_2 = \sqrt{\frac{\sum w (F_o^2 - F_o^2)^2}{\sum w (F_o^2)^2}}$
[c] $w = \frac{1}{\sigma^2 F_o^2 + (aP)^2 + bP} \quad p = \frac{Max (F_o^2 \cdot 0) + 2F_o^2}{3}$; [d] located at the gold-atoms,

Hz, P(Au)]. $-{}^{13}C{}^{1}H$ NMR (CDCl₃, 20°C): $\delta = 9.57$ [d, ${}^{2}J(CP) = 5.3$ Hz, CH₃ (cis-P)], 16.2 [dd, ${}^{2}J(CP) = 123$, ${}^{4}J(CP) =$ 2.9 Hz, CH₃ (trans-P)], 128-134 (m, Ph). - C₂₆H₂₇AuClNOP₂ (663.9): calcd. C 47.04, H 4.10, Cl 5.34, N 2.11; found C 45.75, H 4.18, Cl 5.48, N 1.94.

[Bis(diphenylphosphanyl)amine-P,P']-cis-dimethylgold(III) Nitrate (1g): A solution of AgNO₃ (0.080 g, 0.471 mmol) in 10 ml of methanol was added to a solution of [Me₂AuBr]₂ (0.144 g, 0.235 mmol) in 10 ml of methanol kept at -10 °C, and the reaction mixture was stirred for 2 h. The AgBr precipitate was filtered off and the clear and colorless filtrate added to a suspension of dppa (0.181 g, 0.471 mmol) in 10 ml of Et₂O/THF. After stirring for 2 h all volatile compounds were evaporated in vacuo, and the residue was crystallized from CH₂Cl₂/Et₂O to afford 1g as a colorless solid, yield 0.166 g (86%), m.p. 138 °C (dec.). – ¹H NMR (CDCl₃, 20 °C): $\delta = 1.39$ (broad s, A₃XX'A'₃, CH₃), 7.4–7.9 (m, Ph). – ³¹P NMR (CDCl₃, 20 °C): $\delta = 36.2$ s. $-C_{26}H_{27}AuN_2O_3P_2$ (674.4): calcd. C 46.30, H 4.04, N 4.15; found C 45.13, H 3.93, N 4.09. - DTG/MS (T = 138 °C): weight decrease: calcd. 4.4%, found 4.7%; obs. mass: m/z 30; (T = 350 °C): weight decrease: calcd. 66.3%, found 65.8%.

Crystal Structure Determination: Suitable crystals of compounds 1d, 2a, 2e, and 3b were sealed into glass capillaries and examined with an Enraf Nonius CAD4-diffractometer with Mo- K_{α} radiation. Intensity data were corrected for Lorentz polarization and absorption effects. Structures were solved by direct methods and refined by full-matrix least-squares calculations against F^2 . Details of solution and refinement are given in Table 1. Further information may be obtained from Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-59205, the names of the authors, and the journal citation.

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