Neutral Gold(I) Complexes with Mixed Phosphorus Ligands[☆]

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The reaction of compounds $(R_3P)AuMe$ with diphenylphosphinous acid $Ph_2P(O)H$ affords methane and neutral complexes of the type $(R_3P)AuP(O)Ph_2$ (**1a**: R = Me; **1b**: R = Ph; **1c**: R = *o*-Tol). **1a**, **b** are obtained in high yield, but the yield of **1c** is lower owing to a side-reaction which leads to a different product: $Ph_2P(OH)-Au-P(O)Ph_2$ (**2**). The crystal structure of **1a** was determined by a single-crystal X-ray diffraction study. The compound is a monomer with a linear P−Au−P' axis and the phosphane and phosphinite ligands in a staggered conformation. In solution ($CHCl_3$, CH_2Cl_2) compounds **1a**−**c** undergo a ligand redistribution, establishing equilibria that involve ionic isomers of the type $[(R_3P)_2Au]^+$ $[Au(P(O)Ph_2)_2]^-$, which are readily identified through their NMR data. The analogous reaction of $(R_3P)AuMe$ with dimethylphosphite $(MeO)_2P(O)H$ gives methane and the corresponding dimethylphosphites of the type $(R_3P)AuP(O)(OMe)_2$ (**3a**: R = Me; **3b**: R = Ph; **3c**: R = *o*-Tol). The crystal structure of **3b** has also been determined. It features a linear structure with an eclipsed conformation of the ligands. In polar solvents ($CHCl_3$, methanol) there is again an equilibrium between neutral and ionic isomers, the latter comprising bis(phosphane)gold cations $[(R_3P)_2Au]^+$ and $[Au[P(O)(OMe)_2]_2]^-$ anions, as confirmed by NMR spectroscopy and mass spectrometry.

Introduction

The use of gold compounds in modern technology is largely based on sulfur and phosphorus compounds of gold(I)[1]. In gold-sulfur chemistry the sulfide S^{2-} and thiolate RS^- anions are far superior to neutral diorganosulfides R_2S as ligands for Au(I) and are therefore the preferred auxiliary components of compounds applied in medicine, modern surface technology and traditional gilding preparations[2]. Self-assembled monolayers of thiols on gold surfaces are also assumed to have a gold/thiolate interface[3].

By contrast, in gold−phosphorus chemistry the neutral tertiary phosphanes R_3P are the predominant groups of ligands, and anionic phosphorus components have not been developed systematically as an alternative for gold(I) complexation. There are scattered reports on compounds with diorganophosphide ligands, which are generally oligo- or polymeric owing to the four-electron donor capacity of the R_2P^- anions[4]. Only very limited information is available on the role of monodentate phosphinite $R_2(O)P^-$ and phosphite ligands $(RO)_2(O)P^-$, and the few examples described in the literature were mostly encountered by chance as oxidation or hydrolysis products of other complexes[5].

Because of the growing interest in gold compounds that are volatile, or that are soluble in common organic solvents, stable to light, air and moisture, and that undergo controlled thermal degradation to gold and byproducts amenable to rapid decontamination, we have investigated mononuclear gold(I) complexes bearing a neutral phosphane R_3P group and an anionic diorgano phosphinite $R_2(O)P^-$ or diorganophosphite $(RO)_2(O)P^-$ group as ligands. This combination can give rise either to neutral compounds with a mixed complexation of gold(I), e.g. R_3P-$AuP(O)R_2$, or to ionic species with homoleptic cations and anions, e.g. $[(R_3P)_2Au]^+$ $[Au(P(O)R_2)_2]^-$.

Preparation, Characterization and Structures of the Compounds

(Phosphane)gold(I) Diphenylphosphinites: After a few unsuccessful exploratory experiments with (phosphane)gold halides and metal phosphinites or related precursors, (phosphane)gold(I) *alkyls* were finally chosen as the starting materials for the title compounds. Treatment of substrates of the type $(R_3P)Au$-Me with equivalent quantities of diphenylphosphinous acid in boiling toluene leads to the evolution of methane and affords the desired products **1** without any noticeable decomposition. This route has the disadvantage that the goldalkyl complexes have to be prepared in a separate, critical step[6], but there is also the advantage of high yields (of **1a**, **b**) and an easy workup in the final reaction (eq. 1).

$$(R_3P)Au-Me + Ph_2P(O)H \rightarrow CH_4 + (R_3P)AuP(O)Ph_2 \qquad (1)$$

(**1a**, **b**, **c**: R = Me, Ph, *o*-Tol, respectively)

The reaction of $(o\text{-Tol})_3PAu-Me$ with $Ph_2P(O)H$ gives product **1c** in much lower yields, and there is a byproduct which has the net composition $[Ph_2P(OH)-Au-P(O)Ph_2]_n$ (**2**) and is also available by different routes[7].

$$2\ (o\text{-Tol})_3P-Au-Me + 3\ Ph_2P(O)H \rightarrow 2CH_4 + (o\text{-Tol})_3P + \mathbf{1c} + \tfrac{1}{n}\ \mathbf{2} \quad (2)$$

The products **1a**−**c** are colorless to beige crystalline compounds, stable to air and moisture, and soluble in chloroform, dichloromethane and tetrahydrofuran, sparingly soluble in toluene, and insoluble in diethyl ether and pentane. Their composition was confirmed by elemental analysis, mass spectrometry and NMR spectroscopy. The mass spectra (FAB) show the cations of the intact molecules as the parent peaks, but the ions of homoleptic complexes are also observed. This result indicates at least a partial ligand redistribution to give cations $[(R_3P)_2Au]^+$ and anions $[Au(P(O)Ph_2)_2]^-$.

