Chiral Phosphine Ligands in the Structural Chemistry of Gold

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The reaction of chloro(dimethylsulfide)gold(I) with (2-hydroxybutyl)diphenylphosphine (L) (racemic mixture) in dichloromethane affords high yields of the racemic chiral complex (L)AuCl. Metathesis reactions with KBr or KI, respectively, in a two-phase solvent mixture (CH₂Cl₂/H₂O) lead to a conversion into the corresponding bromide and iodide complexes (L)AuBr and (L)AuI. Treatment of silver chloride with the ligand L in acetonitrile yields the analogous 1:1 adduct (L)AgCl. The compounds have been characterized by their analytical and spectroscopic data, and the structures of (L)AuCl and (L)AuBr have been determined by single-crystal X-ray diffraction. The compounds build isomorphous crystal lattices (monoclinic, P2₁/c) in which pairs of enantiomers (R- and S-configuration of L) are aggregated by two long hydrogen bonds between the hydroxyl group of the ligand and the halogen substituent of the neighbouring molecule. Cationic, linear two-coordinate 1:2 complexes (L)₂Au⁺ X⁻ (X = BF₄, ClO₄, SO₃CF₃) and (L)₂Ag⁺ X⁻ (X = BF₄) are obtained in good yields by reaction of L with Me₂SAuCl and AgX (molar ratio 2:1:1) or with AgBF₄ (molar ratio 2:1), respectively. ³¹P NMR studies at variable temperature show an equilibrium between all possible stereoisomers (RR, SS, RS, SR) in solution with rapid ligand exchange at ambient temperatures.

Introduction

Phosphine ligands play a key role in the coordination chemistry of gold in its lower oxydation state Au(I). Many of the compounds used for the most important applications of gold in contemporary medicine and technology are phosphine complexes [1]. The primary, secondary or tertiary phosphine donor functions in mono- or polydentate ligands are superior to most other ligands and lead to the most stable complexes which adopt a linear twocoordinate structure in standard cases. The unusual structural chemistry of many gold(I) complexes is based on non-classical inter- and intramolecular Au(I)-Au(I) contacts [2]. In their bond energy, these interactions between seemingly closed-shell metal centers (5d¹⁰), arising mainly from relativistic and correlation effects [3], are comparable to hydrogen bonds [4]. Surprisingly, the effect of chirality of phosphine ligands on the chemical properties and structure has not been probed in more than a few sporadic cases [5].

Stereoisomerism at two-coordinate metal atoms is generally not a very common phenomenon [6],

and therefore we have undertaken a preparative and structural study of a few representative model systems using a tertiary phosphine with an asymmetrically substituted carbon atom (a "center of chirality") in one of the organic substituents of the ligand.

Both 1:1 and 1:2 complexes were included in order to obtain enantiomers and diastereomers of this most simple type of metal coordination (linear twocoordinate). Analogous silver(I) complexes have also been considered, because NMR spectroscopy is more informative with this lighter coinage metal with its two spin 1/2 isotopes. It was also anticipated that the presence of a hydroxyl group at the chiral ligand would lead to a directional influence on the solid state structure through the build-up of hydrogen bonds supporting the aggregation through other forces like aurophilicity [7].

Synthesis and Structure of 1:1 Complexes

A racemic mixture of (2-hydroxybutyl)diphenylphosphine (L) was chosen as a ligand prototype with a center of chirality in its alkyl substituent and with a hydroxyl group as one of the functions at the asymetrical carbon atom. This compound is readily prepared from potassium diphenylphosphide and

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1,2-epoxy-butane following a modified literature procedure [8] and may also serve as synthon to prepare further functionalized chiral phosphines or diphosphines.

Treatment of chloro(dimethylsulfide)gold(I) with this ligand L in the molar ratio 1:1 in dichloromethane affords high yields of the expected 1:1 complex (L)AuCl as colourless crystals (91%, m.p. 152°C). This product is readily converted into the corresponding bromide and iodide complexes, (L)AuBr and (L)AuI, in metathesis reactions with KBr or KI, respectively, in a two-phase system $(H_2O/CH_2Cl_2; yields 85/81\%, m.p. 140/109°C).$

The analogous 1:1 complex with silver chloride, (L)AgCl, is obtained by reacting freshly prepared, dry AgCl with the ligand L in acetonitrile (62% yield, m.p. 165° C).

