

Diphenyl(2-hydroxy-phenyl)phosphine and its Trimethylsilyl Ether as Ligands for Gold(I) Complexes

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Diphenyl(2-hydroxy-phenyl)phosphine was introduced as a ligand for gold(I) halides and pentafluorophenyl gold(I) in order to probe the interplay of intra- and intermolecular interactions based on $\text{Au} \cdots \text{Au}$ (aurophilic) and hydrogen bonding. 1:1 complexes of the type $\text{Ph}_2(2\text{-HO-C}_6\text{H}_4)\text{P-Au-X}$ with $\text{X} = \text{Cl, Br, C}_6\text{F}_5$ have been prepared and characterized by analytical and spectroscopic data. The crystal structure of the chloro complex (**1**) has been determined. In the lattice the molecules form dimers through $\text{O-H} \cdots \text{Cl}$ hydrogen bonds. $\text{Au} \cdots \text{Au}$ contacts are ruled out by steric congestion. Reaction of **1** with triethylamine yields a 1:1 adduct with $\text{O-H} \cdots \text{NEt}_3$ hydrogen bonding. The trimethylsilyl ether of the title ligand also forms 1:1 complexes with AuCl , AuBr , AuI , and AuC_6F_5 . The crystal structures of the chloro (**5**) and iodo (**7**) compound have been determined. In both cases the lattices are built from monomers which show only minor differences in their conformations. The silylether groups are not acting as intra- or intermolecular donor functions to the gold atoms.

Introduction

Linear two-coordinate gold(I) complexes L-Au-X show very special intermolecular interactions which often give rise to novel supramolecular structures based on $\text{Au} \cdots \text{Au}$ (aurophilic) bonding [1–3]. If suitable functional groups are provided, these interactions are complemented by standard coordinative or – most importantly – hydrogen bonding to give robust extended structures [4–6]. With certain geometrical restraints, the intermolecular bonding can also lead to more limited, package-like entities [7–9].

In attempts to further delineate the scope of this supramolecular chemistry of gold(I) complexes, we have now introduced ortho-hydroxy-functionalized triphenylphosphine and its trimethylsilyl ether as ligands for gold(I) halides. The results show that this type of ligand is just too bulky to leave enough space for a close approach of the gold atoms. Thus only hydrogen bonding remains as a means of aggregation, and the silylated derivatives finally appear as monomeric molecules. These studies are an extension also of recent investigations in the coordination

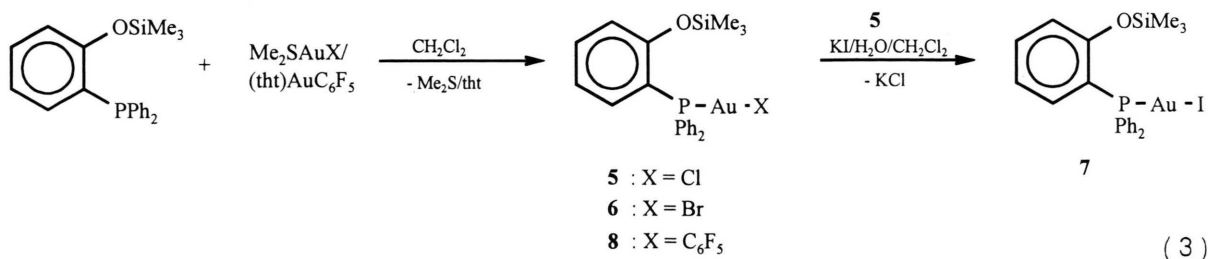
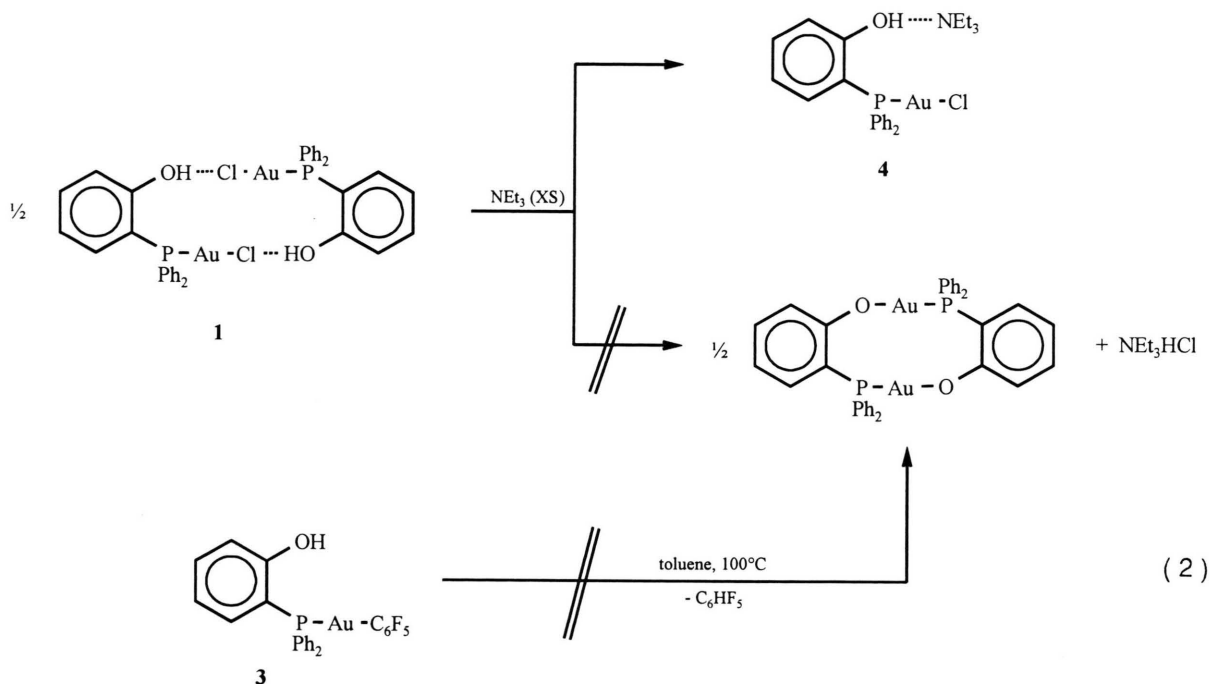
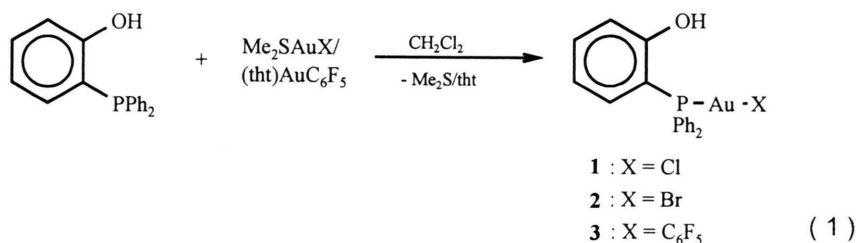
chemistry of the title ligand with other transition elements [10].