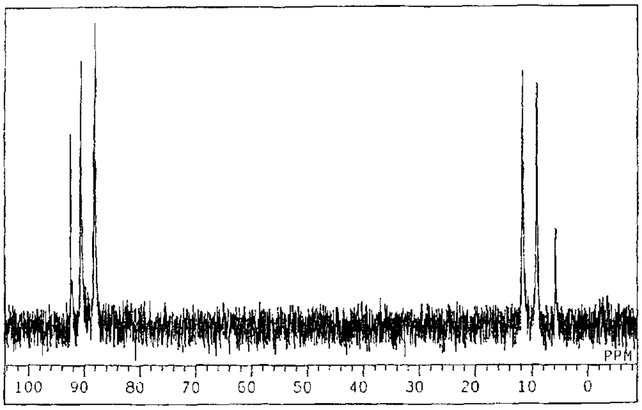
The $^{31}P\{^1H\}$ spectra of solutions in chloroform show AB patterns with large $^2J(P_AP_B)$ couplings, indicative of strong covalent P_A-Au-P_B bonding in *trans* positions. The ^1H and $^{13}C\{^1H\}$ spectra show the two sets of signals expected for the phosphane and diphenylphosphinite ligands, respectively (see the Experimental Section).

At low temperature (−60°C) a diagnostic long-range coupling $^4J(H-C-P_A-Au-P_B)$ of the methyl hydrogen atoms is observed for **1a**, but there is coalescence of the pertinent doublet splitting upon warming of the samples. This temperature dependence indicates some ligand exchange, which is also evident from the collapse of the AB patterns in the ^{31}P spectra at different coalescence temperatures. The most probable origin of this exchange is again the ligand redistribution to give ionic species (eq. 3).

$$2\ (R_3P)AuP(O)Ph_2 \rightleftarrows [(R_3P)_2Au]^+\ [Au(P(O)Ph_2)_2]^- \qquad (3)$$

Upon close inspection of the $^{31}P\{^1H\}$-NMR spectra, the ionic species can indeed also be detected as minor components of the solution equilibria. The AB spin system of **1a** (Figure 1) is accompanied by two smaller singlet resonances which are readily assigned to $[(Me_3P)_2Au]^+$ and $[Au(P(O)Ph_2]^-$ from their chemical shift values[5,8]. The relative concentrations show little temperature dependence in the low-temperature region. At elevated temperatures coalescence occurs (see above). Finally, small $A_9XX'A'_9$ and AXX' patterns, respectively, were observed in the ^1H and $^{13}C\{^1H\}$ spectra of **1a**, due to the presence of the $[(Me_3P)_2Au]^+$ cation. These results are consistent evidence for the validity of the ligand redistribution model in chloroform and dichloromethane solutions.

Figure 1. $^{31}P\{^1H\}$-NMR spectrum of compound **1a** in $CDCl_3$ at 20°C



Careful layering of dichloromethane solutions of compound **1a** with pentane induces exclusive crystallization of the neutral component, however. Crystals of **1a** are orthorhombic, space group $Cmc2_1$, with 4 formula units per unit cell. In the lattice the molecules have crystallographic mirror symmetry (Figure 2). The P1−Au−P2 axis is linear [179.0(2)°] and the two Au−P bonds are of equal length within the standard deviations of the experiment. The Me_3P and $P(O)Ph_2$ units are in a staggered conformation, with the oxygen atom and one of the methyl carbon atoms (C22) mutually *trans* in the mirror plane (Figure 3). The geometries of the PMe_3 and $P(O)Ph_2$ units show no anomalies[5,8]. Owing to the bulk of the ligands there are no close intermolecular contacts between the metal atoms or the metal and the oxygen atoms.