All four 1:1 complexes are air-stable solids, soluble in tetrahydrofuran and di- or trichloromethane. In the NMR spectra, the resulting solutions show the expected sets of ¹H, ³¹P and ¹³C resonances

Fig. 1. Molecular structures of compounds (L)AuCl (a) and (L)AuBr (b).(ORTEP drawing with 50% probability ellipsoids, CH-atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: (a): Au-Cl 2.2973(13), Au-P 2.2285(13); Cl-Au-P 176.03(5); O-H 1.077, H···Cl' 2.347, O-H···Cl' 161.3; (b): Au-Br 2.4129(9), Au-P 2.232(2); Br-Au-P 176.33(6); O-H 1.035: H···Br' 2.535: O-H···Br' 152.5.

with only slight variations in the chemical shifts and coupling constants as a function of the nature of the halogen co-ligand. The influence of the metal atoms is much greater as shown by the differences between the data for the AuCl and AgCl complexes (Exp. Part). Owing to the neighbouring center of chirality, the two phenyl groups at the phosphorus atom are diastereotopic and give two sets of ¹³C resonances. The non-equivalence of the hydrogen atoms of each of the two CH₂ groups leads to the expected multiplicity in the ¹H spectra.

In CDCl₃ at 25°C, the complex (L)AgCl shows no splitting of the ³¹P resonance by the spin 1/2 nuclei of the two silver isotopes ¹⁰⁷Ag and ¹⁰⁹Ag, probably owing to a rapid ligand exchange. At -90°C complex sets of resonances with multiplet patterns appear, which suggest that not only a simple ligand exchange, but also a complex oligomerisation equilibrium (with mainly dimers and various tetrameric forms) are contributing to the processes involved. There is extensive literature on the various forms of

aggregates of (phosphine)silver halides which are mainly determined by the steric and electronic effect of the ligands [9]. No attempt was made to clarify this aspect for the present example (L)AgCl. Crystals grown from various solvents turned out to be twinned in all cases.

In the mass spectra (FAB) of the gold complexes the molecular ions $[(L)AuX]^+$ are present in low intensity. The halogenonium ions $\{[(L)Au]_2X\}^+$ are detected as the ions of highest mass (X = Cl, Br, I;), and the ions $[(L)Au]^+$ are the most abundant. This result confirms earlier reports on the high stability of digold(I) halogenonium cations with their A-shaped structure where the horizontal bar represents Au–Au bonding [10].

Single crystals of (L)AuCl and (L)AuBr are obtained by careful layering of solutions in CH_2Cl_2 with pentane. The crystals are isomorphous, monoclinic, space group $P2_1/c$, with four formula units in the unit cell. In the lattices, the two enantiomers (containing the R- or S-configuration of the ligand) appear in pairs, the components of which are related by a center of inversion (Figures 1a, b). The only discernible bonding relations between the enantiomers are two long hydrogen bonds extending from the hydroxyl groups of the ligand to the halogen atoms of the neighbouring molecule.

The bond lengths and angles of the monomers are within the range of standard data in the literature for L-Au-X molecules with phosphine and halogen ligands (captions to Figures 1a, b).

Of the iodine homologue, (L)AuI, no single crystals could be grown.

Synthesis, Spectroscopy and Isomerism of the 2:1 Complexes

Treatment of Me₂SAuCl with two equivalents of the ligand L in the presence of one equivalent of AgBF₄ in a mixture of dichloromethane and tetrahydrofuran leads to a precipitate of AgCl, and the supernatant solution contains the complex $[(L)_2Au]^+$ BF₄⁻ (87% yield, m.p. 69°C). With AgClO₄ or AgOSO₂CF₃ instead of AgBF₄ the corresponding perchlorate and triflate salts are obtained, respectively.

The reaction of AgBF₄ with two mole equivalents of L in tetrahydrofuran gives the complex $[(L)_2Ag]^+$ BF₄⁻ in 96% yield, m.p. 108°C.



Fig. 2. Temperature-dependent ^{31}P NMR spectra of $[(L)_2Au]^+$ BF_4^- (a) and $[(L)_2Ag]^+$ BF_4^- (b).

The four 2:1 complexes are colourless, air-stable crystalline solids with excellent solubility in alcohols, tetrahydrofuran, and di- or trichloromethane. The NMR spectra of solutions in chloroform at room temperature are similar to those of the 1:1 compounds (above) reflecting the chirality of the ligands.