Preparation and Characterization of the Complexes

Treatment of chloro(dimethylsulfide)gold(I) [11] with equivalent quantities of diphenyl(2-hydroxy-phenyl)phosphine [12] in dichloromethane as a solvent at room temperature leads to the precipitation of virtually quantitative yields of a colourless, microcrystalline product (**1**, m.p. 251°C [dec.]). The complex can be obtained as single crystals on slow evaporation of the solvent from saturated solutions in CH_2Cl_2 . The corresponding bromide complex is obtained similarly using $(\text{Me}_2\text{S})\text{AuBr}$ [13] as the starting material (**2**, 92% yield, m.p. 226°C) (eq. (1)).

The pentafluorophenylgold(I) complex (**3**) is generated in the reaction of $(\text{C}_6\text{F}_5)\text{Au}(\text{tetrahydrothiophene})$ [14] with $(2\text{-HO-C}_6\text{H}_4)\text{Ph}_2\text{P}$ as shown by the spectroscopic data of the reaction mixture and of the products obtained after standard work-up (eq. (1)). The spectra indicate that significant amounts of a phosphine oxide are also present, which render the separation of complex **3** very difficult, and no satisfactory purity could be achieved.

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The chloro complex **1** forms a weak adduct with triethylamine (**4**), which can be precipitated from a toluene solution upon addition of pentane. It loses NEt_3 upon attempted crystallization. The primary product has been identified by spectroscopic data which suggest a fixation of the amine via hydrogen bonding at the phenolic function (eq. (2)). A similar type of adduct formation has previously been

observed with gold(I) complexes of phosphinous acid [15].

The trimethylsilyl ether of the above ligand, (2-Me₃SiO-C₆H₄)Ph₂P [12], undergoes the same set of reactions with (Me₂S)AuCl, (Me₂S)AuBr or C₆H₅Au(tht) to give the corresponding 1:1 complexes in high yields (eq. (3)). The chloro complex **5** can be converted into the iodo complex **7**

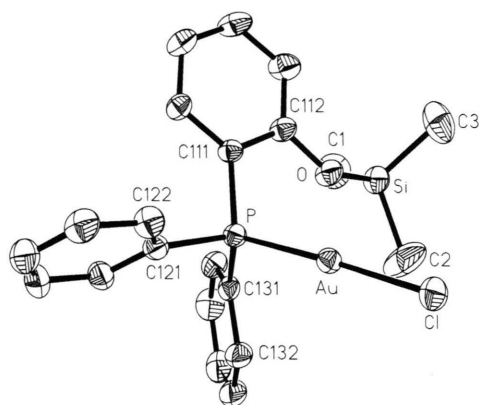


Fig. 1. Molecular structure of compound **5** (ORTEP drawing with 50% probability ellipsoids, H-atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: Au-P 2.2294(8), Au-Cl 2.2851(8); P-Au-Cl 177.30(3), Si-O-C112 132.8(2).

by treatment with aqueous potassium iodide. While isolation of the products presents no problems for the halide complexes, the pentafluorophenyl compound **8** is again difficult to purify. Attempted thermolysis of **3** to liberate C_6F_5H did not lead to the expected O-Au-P bonded oligomer, but gave complex mixtures of products.