Figure 2. Molecular structure of compound **1a** with atomic numbering (ORTEP drawing, 50% probablility ellipsoids, hydrogen atoms omitted for clarity); selected bond lengths [Å] and angles [°]: Au−P1 2.311(1), Au−P2 2.313(2), P1−O 1.524(8), P1−C11 1.820(7), P2−C21 1.818(9), P2−C22 1.801(12); P1−Au−P2 179.0(2), O−P1−Au 117.4(4), O−P1−C11 109.2(3), C11−P1−C11' 101.3(4), Au−P2−C21 113.6(3), Au−P2−C22 116.3(5), C21−P2−C22 104.2(4), C21−P2−C21' 103.6(6)

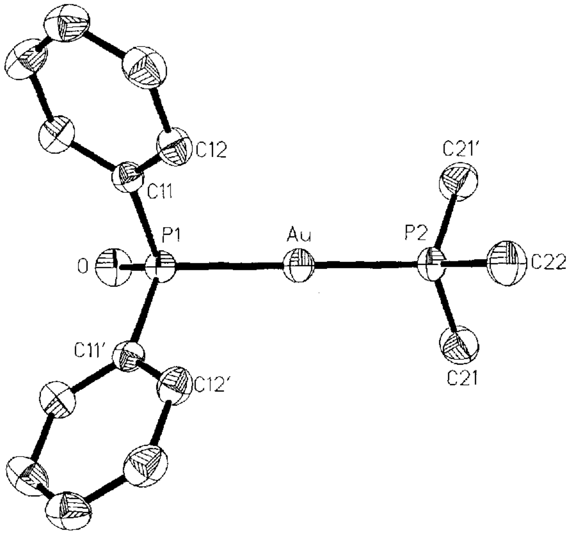
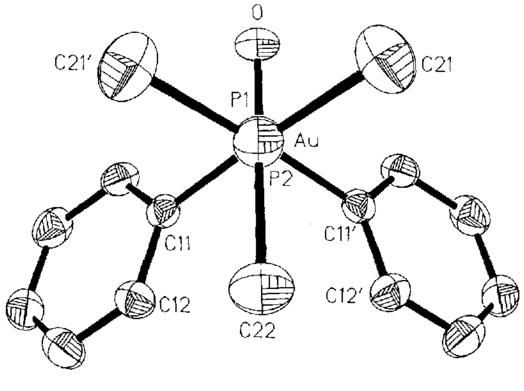


Figure 3. View of compound **1a**, showing the staggered conformation of the Me_3P and $P(O)Ph_2$ units



(Phosphane)gold(I) Dimethylphosphites: (Phosphane)gold methyl compounds were found to undergo a clean reaction also with dimethylphosphite $(MeO)_2P(O)H$ in refluxing toluene with evolution of methane. High yields of products **3a**−**c** were isolated as orange (**3a**) or colorless solids (**3b, c**), which are stable to air and moisture, soluble

in chloroform, dichloromethane and tetrahydrofuran, sparingly soluble in toluene, and insoluble in diethyl ether or pentane.

$$(R_3P)Au{-}Me + (MeO)_2P(O)H \rightarrow CH_4 + (R_3P)Au{-}P(O)(OMe)_2$$

(**3a**, **b**, **c**: R = Me, Ph, *o*-Tol, respectively) (4)

Attempts to prepare compounds **3** through the reaction of the halide complexes $(R_3P)AuX$ wit $P(OMe)_3$ were unsuccessful. No Arbusov-type process occurred and only mixtures of unidentified products were obtained.

Compounds **3a–c** were characterized by microanalytical and spectroscopic data. The $^{31}P\{^1H\}$-NMR spectra show AB spin systems with large $^2J(P_AP_B)$ coupling constants. For complex **3a** these signals are accompanied by two small singlet resonances, which are readily assigned to the ionic species drawn in the ligand redistribution equilibrium according to eq. 5.

$$2\ (Me_3P)Au{-}P(O)(OMe)_2 \rightleftarrows [(Me_3P)_2Au]^+\ \{Au[P(O)(OMe)_2]_2\}^- \qquad (5)$$

The ^1H and ^{13}C spectra of **3a** contain signal patterns in full agreement with these components. A long-range ^4J(H–C–P–Au–P) coupling is again detectable (see **1a** above). In $CDCl_3$ solution the mixed-ligand species is strongly dominant and accounts for about 85% of the total (at ambient temperature). In methanol the amount of neutral **3a** is strongly reduced, to about 60% under comparable conditions. As expected, this result shows that the equilibrium (eq. 5) is shifted to the side of the ionic compound as the polarity of the solvent is increased. Ligand exchange processes are slow on the NMR timescale for compound **3a** and no coalescence phenomena are observed in the spectra at temperatures up to 50°C (in $CDCl_3$). The ligand exchange processes are thus much slower than with compound **1a**.

Compounds **3b**, **c** do not take part in ligand redistribution equilibria in solution. The NMR spectra show only the resonances of the mixed-ligand complexes. This result is explained on the basis of steric effects, which prevent close metal–phosphorus and metal–metal contacts between molecules. Note that compound **3a** has the two smallest ligands of the series.

Compound **3b** was crystallized by layering solutions in dichloromethane with diethyl ether. The crystals are triclinic, space group $P\bar{1}$, with 4 formula units per unit cell. The asymmetric unit contains two independent molecules, one of which is disordered (Figure 5). The discussion therefore refers to the non-disordered molecule, which has no crystallographically imposed symmetry (Figure 4). The coordination of the gold atom is linear [P3–Au–P4 176.08(4)°] and the two ligands are in an eclipsed conformation (Figure 5). The Au–P bond to the Ph_3P ligand [Au2–P3 2.317(1) Å] is significantly longer than the Au–P bond to the phosphite ligand [Au2–P4 2.289(1) Å]. The internal geometries of the ligands show no anomalies. There are no unusual intermolecular contacts. For crystals of **3a** such intermolecular contacts are more likely because the small ligands should minimize steric effects. The orange color of solid **3a**, which disappears in solution, is evidence of such a structural anomaly, since color and luminescence have previously been observed for a large number of gold(I) complexes with short intermolecular Au···Au contacts[9]. This effect is quenched in solution by efficient solvation.