Again, the ³¹P spectra give singlet resonances at 25°C due to rapid ligand exchange. Already at -40°C (for the silver compound at -60°C), however, these signals are split into two resonances (of equal intensity) for the three gold compounds, and into two doublets of doublets for the silver compound (Figures 2a, b). This splitting has its origin in the presence of the four diastereomeric cations $[R,R]^+$, $[S,S]^+$, $[R,S]^+$, and $[S,R]^+$, in which the phosphorus atoms are either related by a center of inversion or by a mirror plane.

These signals split further into doublets of doublets for the silver compound through coupling with the two isotopic silver nuclei (¹⁰⁹Ag, ¹⁰⁷Ag). The coupling constants J(P-Ag) are in the ratio of the gyromagnetic factors (1.15). Upon warming to 30°C coalescence of the signals occurs owing to the increasing ligand exchange rates.

Both in the coalesced spectrum at the high temperature limit and at -50°C the proton resonance of the OH groups is detected at remarkably low field suggesting strong intra- or intermolecular hydrogen bonding. It is conceivable that the proximity of the ligands in the 2:1 complexes favours the close approach necessary for interactions between hydroxyl groups. Unfortunately, no single crystals could be obtained from any of the four 2:1 compounds. All predictions regarding the structure therefore remain only tentative.

Experimental Part

All experiments were carried out under dry, purified nitrogen. Solvents were dried, distilled and stored over molecular sieves in a nitrogen atmosphere. Glassware was ovendried, evacuated and filled with nitrogen.

Racemic (2-hydroxybutyl)diphenylphosphine was prepared according to a modified literature procedure by reaction of potassium diphenylphosphide with 1,2epoxybutane followed by hydrolysis [8].

NMR: Jeol GX 400, Jeol JNM-LA400; CDCl₃ as solvent and internal standard, converted to TMS for ¹H and ${}^{13}C{}^{1}H{}; H_{3}PO_{4}$ (85%) as external standard for ${}^{31}P{}^{1}H{};$ spectra were measured at room temperature, unless noted otherwise. - MS: Finnigan MAT 90 (fast atom bombardment).

[R/S-(2-Hydroxybutyl)diphenylphosphine]gold(I)chloride

(2-Hydroxybutyl)diphenylphosphine (263 mg, 1.0 mmol) and Me₂SAuCl (300 mg, 1.0 mmol) were dissolved in 10 ml of CH₂Cl₂ to give a clear colourless solution, which was stirred for 1 h at ambient temperature. Careful layering of the solution with pentane precipitated the product as colourless crystals suitable for X-ray diffraction; yield 455 mg (91%), m.p. 152 °C. - ¹H NMR:

$$\begin{split} &\delta = 0.97 \ (\text{t},\,{}^{3}J_{\text{H},\text{H}} = 7.4 \ \text{Hz},\, 3\text{H}) \ \text{CH}_{3:} \ 1.66 \ (\text{m},\, 2\text{H}) \ \text{CH}_{2}\text{-}\\ &\text{CH}_{3:} \ 1.95 \ (\text{br},\,\text{s},\, 1\text{H}) \ \text{OH}; \ 2.56 \ (\text{ddd},\,{}^{2}J_{\text{H},\text{H}} = 14.6 \ \text{Hz},\,{}^{2}J_{\text{H},\text{P}}\\ &= 10.7 \ \text{Hz},\,\,{}^{3}J_{\text{H},\text{H}} = 3.3 \ \text{Hz},\, 1\text{H}),\, 2.77 \ (\text{ddd},\,{}^{2}J_{\text{H},\text{H}} = 14.6 \ \text{Hz},\,{}^{2}J_{\text{H},\text{P}}\\ &= 10.7 \ \text{Hz},\,\,{}^{3}J_{\text{H},\text{H}} = 3.3 \ \text{Hz},\, 1\text{H}),\, 2.77 \ (\text{ddd},\,{}^{2}J_{\text{H},\text{H}} = 14.6 \ \text{Hz},\,{}^{2}J_{\text{H},\text{P}}\\ &= 11.0 \ \text{Hz},\,\,{}^{3}J_{\text{H},\text{H}} = 9.2 \ \text{Hz},\, 1\text{H}) \ \text{CH}_2\text{-P};\, 4.11 \ (\text{m},\, 1\text{H}) \ \text{CH}_2\text{-P};\, 4.11 \ (\text{m},\, 1\text{H}) \ \text{CH}_2\text{-P};\, 31.9 \ (\text{d},\,\,{}^{3}J_{\text{C},\text{P}} = 11.6 \ \text{Hz}) \ \text{CH}_2\text{-CH}_3;\, 36.1 \ (\text{d},\,\,{}^{1}J_{\text{C},\text{P}} = 38.9 \ \text{Hz}) \ \text{CH}_2\text{-P};\, 71.0 \ (\text{d},\,\,{}^{2}J_{\text{C},\text{P}} = 2 \ \text{Hz}) \ \text{CH}; \\ 129.1 \ (\text{d},\,\,{}^{3}J_{\text{C},\text{P}} = 12.0 \ \text{Hz}),\, 129.3 \ (\text{d},\,\,{}^{3}J_{\text{C},\text{P}} = 21.6 \ \text{Hz}) \ \text{C}_{3/5}; \\ 129.8 \ (\text{d},\,\,{}^{1}J_{\text{C},\text{P}} = 58.6 \ \text{Hz}),\, 130.0 \ (\text{d},\,\,{}^{1}J_{\text{C},\text{P}} = 61.2 \ \text{Hz}) \ \text{C}_{1}; \\ 131.8 \ (\text{d},\,\,{}^{4}J_{\text{C},\text{P}} = 2.5 \ \text{Hz}),\, 131.9 \ (\text{d},\,\,{}^{4}J_{\text{C},\text{P}} = 2.5 \ \text{Hz}) \ \text{C}_{2}; \\ \text{c}_{3}.2 \ (\text{d},\,\,{}^{2}J_{\text{C},\text{P}} = 12.0 \ \text{Hz}),\, 133.3 \ (\text{d},\,\,{}^{2}J_{\text{C},\text{P}} = 12.0 \ \text{Hz}) \ \text{C}_{2}; \\ \text{c}_{3}.^{3}1\text{P}_{1}^{1}\text{H} \ \text{NMR}: \ \delta = 25.9 \ (\text{s}). - \text{MS} \ (\text{FAB}), \ m/z \ (\%): 947 \ (16) \ \{[(\text{L})\text{Au}]_{2}^{3^{7}}\text{Cl}\}^{+},\, 945 \ (42) \ \{[(\text{L})\text{Au}]_{2}^{3^{5}}\text{Cl}\}^{+},\, 490 \ (2) \ [(\text{L})\text{Au}\text{Cl}]^{+},\, 455 \ (100) \ [(\text{L})\text{Au}]^{+}. \end{split}$$

[R/S-(2-Hydroxybutyl) diphenylphosphine]gold(I)-bromide

15 ml of an aqueous solution of KBr (1.0 g, excess) was added to a solution of (L)AuCl (98 mg, 0.2 mmol) in 15 ml of CH₂Cl₂. The resulting two-phase system was stirred vigorously for 5 h, upon which the aqueous layer was separated and washed with 10 ml of CH₂Cl₂. The dichloromethane extracts were combined, dried with MgSO₄, and the solvent was evaporated under vacuum to leave a white crystalline product. Single crystals suitable for X-ray diffraction were obtained from dichloromethane/pentane at room temperature; yield 91 mg (85%), m.p. 140 °C. - ¹H NMR: $\delta = 0.92$ (t, ³ $J_{H,H} =$ 7.4 Hz, 3H) CH₃: 1.61 (m, 2H) CH₂-CH₃: 1.75 (br. s, 1H) OH; 2.51 (ddd, ${}^{2}J_{H,H} = 14.7$ Hz, ${}^{2}J_{H,P} = 10.4$ Hz, ${}^{3}J_{H,H}$ = 3.3 Hz, 1H), 2.77 (ddd, ${}^{2}J_{H,H}$ = 14.7 Hz, ${}^{2}J_{H,P}$ = 11.0 Hz, ${}^{3}J_{H,H} = 9.1$ Hz, 1H) CH₂-P; 4.09 (m, 1H) CH; 7.37 - 7.78 (m, 10 H) arene H. - ${}^{13}C{}^{1}H{}$ NMR: $\delta = 9.7$ (s) CH₃; 31.9 (d, ${}^{3}J_{C,P} = 11.0$ Hz) CH₂-CH₃; 36.3 (d, ${}^{1}J_{C,P}$ = 37.7 Hz) CH₂-P; 71.9 (d, ${}^{2}J_{C,P}$ = 2 Hz) CH; 129.1 (d, ${}^{3}J_{C,P} = 12.0 \text{ Hz}$, 129.3 (d, ${}^{3}J_{C,P} = 12.0 \text{ Hz}$) C_{3/5}; 130.0 $(d, {}^{1}J_{C,P} = 59.8 \text{ Hz}), 130.2 (d, {}^{1}J_{C,P} = 58.8 \text{ Hz}) C_{1}; 131.8$ (d, ${}^{4}J_{C,P} = 2.8$ Hz), 131.9 (d, ${}^{4}J_{C,P} = 2.8$ Hz) C₄; 133.2 (d, ${}^{2}J_{C,P} = 11.0 \text{ Hz}$), 133.3 (d, ${}^{2}J_{C,P} = 11.0 \text{ Hz}$) C_{2/6}. -³¹P{¹H} NMR: $\delta = 28.5$ (s). - MS (FAB), *m/z* (%): 991 $(24) \{ [(L)Au]_2^{81}Br \}^+, 989 (23) \{ [(L)Au]_2^{79}Br \}^+, 536 (6) \}$ $[(L)Au^{81}Br]^+$, 534 (6) $[(L)Au^{79}Br]$, 455 (100) $[(L)Au]^+$.