The results of elemental analyses and of the NMR spectroscopic and mass spectrometric investigations confirmed the proposed stoichiometry and L-Au-X structure. Redistribution of ligands [16], to give *e.g.* homoleptic ionic species $[L_2Au]^+[AuX_2]^-$, was not observed for any of the solutions in chloroform at ambient temperature. However, in the FAB mass spectra this ligand exchange was observed and cations $[L_2Au]^+$ could be detected. It should be noted that in the homoleptic cation there is a chance for inter-ligand hydrogen bonding, but obviously this opportunity is not a sufficient driving force for the exchange of ligands. The NMR chemical shifts and multiplicities were as expected on the basis of literature data for related neutral compounds.

Structural Investigations

Crystals of the chloro (**5**) and iodo (**7**) complexes are not isomorphous. The lattice of the former (**5**, triclinic, space group $P\bar{1}$, $Z = 2$) contains individual molecules with no sub-van der Waals contacts (Fig. 1). These molecules are chiral and the enantiomers are related by an inversion center.

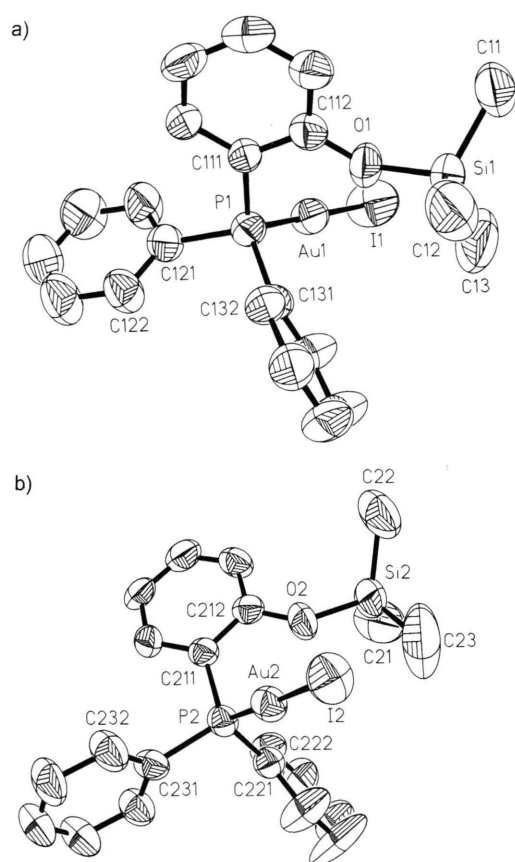


Fig. 2a, b. Molecular structure of the two crystallographically independent molecules of compound **7** (ORTEP drawing with 50% probability ellipsoids, H-atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: Au1-P1 2.247(2), Au1-I1 2.5381(9); P1-Au1-I1 179.52(6), Si1-O1-C112 133.7(6) - Au2-P2 2.252(2), Au2-I2 2.5677(7); P2-Au2-I2 178.53(6), Si2-O2-C212 132.0(5).

The ligand has a propeller-type conformation distorted by the presence of the ortho-trimethylsiloxy substituent at one of the phenyl rings. The C-P-C and C-P-Au angles at phosphorus are as yet in the narrow ranges from 104.24(13) to 107.91(13)° and from 111.41(9) to 114.68(10)°, respectively. The P-Au-Cl unit is linear [177.30(3)°] with standard Au-P and Au-Cl bond lengths. The distance O...Au [3.353 Å] is too large to suggest coordinative bonding. The Si-O-C angle [132.8(2)°] also indicates a configuration typical for free silyl ethers.

Crystals of the iodo analogue **7** are also triclinic (space group $P\bar{1}$, $Z = 4$), but the lattice contains two independent molecules which differ in some

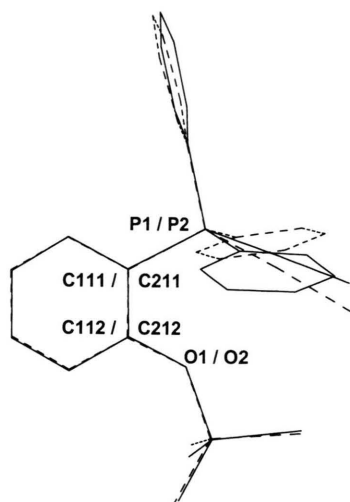


Fig. 3. Superposition of the two crystallographically independent molecules of compound 7.

details of conformation (Fig. 2a, b). A superposition of the two structures (Fig. 3) shows that the molecules are almost (non-crystallographic) mirror images (two enantiomers). For each of the independent molecules there is an enantiomer related by a crystallographic center of inversion. The P-Au-I units are both linear [179.52(6) and 178.53(6)° for Au1 and Au2, respectively], and there is only a minor difference between the two Si-O-C angles [133.7(6) and 132.9(5)°].