Figure 4. Molecular structure of compound **3b** with atomic numbering of the non-disordered molecule (ORTEP drawing, 50% probability ellipsoids, only the non-disordered molecule of the two crystallographically independent molecules is shown, hydrogen atoms are omitted for clarity); selected bond lengths [Å] and angles [°]: Au2–P3 2.317(1), Au2–P4 2.288(1), P4–O41 1.479(3), P4–O42 1.603(4), P4–O43 1.593(4); P3–Au2–P4 176.08(4)

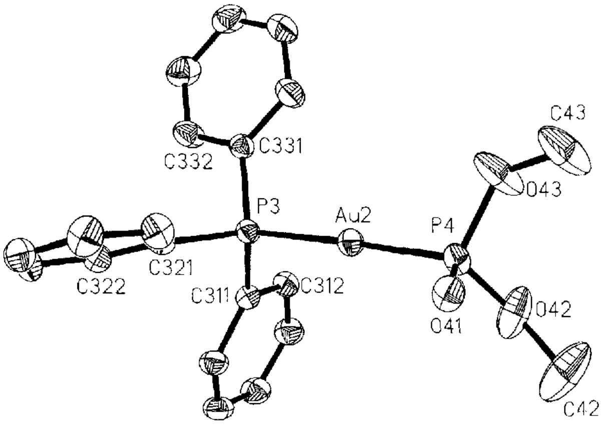
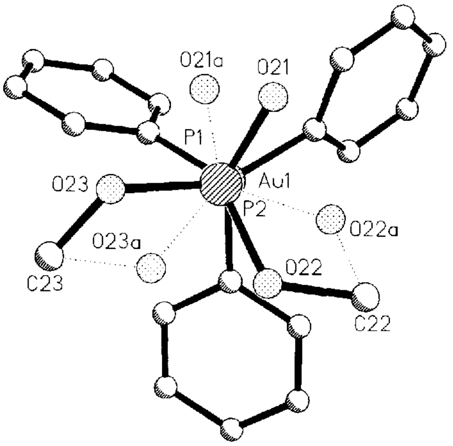


Figure 5. View of compound **3b**, showing the eclipsed conformation of the two ligands in the molecule where the methoxy groups are disordered



Discussion and Conclusions

Phosphinite and phosphite anions can be used as powerful P-monodentate ligands for gold(I). Together with tertiary phosphines, robust neutral mixed-ligand complexes are obtained (eqs. 1 and 4). In the crystal mononuclear compounds with a linear P–Au–P′ axis are present (Figures 2 and 4), but in polar solvents some ligand redistribution may occur to give ionic compounds with homoleptically coordinated cations and anions (eqs. 3 and 5). For the phophinite complexes (e.g. **1b**) a ligand exchange process is observed which is rapid on the NMR time scale at ambient temperature. With large substituents [$(o\text{-Tol})_3P$, **1c**] this process is much slower owing to steric hindrance in the transition states of exchange and in the homoleptic ionic products. For the phosphite complexes this exchange is also absent (or slow) in the temperature region up to 60°C, indicating stronger bonding of the $P(O)(OMe)_2$ ligands than of the $P(O)Ph_2$ ligands. This is consistent with the observation of a significantly shorter Au−P bond in the former as determined in the structural studies.

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Experimental Section

General: All experiments were routinely carried out in an atmosphere of dry nitrogen. Solvents were dried and saturated with nitrogen; glassware was oven-dried and filled with nitrogen. Standard analytical and spectroscopic equipment was used throughout. Starting materials were commercially available or prepared and purified following published procedures. All NMR data were recorded in $CDCl_3$ at 23°C unless otherwise stated.