[R/S-(2-Hydroxybutyl)diphenylphosphine]gold(I)-iodide

Following the procedure given above using 1.0 g of KI and 147 mg (0.3 mmol) of (L)AuCl; yield 141 mg (81%), m.p. 109 °C. - ¹H NMR: δ = 0.88 (t, ³*J*_{H,H} = 7.3 Hz, 3H) CH₃; 1.57 (m, 2H) CH₂-CH₃; 1.80 (br. s, 1H) OH; 2.49 (ddd, ²*J*_{H,H} = 14.6 Hz, ²*J*_{H,P} = 11.0 Hz, ³*J*_{H,H} = 2.9 Hz, 1H), 2.70 (ddd, ²*J*_{H,H} = 14.6 Hz, ²*J*_{H,P} = 11.0 Hz, ³*J*_{H,H} = 9.5 Hz, 1H) CH₂-P; 4.04 (m, 1H) CH; 7.35 - 7.80 (m,

10 H) arene H. - ¹³C{¹H} NMR: δ = 9.7 (s) CH₃; 31.9 (d, ³*J*_{C,P} = 11.6 Hz) CH₂-CH₃; 36.6 (d, ¹*J*_{C,P} = 35.6 Hz) CH₂-P; 70.6 (d, ²*J*_{C,P} = 2 Hz) CH; 129.1 (d, ³*J*_{C,P} = 12.0 Hz), 129.3 (d, ³*J*_{C,P} = 11.6 Hz) C_{3/5}; 130.4 (d, ¹*J*_{C,P} = 57.5 Hz), 130.5 (d, ¹*J*_{C,P} = 57.5 Hz) C₁; 131.7 (d, ⁴*J*_{C,P} = 2.5 Hz), 131.8 (d, ⁴*J*_{C,P} = 2.5 Hz) C₄; 133.2 (d, ²*J*_{C,P} = 13.6 Hz), 133.2 (d, ²*J*_{C,P} = 13.6 Hz) C_{2/6}. - ³¹P{¹H} NMR: δ = 31.9 (s). - MS (FAB), *m/z* (%): 1037 (16) {[(L)Au]₂I}⁺, 582 (8) [(L)AuI]⁺, 455 (43) [(L)Au]⁺.

C₁₆H₁₉AuIOP (582.21)

Calcd C 33.01 H 3.29 Au 33.84 %; Found C 32.99 H 3.35 Au 34.0 %.