The structures of compounds **5** and **7** show that there is very efficient steric shielding of the P-Au-X units which prevents any intermolecular contact between gold atoms or between gold and halogen atoms. There is a parallel head-to-tail arrangement of these units in the lattice, but the distances [*e.g.* Au1...Au2 6.163 Å] are too large to allow any direct interaction. It is interesting to note that the siloxy groups are not accepted by the gold atoms as auxiliary (intra- or intermolecular) ligands. Clean twofold coordination is maintained.

Crystals of complex **1** are monoclinic (space group $P2_1/n$, with $Z = 4$), and the lattice contains pairs of molecules, the individual units of which are related by symmetry (Fig. 4). Bond lengths and angles of the C_3P -Au-Cl unit in the monomer are very similar to those in the silylether **5**, but the conformation of the triphenylphosphine propeller is changed such that the phenolic groups can maintain hydrogen bonds with the chloro ligand of a neighbour-

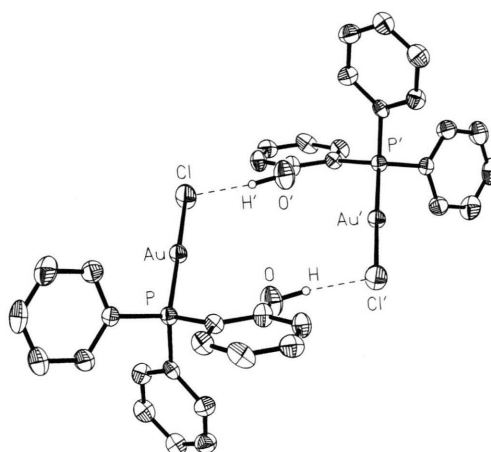


Fig. 4. Molecular structure of the pairs of molecules of compound **1** (ORTEP drawing with 50% probability ellipsoids, C-H atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: Au-P 2.2226(2), Au-Cl 2.285(2); P-Au-Cl 176.85(8); hydrogen bonding: O-H 1.049, Cl...H 2.040; O-H...Cl 169.0°.

ing molecule. This hydrogen bonding is responsible for the formation of dimeric units. The details of these hydrogen bonds [O-H 1.049 Å, Cl...H 2.040 Å, O-H...Cl 169.0°] are consistent with parameters for other hydrogen-bonded contacts of this type [17 - 19].

The oligomerization of compound **1** in the crystal is probably responsible for the rather poor solubility of the complex in di- or trichloromethane and methanol. The solubility is increased upon addition of triethylamine owing to the cleavage of the dimer and formation of new hydrogen bonds of the monomers with NEt_3 (eq. (2)). Evidence for the different types of hydrogen bonding is available also from NMR and IR investigations, although the effects are not always fully convincing due to solubility problems and to the sensitivity of the samples to traces of moisture.

In summary, the present study has shown that a triphenylphosphine ligand with only one ortho-substituent at one of the phenyl groups is already too large to allow an intimate intermolecular mutual approach of the gold atoms. The metal atoms are also reluctant to accept the phenolic function as an auxiliary donor, and this is also true for the trimethylsilyl ethers of the title ligand. The complexes with this even bulkier substituent are monomers with a standard linear two-coordinate structure. No significant ligand redistributions to give homoleptic ionic

isomers $[\text{L}_2\text{Au}]^+$ and $[\text{AuX}_2]^-$ have been observed by NMR spectroscopy in solution, although mass spectrometric studies have indicated that cations $[\text{L}_2\text{Au}]^+$ are formed in the vaporization and ionization process. Thus inter-ligand hydrogen bonding (-OH/-OH) in homoleptic cations $[\text{L}_2\text{Au}]^+$ is also not competing effectively with the O-H...Cl hydrogen bonding observed for the heteroleptic compound **1** as the sole binding contacts between the molecules. Similar results have been obtained for analogous phosphinous acid complexes [15].

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.