(Trimethylphosphane)gold(I) Diphenylphosphinite (**1a**): A mixture of methyl(trimethylphosphane)gold(I), Me_3PAuMe[6] (176 mg, 0.61 mmol), and diphenylphosphinous acid, $Ph_2P(O)H$ (123 mg, 0.61 mmol), was dissolved in toluene (20 ml) and the resulting colorless solution was refluxed for 5 h with stirring until its color turned golden. The solvent (5 ml) was evaporated under vacuum and pentane (20 ml) was added to precipitate product **1a** as a white solid, which was recrystallized from dichloromethane/pentane to give colorless needles [247 mg, 85% yield; m.p. 185°C (dec.), stable to air and moisture, soluble in dichloromethane and tetrahydrofuran, sparingly soluble in toluene, and insoluble in diethyl ether and pentane]. − ^{1}H NMR: δ = 7.31−7.76 [m, Ph], 7.31−7.76 [m, $\{Au[P(O)Ph_2]_2\}^-$], 1.38 [s br., $\{Au(PMe_3)_2\}^+$], 1.49 [d, ^{2}J(P,H) = 9.8 Hz, Me]. − ^{1}H NMR (−60°C): δ = 7.31−7.76 [m, Ph], 7.31−7.76 [m, $\{Au[P(O)Ph_2]_2\}^-$], 1.37 [s br., $\{Au(PMe_3)_2\}^+$], 1.48 [dd, ^{2}J(P,H) = 9.8 Hz, ^{4}J(P,H) = 2.2 Hz, Me]. − ^{1}H NMR (50°C): δ = 7.33−7.74 [m, Ph], 7.33−7.74 [m, $\{Au[P(O)Ph_2]_2\}^-$], 1.46 [s br., $\{Au(PMe_3)_2\}^+$], 1.46 [s, br., Me]. − $^{13}C\{^{1}H\}$ NMR: δ = 130.7 [d, ^{2}J(P,C) = 13.8 Hz, *ortho*-CH], 129.4 [d, ^{4}J(P,C) = 2.8 Hz, *para*-CH], 128.1 [d, ^{3}J(P,C) = 11.0 Hz, *meta*-CH], *ipso*-C was not detected, 15.4 [d, ^{1}J(P,C) = 31.3 Hz, Me], 16.0 [pseudo-t, *N* = 34.9 Hz, $\{Au(PMe_3)_2\}^+$]. − $^{31}P\{^{1}H\}$ NMR: δ = 92.5 [s, $\{Au(P(O)Ph_2)_2\}^-$], 88.9 [d, ^{2}J(P,P) = 404.4 Hz, $P(O)Ph_2$], 10.0 [d, ^{2}J(P,P) = 404.4 Hz, PMe_3], 5.9 [s, $\{Au(PMe_3)_2\}^+$]. − $^{31}P\{^{1}H\}$ NMR (−60°C): δ = 93.2 [s, $\{Au[P(O)Ph_2]_2\}^-$], 90.9 [d, ^{2}J(P,P) = 400.7 Hz, $P(O)Ph_2$], 10.6 [d, ^{2}J(P,P) = 400.7 Hz, PMe_3], 7.0 [s, $\{Au(PMe_3)_2\}^+$]. − $^{31}P\{^{1}H\}$ NMR (50°C): δ = 92.4 [s, $\{Au[P(O)Ph_2]_2\}^-$], 88.8 [s, br., $P(O)Ph_2$], 10.6 [s, br., PMe_3], 5.3 [s, $\{Au(PMe_3)_2\}^+$]. − MS (FAB): *m/z* = 948 [2 M^+], 872 [2 M^+ − Me_3P], 747 [2 M^+ − $Ph_2P(O)$], 671 [2 M^+ − Me_3P − $Ph_2P(O)$], 600 [$\{Au(P(O)Ph_2)_2\}^-$], 474 [M^+], 398 [M^+ − Me_3P], 349 [$\{Au(PMe_3)_2\}^+$], 273 [M^+ − $Ph_2P(O)$], 201 [M^- − Me_3P − Au]. − $C_{15}H_{19}AuOP_2$ (474.23): calcd. C 37.99, H 4.04; found C 37.86, H 4.12.

(Triphenylphosphane)gold(I) Diphenylphosphinite (**1b**): The procedure was the same as described for **1a**, using 142 mg of methyl(triphenylphosphane)gold(I), Ph_3PAuMe[6] (0.30 mmol), and 61 mg of $Ph_2P(O)H$ (0.30 mmol); yield 191 mg, 96%; beige solid, m.p. 215°C (dec.), stable to air and moisture, soluble in dichloromethane and tetrahydrofuran, sparingly soluble in toluene and insoluble in diethyl ether and pentane. − ^{1}H NMR: δ = 7.78−7.83 [m, $P(O)Ph_2$], 7.31−7.51 [m, PPh_3]. − $^{13}C\{^{1}H\}$ NMR: δ = 144.8 [d, ^{1}J(P,C) = 56.2 Hz, *ipso*-C of $P(O)Ph_2$], 130.7 [d, ^{2}J(P,C) = 13.2 Hz, *ortho*-CH of $P(O)Ph_2$], 129.5 [s, *para*-CH of $P(O)Ph_2$], 128.2 [d, ^{3}J(P,C) = 8.2 Hz, *meta*-CH of $P(O)Ph_2$], 134.1 [d, ^{2}J(P,C) = 12.1 Hz, *ortho*-CH of PPh_3], 131.7 [s, *para*-CH of PPh_3], 129.3 [d, ^{3}J(P,C) = 9.4 Hz, *meta*-CH of PPh_3], *ipso*-C was not detected. − $^{31}P\{^{1}H\}$ NMR: δ = 88.6 [s br., $P(O)Ph_2$], 44.9 [s br., PPh_3]. − $^{31}P\{^{1}H\}$ NMR (−60°C): δ = 89.5 [d, ^{2}J(P,P) = 377.1 Hz, $P(O)Ph_2$], 44.8 [d, ^{2}J(P,P) = 377.1 Hz, PPh_3]. − MS (FAB): *m/z* = 721 [$\{Au(PPh_3)_2\}^+$], 660 [M^+], 600 [$\{Au(P(O)Ph_2)_2\}^-$], 459 [M^+ − $Ph_2P(O)$], 398 [M^+ − Ph_3P], 262 [M^+ − $Ph_2P(O)$ − Au], 201 [M^+ − Ph_3P − Au]. − $C_{30}H_{25}AuOP_2$ (660.44): calcd. C 54.56, H 3.82; found C 52.75, H 4.06.

(Tri-o-tolylphosphane)gold(I) Diphenylphosphinite (**1c**): The procedure was the same as described for **1a**, using 155 mg of methyl(tri-*o*-tolylphosphane)gold(I), *o*-Tol_3PAuMe[6] (0.30 mmol), and 61 mg of $Ph_2P(O)H$ (0.30 mmol). The reaction mixture contained the desired product **1c** in low yield as detected by NMR spectroscopy. Byproduct **2** was isolated from dichloromethane/pentane as colorless needles [yield of **2**: 65 mg, 36%; m.p. 195°C (dec.), stable to air and moisture, soluble in dichloromethane and tetrahydrofuran and insoluble in diethyl ether and pentane][7]. − **1c**: $^{31}P\{^{1}H\}$ NMR: δ = 85.9 [d, ^{2}J(P,P) = 379.2 Hz, $P(O)Ph_2$], 29.7 [d, ^{2}J(P,P) = 379.2 Hz, *o*-Tol_3P].

(Trimethylphosphane)gold(I) Dimethylphosphite (**3a**): Dimethyl phosphite $(MeO)_2P(O)H$ (30 µl, 0.33 mmol) was added to a solution of Me_3PAuMe[6] (95 mg, 0.33 mmol) in toluene (20 ml). The resulting colorless solution was refluxed for 5 h with stirring until its color turned golden. The solvent was evaporated under vacuum (5 ml) and pentane (20 ml) was added to precipitate product **3a** as an orange solid [110 mg, 87% yield; m.p. 161°C (dec.), stable to air and moisture, soluble in dichloromethane and tetrahydrofuran, sparingly soluble in toluene, and insoluble in diethyl ether and pentane]. − ^{1}H NMR: δ = 3.60 [d, ^{3}J(P,H) = 12.2 Hz, OMe], 3.50 [*pseudo*-t, *N* = 12.2 Hz, $\{Au[P(O)(OMe)_2]_2\}^-$], 1.69 [pseudo-t, *N* = 8.5 Hz, $\{Au(PMe_3)_2\}^+$], 1.48 [dd, ^{2}J(P,H) = 10.4 Hz, ^{4}J(P,H) = 3.1 Hz, Me]. − ^{1}H NMR ([D_4]methanol): δ = 3.49 [d, ^{3}J(P,H) = 12.8 Hz, OMe], 3.49 [pseudo-t, overlapped, $\{Au[P(O)(OMe)_2]_2\}^-$], 1.58 [pseudo-t, *N* = 8.6 Hz, $\{Au(PMe_3)_2\}^+$], 1.50 [dd, ^{2}J(P,H) = 10.4 Hz, ^{4}J(P,H) = 3.1 Hz, Me]. − ^{1}H NMR ([D_4]methanol, −60°C): δ = 3.55 [d, ^{3}J(P,H) = 12.5 Hz, OMe], 3.55 [pseudo-t, overlapped, $\{Au(P(O)(OMe)_2)_2\}^-$], 1.66 [pseudo-t, *N* = 8.5 Hz, $\{Au(PMe_3)_2\}^+$], 1.62 [dd, ^{2}J(P,H) = 10.7 Hz, ^{4}J(P,H) = 3.0 Hz, Me]. − ^{1}H NMR ([D_4]methanol, 50°C): δ = 3.55 [d, ^{3}J(P,H) = 12.8 Hz, OMe], 3.54 [pseudo-t, *N* = 12.8 Hz, $\{Au[P(O)(OMe)_2]_2\}^-$], 1.63 [pseudo-t, *N* = 7.9 Hz, $\{Au(PMe_3)_2\}^+$], 1.55 [dd, ^{2}J(P,H) = 10.4 Hz, ^{4}J(P,H) = 3.1 Hz, Me]. − $^{13}C\{^{1}H\}$ NMR: δ = 49.2 [d, ^{2}J(P,C) = 4.4 Hz, OMe], 48.7 [pseudo-t, *N* = 3.3 Hz, $\{Au[P(O)(OMe)_2]_2\}^-$], 16.4 [pseudo-t, *N* = 36.9 Hz, $\{Au(PMe_3)_2\}^+$], 15.5 [dd, ^{1}J(P,C) = 32.5 Hz, ^{3}J(P,C) = 2.8 Hz, Me]. − $^{13}C\{^{1}H\}$ NMR ([D_4]methanol): δ = 15.0 [pseudo-t, *N* = 37.8 Hz, $\{Au(PMe_3)_2\}^+$], 14.4 [dd, ^{1}J(P,C) = 34.0 Hz, ^{3}J(P,C) = 2.8 Hz, Me]. − $^{31}P\{^{1}H\}$ NMR: δ = 125.4 [s, $\{Au[P(O)(OMe)_2]_2\}^-$], 116.6 [d, ^{2}J(P,P) = 553.7 Hz, $P(O)(OMe)_2$], 8.9 [d, ^{2}J(P,P) = 553.7 Hz, PMe_3], 4.3 [s, $\{Au(PMe_3)_2\}^+$]. − $^{31}P\{^{1}H\}$ NMR ([D_4]methanol): δ = 129.8 [s, $\{Au[P(O)(OMe)_2]_2\}^-$], 124.0 [d, ^{2}J(P,P) = 544.9 Hz, $P(O)(OMe)_2$], 10.0 [d, ^{2}J(P,P) = 547.2 Hz, PMe_3], 7.2 [s, $\{Au(PMe_3)_2\}^+$]. − $^{31}P\{^{1}H\}$ NMR ([D_4]methanol, −60°C): δ = 127.9 [s, $\{Au[P(O)(OMe_2]_2\}^-$], 124.1 [d, ^{2}J(P,P) = 534.0 Hz, $P(O)(OMe)_2$], 9.4 [d, ^{2}J(P,P) = 534.1 Hz, PMe_3], 7.0 [s, $\{Au(PMe_3)_2\}^+$]. − $^{31}P\{^{1}H\}$ NMR ([D_4]methanol, 50°C): δ = 131.3 [s, $\{Au[P(O)(OMe)_2]_2\}^-$], 124.2 [d, ^{2}J(P,P) = 547.2 Hz, $P(O)(OMe)_2$], 10.4 [d, ^{2}J(P,P) = 549.3 Hz, PMe_3], 8.1 [s, $\{Au(PMe_3)_2\}^+$]. − MS (FAB): *m/z* = 655 [$\{Au(PMe_3)_2\}^+$ + Au-