[Diphenyl-(2-hydroxy-phenyl)phosphine]gold(I) chloride (1): (Dimethylsulfide)gold(I) chloride (88 mg, 0.3 mmol) and $\text{Ph}_2\text{P}(\text{C}_6\text{H}_4\text{OH})$ (84 mg, 0.3 mmol) were dissolved in CH_2Cl_2 (20 ml) and the reaction mixture stirred at room temperature. The product precipitated as a white solid, which was collected by filtration after a reaction time of 1 h. The solvent of the filtrate was evaporated in a vacuum to leave a volume of 3 ml. Pentane (30 ml) was added to precipitate the remainder of the product. Colourless crystals were obtained by slow evaporation of a saturated CH_2Cl_2 solution; 150 mg, 98% yield; m. p. 251°C (dec.), stable to air and moisture, sparingly soluble in dichloromethane, chloroform and methanol, and insoluble in diethylether and pentane. - ^1H NMR: δ = 7.29-7.68 [m, Ph]; 6.82-7.23 [m, C_6H_4]; 5.80 [s br, OH]. - $^{13}\text{C}\{^1\text{H}\}$ NMR: δ = 134.2 [d, $^2J(\text{P,C})$ = 13.82 Hz, C2/6-Ph]; 134.0 [s, C6-C $_6\text{H}_4$]; 131.9 [d, $^4J(\text{P,C})$ = 3.07 Hz, C4-Ph]; 130.7 [s, C4-C $_6\text{H}_4$]; 129.2 [d, $^3J(\text{P,C})$ = 12.28 Hz, C3/5-Ph]; 127.9 [d, $^1J(\text{P,C})$ = 63.72 Hz, C1-Ph]; 121.4 [d, $^3J(\text{P,C})$ = 10.75 Hz, C5-C $_6\text{H}_4$]; 117.0 [d, $^{31}\text{P}(\text{C})$ = 5.37 Hz, C3-C $_6\text{H}_4$]; C1-C $_6\text{H}_4$ and C2-C $_6\text{H}_4$ were not detected. - $^{31}\text{P}\{^1\text{H}\}$ NMR: δ = 22.4 [s]. - MS (FAB): m/z = 753 $[\{\text{Ph}_2\text{P}(\text{C}_6\text{H}_4\text{OH})\}_2\text{Au}]^+$, 475 $[\text{M} - \text{Cl}]^+$.

$\text{C}_{18}\text{H}_{15}\text{AuClOP}$ (510.69)

Calcd C 42.33 H 2.96 %,

Found C 42.25 H 3.03 %.

[Diphenyl-(2-hydroxy-phenyl)phosphine]gold(I) bromide (2): The procedure was the same as described for **1**, using 102 mg of (dimethylsulfide)gold(I) bromide (0.3 mmol) and 84 mg of $\text{Ph}_2\text{P}(\text{C}_6\text{H}_4\text{OH})$ (0.3 mmol); yield

153 mg, 92% ; white solid, m. p. 226°C, stable to air and moisture, sparingly soluble in dichloromethane, chloroform and methanol, and insoluble in diethylether and pentane. - ^1H NMR: δ = 7.36-7.71 [m, Ph]; 6.77-7.00 [m, C_6H_4]. - $^{13}\text{C}\{^1\text{H}\}$ NMR: δ = 157.9 [d, $^{21}\text{P}(\text{C})$ = 5.37 Hz, C2-C $_6\text{H}_4$]; 134.2 [d, $^2J(\text{P,C})$ = 13.81 Hz, C2/6-Ph]; 134.1 [s, C6-C $_6\text{H}_4$]; 133.8 [s, C4-C $_6\text{H}_4$]; 131.8 [s, C4-Ph]; 129.1 [d, $^3J(\text{P,C})$ = 12.28 Hz, C3/5-Ph]; 128.3 [d, $^1J(\text{P,C})$ = 62.93 Hz, C1-Ph]; 121.0 [d, $^3J(\text{P,C})$ = 10.74 Hz, C5-C $_6\text{H}_4$]; 116.8 [d, $^3J(\text{P,C})$ = 5.37 Hz, C3-C $_6\text{H}_4$]; C1-C $_6\text{H}_4$ was not detected. - $^{31}\text{P}\{^1\text{H}\}$ NMR: δ = 25.9 [s]. - MS (FAB): m/z = 1029 $[2\text{M} - \text{Br}]^+$, 556 $[\text{M} + 1]^+$, 554 $[\text{M} - 1]^+$, 475 $[\text{M} - \text{Br}]^+$.

$\text{C}_{18}\text{H}_{15}\text{AuBrOP}$ (555.16)

Calcd C 38.94 H 2.72 %,

Found C 38.69 H 2.93 %.