P(O)(OMe)$_2$], 382 [M$^+$], 349 [{Au(PMe$_3$)$_2$}$^+$], 273 [M$^+$ − P(O)(OMe)$_2$]. − $C_5H_{15}AuO_3P_2$ (382.09): calcd. C 15.72, H 3.96, Au 51.55; found C 15.69, H 4.05, Au 51.20.

(Triphenylphosphane)gold(I) Dimethylphosphite (**3b**): The procedure was the same as described for **3a**, using 157 mg of Ph$_3$PAuMe[6] (0.33 mmol) and 30 µl of (MeO)$_2$P(O)H (0.33 mmol). **3b** was recrystallized from dichloromethane/diethyl ether to give colorless crystals; yield 154 mg, 82%; m.p. 148°C (dec.), stable to air and moisture, soluble in dichloromethane and tetrahydrofuran, sparingly soluble in toluene, and insoluble in diethyl ether and pentane. − ^{1}H NMR: δ = 7.44−7.48 [m, Ph], 3.66 [d, ^3J(P,H) = 12.2 Hz, OMe]. − ^{13}C{^{1}H} NMR: δ = 134.2 [d, ^2J(P,C) = 13.8 Hz, *ortho*-CH], 131.8 [d, ^4J(P,C) = 2.21 Hz, *para*-CH], 129.3 [d, ^3J(P,C) = 11.0 Hz, *meta*-CH], 129.0 [d, ^1J(P,C) = 52.3 Hz, *ipso*-C], 49.0 [d, ^2J(P,C) = 3.86 Hz, OMe]. − ^{31}P{^{1}H} NMR: δ = 113.7 [d, ^2J(P,P) = 521.0 Hz, P(O)(OMe)$_2$], 44.9 [d, ^2J(P,P) = 518.8 Hz, PPh$_3$]. − MS (FAB): *m/z* = 1027 [{Au(PPh$_3$)$_2$}$^+$ + AuP(O)(OMe)$_2$], 721 [{Au(PPh$_3$)$_2$}$^+$], 568 [M$^+$], 459 [M$^+$ − P(O)(OMe)$_2$]. − $C_{20}H_{21}AuO_3P_2$ (568.29): calcd. C 42.27, H 3.72; found C 42.07, H 3.67.