Pentafluorophenyl[diphenyl-(2-hydroxy-phenyl)phosphine]gold(I) (3): Pentafluorophenyl(tetrahydrothiophene)gold(I) (136 mg, 0.3 mmol) and $\text{Ph}_2\text{P}(\text{C}_6\text{H}_4\text{OH})$ (84 mg, 0.3 mmol) were dissolved in CH_2Cl_2 (20 ml) and the reaction mixture stirred for 1 h at room temperature. The solvent was evaporated in a vacuum to leave a volume of 3 ml. Pentane (30 ml) was added to precipitate a white solid, that contained small amounts of the phosphine oxide $\text{Ph}_2\text{P}(\text{O})(\text{C}_6\text{H}_4\text{OH})$, which could not be separated. - ^1H NMR: δ = 7.21-7.74 [m, Ph]; 6.76-7.05 [m, C_6H_4]. - $^{13}\text{C}\{^1\text{H}\}$ NMR: δ = 157.9 [d, $^2J(\text{P,C})$ = 6.91 Hz, C2-C $_6\text{H}_4$]; 148.7 [d, $^1J(\text{F,C})$ = 258.60 Hz, C2/6-C $_6\text{F}_5$]; 141.3 [s br, C4-C $_6\text{F}_5$]; 137.2 [d, $^1J(\text{F,C})$ = 271.67 Hz, C3/5-C $_6\text{F}_5$]; 134.4 [s, C6-C $_6\text{H}_4$]; 134.3 [d, $^2J(\text{P,C})$ = 13.82 Hz, C2/6-Ph]; 134.3 [s, C4-C $_6\text{H}_4$]; 131.7 [d, $^4J(\text{P,C})$ = 3.07 Hz, C4-Ph]; 129.3 [d, $^3J(\text{P,C})$ = 11.52 Hz, C3/5-Ph]; 128.8 [d, $^1J(\text{P,C})$ = 56.79 Hz, C1-Ph]; 121.4 [d, $^3J(\text{P,C})$ = 8.44 Hz, C5-C $_6\text{H}_4$]; 117.2 [d, $^3J(\text{P,C})$ = 4.61 Hz, C3-C $_6\text{H}_4$]; 115.0 [d, $^1J(\text{P,C})$ = 55.25 Hz, C1-C $_6\text{H}_4$]. - $^{31}\text{P}\{^1\text{H}\}$ NMR: δ = 41.0 [s, $\text{Ph}_2\text{P}(\text{O})(\text{C}_6\text{H}_4\text{OH})$]; 31.9 [t, $^4J(\text{F,P})$ = 7.40 Hz, $\text{Ph}_2\text{P}(\text{C}_6\text{H}_4\text{OH})\text{AuC}_6\text{F}_5$ **3**]. - $^{19}\text{F}\{^1\text{H}\}$ NMR (CF_3COOH as reference): δ = -85.8 [t, $^3J(\text{F,F})$ = 20.60 Hz, *meta*-F]; -83.3 [t, $^3J(\text{F,F})$ = 19.72 Hz, *para*-F]; -43.1 [d, $^3J(\text{F,F})$ = 14.85 Hz, *ortho*-F]. - $\text{C}_{24}\text{H}_{15}\text{AuF}_5\text{OP}$ (642.31).

Triethylamine-[diphenyl-(2-hydroxy-phenyl)phosphine]gold(I) chloride (4): [Diphenyl-(2-hydroxy-phenyl)phosphine]gold(I) chloride (**1**) (51 mg, 0.1 mmol) was dissolved in toluene (50 ml) and the clear colourless solution was treated with an excess of NEt_3 (1 ml). After stirring for 1 h at room temperature the solvent was evaporated in a vacuum to leave a volume of 3 ml. Pentane (40 ml) was added to precipitate a white solid, that contained small amounts of the phosphine oxide $\text{Ph}_2\text{P}(\text{O})(\text{C}_6\text{H}_4\text{OH})$. Attempted purification by crystallization led to the formation of compound **1** with the free hydroxy function. - ^1H NMR: δ = 7.17-7.67 [m, 10H,

Table I. Crystal data, data collection, and structure refinement for compounds **1**, **5**, and **7**.

	1	5	7
<i>Crystal data</i>			
Formula	C ₁₈ H ₁₅ AuClOP	C ₂₁ H ₂₃ AuClOPSi	C ₂₁ H ₂₃ AuIOPSi
M _r	510.69	582.87	674.32
Crystal system	monoclinic	triclinic	triclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> (Å)	8.949(1)	9.823(1)	10.273(1)
<i>b</i> (Å)	10.894(1)	10.367(1)	14.606(1)
<i>c</i> (Å)	17.388(1)	12.484(1)	17.107(1)
α (°)	90	71.85(1)	80.75(1)
β (°)	102.70(1)	76.18(1)	79.26(1)
γ (°)	90	67.59(1)	71.70(1)
<i>V</i> (Å ³)	1653.7(4)	1106.3(2)	2379.9(3)
ρ_{calc} (gcm ⁻³)	2.051	1.750	1.882
<i>Z</i>	4	2	4
<i>F</i> (000)	968	564	1272
μ (MoK α) (cm ⁻¹)	91.52	69.03	76.03
<i>Data collection</i>			
<i>T</i> (°C)	-78	-78	+21
Scan mode	ω - θ	ω	ω -2 θ
<i>hkl</i> Range	-11→11, 0→14, 0→22	0→12, -12→13, -15→15	0→12, -15→17, -19→20
$\sin(\theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.64	0.64	0.62
Measured reflections	4096	5296	8345
Unique reflections	3979 [<i>R</i> _{int} = 0.0651]	5296	8345
Refls. used for refinement	3744	5165	7341
<i>Refinement</i>			
Refined parameters	199	235	469
Final <i>R</i> values [<i>I</i> > 2 σ (<i>I</i>)]			
<i>R</i> 1 ^[a]	0.0421	0.0199	0.0403
<i>wR</i> 2 ^[b]	0.0951	0.0485	0.0982
(shift/error) _{max}	< 0.001	< 0.001	< 0.001
ρ_{fin} (max/min) (eÅ ⁻³)	1.736 / -2.611	0.797 / -1.473	1.247 / -1.444

^[a] $R = \Sigma(|F_o| - |F_c|) / \Sigma|F_o|$; ^[b] $wR2 = \{[\Sigma w(F_o^2 - F_c^2)^2] / \Sigma w(F_o^2)^2\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]$; $p = (F_o^2 + 2F_c^2)/3$; $a = 0.0399$ (**1**), 0.0287 (**5**), 0.0503 (**7**); $b = 14.32$ (**1**), 1.22 (**5**), 7.67 (**7**).

Ph]; 6.53-6.70 [m, 4H, C₆H₄]; 3.05 [q, 6H, ³*J*(H,H) = 7.10 Hz, CH₂]; 1.25 [t, 9H, ³*J*(H,H) = 7.10 Hz, CH₃]. - ³¹P{¹H} NMR: δ = 41.0 [s, Ph₂P(O)(C₆H₄OH)]; 24.0 [s, Ph₂P(C₆H₄OH)· \cdot ·NET₃]₂AuCl **4**]. - MS (FAB): *m/z* = 612 [M + 1]⁺, 611 [M]⁺, 610 [M - 1]⁺, 102 [NET₃ + 1]⁺. - C₂₄H₃₀AuClINOP (611.90).

[Diphenyl-(2-trimethylsiloxyphenyl)phosphine]-gold(I) chloride (**5**): (Dimethylsulfide)gold(I) chloride (88 mg, 0.3 mmol) and diphenyl-(2-trimethylsiloxyphenyl)phosphine (105 mg, 0.3 mmol) were dissolved in CH₂Cl₂ (20 ml) and the reaction mixture was stirred for 1 h at room temperature. The solvent was evaporated in a vacuum to leave a volume of 3 ml. Pentane (30 ml) was added to precipitate the product as a white solid. Colourless crystals were obtained by slow evaporation of the

solvent from solutions in CH₂Cl₂ (157 mg, 90% yield; m.p. 204°C (dec. > 250°C), stable to air and moisture, soluble in dichloromethane, chloroform and tetrahydrofuran, and insoluble in diethylether and pentane). - ¹H NMR: δ = 7.41-7.68 [m, Ph]; 6.62-6.94 [m, C₆H₄]; 0.14 [s, Me]. - ¹³C{¹H} NMR: δ = 157.4 [s, C2-C₆H₄]; 134.2 [d, ²*J*(P,C) = 13.82 Hz, C2/6-Ph]; 133.9 [s, C6-C₆H₄]; 133.5 [s, C4-C₆H₄]; 131.6 [d, ⁴*J*(P,C) = 2.30 Hz, C4-Ph]; 129.0 [d, ³*J*(P,C) = 12.28 Hz, C3/5-Ph]; 128.6 [d, ¹*J*(P,C) = 63.70 Hz, C1-Ph]; 121.1 [d, ³*J*(P,C) = 9.98 Hz, C5-C₆H₄]; 118.8 [d, ¹*J*(P,C) = 66.00 Hz, C1-C₆H₄]; 117.7 [d, ³*J*(P,C) = 5.37 Hz, C3-C₆H₄]; 0.3 [s, Me]. - ³¹P{¹H} NMR: δ = 25.8 [s]. - MS (FAB): *m/z* = 897 [{Ph₂P(C₆H₄OSiMe₃)₂Au}]⁺, 547 [M - Cl]⁺, 475 [M - Cl - SiMe₃ + 1]⁺.

$C_{21}H_{23}AuClOPSi$ (582.87)

Calcd C 43.27 H 3.98 %,

Found C 43.27 H 3.75 %.

[Diphenyl-(2-trimethylsiloxyphenyl)phosphine]-gold(I) bromide (**6**): The procedure was the same as described for **5**, using 102 mg of (dimethylsulfide)gold(I) bromide (0.3 mmol) and 105 mg of the ligand (0.3 mmol); yield 147 mg, 78 %; white solid, m. p. 158°C, stable to air and moisture, soluble in dichloromethane, chloroform and tetrahydrofuran, and insoluble in diethylether and pentane. - 1H NMR: δ = 7.39-7.68 [m, Ph]; 6.68-7.00 [m, C_6H_4]; 0.14 [s, Me]. - $^{31}P\{^1H\}$ NMR: δ = 28.2 [s]. - MS (FAB): m/z = 1174 [2M - Br] $^+$, 628 [M + 1] $^+$, 547 [M - Br] $^+$, 350 [M - AuBr] $^+$.