(Tri-o-tolylphosphane)gold(I) Dimethylphosphite (**3c**): The procedure was the same as described for **3a**, using 90 mg of Ph$_3$PAuMe[6] (0.17 mmol) and 16 µl of (MeO)$_2$P(O)H (0.17 mmol); yield 90 mg, 87%; beige solid, m.p. 156°C (dec.), stable to air and moisture, soluble in dichloromethane and tetrahydrofuran, sparingly soluble in toluene, and insoluble in diethyl ether and pentane. − ^{1}H NMR: δ = 6.85−7.42 [m, 12H, *o*-Tol], 3.58 [d, 6H, ^3J(P,H) = 12.5 Hz, OMe], 2.66 [s, 9H, Me]. − ^{13}C{^{1}H} NMR: δ = 142.8 [d, ^2J(P,C) = 13.8 Hz, C2], 133.6 [d, ^2J(P,C) = 10.1 Hz, C6], 132.1 [d, ^3J(P,C) = 9.2 Hz, C3], 131.8 [d, ^4J(P,C) = 1.83 Hz, C4], 126.9 [d, ^3J(P,C) = 9.19 Hz, C5], 125.8 [d, ^1J(P,C) = 50.6 Hz, C1], 48.9 [d, ^2J(P,C) = 3.7 Hz, OMe], 23.6 [d, ^3J(P,C) = 11.0 Hz, Me]. − ^{31}P{^{1}H} NMR: δ = 110.2 [d, ^2J(P,P) = 518.8 Hz, P(O)(OMe)$_2$], 29.4 [d, ^2J(P,P) = 518.8 Hz, *o*-Tol$_3$P]. − MS (FAB): *m/z* = 1111 [{(o-Tol$_3$P)$_2$Au}$^+$ + AuP(O)(OMe)$_2$], 805 [{(o-Tol$_3$P)$_2$Au}$^+$], 610 [M$^+$], 501 [M$^+$ − P(O)(OMe)$_2$]. − $C_{23}H_{27}AuO_3P_2$ (610.38): calcd. C 45.26, H 4.46; found C 43.86, H 4.77.

Crystal Structure Determinations: Specimens of suitable quality and size were mounted in glass capillaries and used for measurements of precise cell constants and collection of intensity data on an Enraf Nonius CAD4 diffractometer (Mo-K_α radiation, λ(Mo-K_α) = 0.71073 Å). During data collection, three standard reflections were measured periodically as a general check of crystal and instrument stability. No significant changes were observed for either compound. Lp correction was applied and intensity data were corrected for absorption effects. The structures were solved by Patterson methods (SHELXS-86) and completed by full-matrix least-squares techniques against F^2 (SHELXL-93). The thermal motion of all non-hydrogen atoms was treated anisotropically. All hydrogen atoms were placed in idealized calculated positions and allowed to ride on their corresponding carbon atoms with fixed isotropic contributions ($U_{iso(fix)}$ = 1.5 · U_{eq} of the attached C atom). The P(O)(OMe)$_2$ group of one of the two independent molecules of compound **3b** was disordered and refined in split positions. Further information about the crystal data, data collection and structure refinement is summarized in Table 1. Selected interatomic distances and angles are shown in the corresponding figure captions. Anisotropic thermal parameters, tables of distances and angles, and atomic coordinates have been deposited with Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen. The data are available on request on quoting CSD-406832 (**1a**), 406833 (**3b**).

Table 1. Crystal data, data collection, and structure refinement for compounds **1a** and **3b**.

		1a	**3b**
Crystal data			
Formula		$C_{15}H_{19}AuOP_2$	$C_{20}H_{21}AuO_3P_2$
M_r		474.21	568.27
Crystal system		orthorhombic	triclinic
Space group		$Cmc2_1$ [No. 36]	$P\bar{1}$
a	(Å)	13.477(1)	11.432(1)
b	(Å)	10.577(1)	11.991(1)
c	(Å)	10.937(1)	14.581(2)
α	(°)	90	89.01(1)
β	(°)	90	89.93(1)
γ	(°)	90	84.19(1)
V	(Å^3)	1559.0(2)	1988.2(4)
ρ_{calc}	(gcm^{-3})	2.020	1.898
Z		4	4
F(000)		904	1096
µ(Mo K_α)	(cm^{-1})	96.31	75.77
Data collection			
T (°C)		-74	-74
Scan mode		ω	ω
hkl range		0→17, -13→6, -13→13	-13→13, 0→15, -16→17
$\sin(\theta/\lambda)_{max}$	(Å^{-1})	0.64	0.64
Measured reflections		2632	8032
Refls. used for refinement		1688 [R_{int} = 0.0283]	8031
Absorption correction		psi-scans	psi-scans
T_{min}/T_{max}		0.489/0.993	0.746/1.000
Refinement			
Refined parameters		93	497
H atoms (found/calcd.)		0/10	0/21
Flack Parameter		-0.01(2)	-
Final R values [I>2σ(I)]			
$R1$[a]		0.0224	0.0260
$wR2$[b]		0.0637	0.0616
(shift/error)$_{max}$		<0.001	<0.001
ρ_{fin}(max/min)	(eÅ^{-3})	1.004/-1.560	1.117/-1.196

[a] $R = \Sigma(\|F_o\| - \|F_c\|)/\Sigma\|F_o\|$. − [b] $wR2 = \{[\Sigma w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]$; $p = (F_o^2 + 2F_c^2)/3$; a = 0.0379 (**1a**), 0.0351 (**3b**); b = 3.23 (**1a**), 4.48 (**3b**).

☆ Dedicated to Professor *Wolfgang Beck* on the occasion of his 65th birthday.

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