$C_{21}H_{23}AuBrOPSi$ + 1/2 C_5H_{12} (627.34 + 36.07)

Calcd C 42.55 H 4.41 %,

Found C 43.39 H 4.11 %.

[Diphenyl-(2-trimethylsiloxyphenyl)phosphine]-gold(I) iodide (**7**): [Diphenyl-(2-trimethylsiloxyphenyl)phosphine]gold(I) chloride **5** (117 mg, 0.2 mmol) was dissolved in CH_2Cl_2 (20 ml) and treated with an excess of an aqueous solution of KI (10 ml). After stirring for 1 h at room temperature the CH_2Cl_2 phase was collected. The solvent was evaporated in a vacuum to leave a volume of 3 ml. Pentane (30 ml) was added to precipitate the product as a white solid. Colourless crystals were obtained by slow evaporation of a CH_2Cl_2 solution; 69 mg, 51 % yield; m. p. 153°C, stable to air and moisture, soluble in dichloromethane, chloroform and tetrahydrofuran, and insoluble in diethylether and pentane. - 1H NMR: δ = 7.43 - 7.71 [m, Ph]; 6.73-6.99 [m, C_6H_4]; 0.14 [s, Me]. - $^{31}P\{^1H\}$ NMR: δ = 32.7 [s]. - MS (FAB): m/z = 1221 [2M - I] $^+$, 675 [M + 1] $^+$, 674 [M] $^+$, 547 [M - I] $^+$, 350 [M - AuI] $^+$.

$C_{21}H_{23}AuIOPSi$ (674.32)

Calcd C 37.40 H 3.44 %,

Found C 40.64 H 3.75 %.

Pentafluorophenyl[diphenyl-(2-trimethylsiloxyphenyl)phosphine]gold(I) (**8**): Pentafluorophenyl(tetrahydrothiophene)gold(I) (136 mg, 0.3 mmol) and diphenyl-(2-trimethylsiloxyphenyl)phosphine (105 mg, 0.3 mmol) were dissolved in CH_2Cl_2 (20 ml) and the reaction mixture was stirred for 1 h at room temperature. The solvent was evaporated in a vacuum to leave a volume of 3 ml. Pentane (30 ml) was added to precipitate a white solid,

that contained small amounts of the phosphine oxide $Ph_2P(O)(C_6H_4OH)$. Purification of **8** by crystallization was not successful. - 1H NMR: δ = 7.31-7.74 [m, Ph]; 6.61-6.96 [m, C_6H_4]; 0.11 [s, Me]. - $^{13}C\{^1H\}$ NMR: δ = 157.4 [d, $^2J(P,C)$ = 6.14 Hz, C2- C_6H_4]; 134.5 [d, $^2J(P,C)$ = 13.82 Hz, C2/6-Ph]; 134.3 [s, C6- C_6H_4]; 133.1 [s, C4- C_6H_4]; 131.4 [d, $^4J(P,C)$ = 2.31 Hz, C4-Ph]; 129.0 [d, $^3J(P,C)$ = 11.51 Hz, C3/5-Ph]; 121.1 [d, $^3J(P,C)$ = 9.21 Hz, C5- C_6H_4]; 117.5 [d, $^3J(P,C)$ = 4.61 Hz, C3- C_6H_4]; 0.0 [s, Me]; C1-Ph, C1- C_6H_4 and C_6F_5 were not detected. - $^{31}P\{^1H\}$ NMR: δ = 41.0 [s, $Ph_2P(O)(C_6H_4OH)$]; 36.5 [t, $^4J(P,F)$ = 7.04 Hz, $Ph_2P(C_6H_4OSiMe_3)AuC_6F_5$, **8**]. - MS (FAB): m/z = 1261 [2M - C_6F_5] $^+$, 715 [M + 1] $^+$, 714 [M] $^+$, 547 [M - C_6F_5] $^+$, 475 [M - SiMe₃ - C_6F_5 + 1], 350 [M - AuC₆F₅] $^+$. - $C_{27}H_{23}AuF_5OPSi$ (714.49).

Crystal structure determinations. Specimens of suitable quality and size of compounds **1**, **5**, and **7** were mounted in glass capillaries and used for measurements of precise cell constants and intensity data collection on an Enraf Nonius CAD4 diffractometer (Mo- K_α radiation, $\lambda(Mo-K_\alpha)$ = 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. Lp correction was applied and intensity data were corrected for absorption effects (DIFABS). 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 C-H atoms were placed in idealized calculated positions and allowed to ride on their corresponding carbon atoms with fixed isotropic contributions ($U_{iso(fix)} = 1.5 \times U_{eq}$ of the attached C atom). The O-H atom of compound **1** was located and included in the refinement with fixed isotropic contributions ($U_{iso(fix)} = 1.5 \times U_{eq}$ of the attached O atom). Further information on crystal data, data collection and structure refinement are summarized in Table I. Important 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 No. 410462 (**1**), 410463 (**5**), and 410461 (**7**).

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