[R/S-(2-Hydroxybutyl)diphenylphosphine]silver(I)chloride

AgCl (60 mg, 0.4 mmol) was added to a solution of (2-hydroxybutyl)diphenylphosphine (105 mg, 0.4 mmol) in 20 ml of acetonitrile and the resulting suspension was stirred under reflux for 6 h with protection against incandescent light. The hot solution was filtered and the volatiles were removed from the filtrate in a vacuum. Recrystallisation of the residue from dichloromethane/pentane afforded the desired product as white crystalline solid; yield 100 mg (62%), m.p. 165 °C. - ¹H NMR: δ = 0.78 (t, ³J_{H,H} = 7.3 Hz, 3H) CH₃; 1.43 (m, 2H) CH₂-CH₃; 2.33 (ddd, ²J_{H,H} = 14.1 Hz, ²J_{H,P} = 10.9 Hz, ${}^{3}J_{H,H} = 2.7$ Hz, 1H), 2.46 (ddd, ${}^{2}J_{H,H} = 14.1$ Hz, ${}^{2}J_{H,P} = 10.3$ Hz, ${}^{3}J_{H,H} = 5.2$ Hz, 1H) CH₂-P; 3.86 (m, 1H) CH; 4.32 (br. s, 1H) OH; 7.18 - 7.60 (m, 10 H) arene H. - ${}^{13}C{}^{1}H$ NMR: $\delta = 10.0$ (s) CH₃; 32.1 (d, ${}^{3}J_{C,P}$ = 10.3 Hz) CH_2 -CH₃; 37.0 (d, ${}^{1}J_{C,P}$ = 17.0 Hz) CH₂-P; 69.4 (d, ${}^{2}J_{C,P}$ = 6.6 Hz) CH; 128.7 (d, ${}^{3}J_{C,P}$ = 9.5 Hz), 128.9 (d, ${}^{3}J_{C,P} = 9.9 \text{ Hz}$) C_{3/5}; 129.7 (s), 130.4 (s) C₄; 132.6 (d, ${}^{2}J_{C,P} = 15.7 \text{ Hz}$), 133.7 (d, ${}^{2}J_{C,P} = 16.5 \text{ Hz}$) $C_{2/6}$; 132.7 (d, ${}^{1}J_{C,P} = 27.7$ Hz), 133.8 (d, ${}^{1}J_{C,P} = 28.3$ Hz) C₁. - ³¹P{¹H} NMR: δ = -1.9 (s). - MS (FAB), *m/z* (%): 912 (10) $[(L)_2Ag_3Cl_2]^+$, 768 (65) $\{[(L)Ag]_2Cl\}^+$, $626 (76) [(L)_2^{109} Ag]^+, 624 (82) [(L)_2^{107} Ag]^+, 367 (87)$ $[(L)^{109}Ag]^+$, 365 (100) $[(L)^{107}Ag]^+$.

C₁₆H₁₉AgClOP (401.62)

Calcd C 47.85 H 4.77 %; Found C 47.87 H 4.80 %.

Bis[(2-hydroxybutyl)diphenylphosphine]gold(I) tetrafluoroborate

(2-Hydroxybutyl)diphenylphosphine (155 mg, 0.6 mmol) and Me₂SAuCl (88 mg, 0.3 mmol) were dissolved in 10 ml of CH₂Cl₂ and a solution of AgBF₄ (58 mg, 0.3 mmol) in 5 ml of THF was added dropwise at ambient temperature with stirring. After 1 h the AgCl precipitate

was filtered off and the solvent was evaporated under vacuum to leave a white, crystalline product; yield 210 mg (87%), m.p. 69 °C. - ¹H NMR: δ = 0.86 (t, ³*J*_{H,H} = 7.3 Hz, 3H) CH₃: 1.57 (m, 2H) CH₂-CH₃: 2.72 (br. d, 1H), 2.84 (br. dd, 1H) CH₂-P; 3.66 (m, 1H) CH; 4.23 (br. s, 1H) OH; 7.38 - 7.72 (m, 10 H) arene H. - ³¹P{¹H} NMR (25 °C): δ = 35.7 (s); (- 40 °C): δ _A = 35.1 (s), δ _B = 35.2 (s). - MS (FAB), *m/z* (%): 713 (100) [(L)₂Au]⁺, 455 (16) [(L)Au]⁺. The corresponding perchlorate and triflate salts can be obtained in an analogous way. The products give the same ¹H NMR, ³¹P{¹H} NMR and FAB-MS spectra as reported above.

Bis[(2-hydroxybutyl)diphenylphosphine]silver(I) tetrafluoroborate

A solution of AgBF₄ (68 mg, 0.35 mmol) in 5 ml of THF was added dropwise to a solution of (2-hydroxybutyl)diphenylphosphine (180 mg, 0.7 mmol) in 10 ml of THF with constant stirring. Stirring of the solution was continued for 2 h at ambient temperature, and the solvent was removed under vacuum to give the desired product in the form of a white, crystalline solid; yield 239 mg (96%), m.p. 108 °C. - ¹H NMR: δ = 0.86 (t, ³*J*_{H,H} = 7.3 Hz, 3H) CH₃; 1.56 (m, 2H) CH₂-CH₃; 2.52 (d, 2H), CH₂-P; 3.54 (m, 1H) CH; 3.90 (br. s, 1H) OH; 7.18 - 7.60 (m, 10 H) arene H. - ³¹P{¹H} NMR (-60 °C): $\delta_{\rm A}$ = 0.48 (2d, ¹*J*_{P,Ag} = 604.4 and 523.3 Hz), $\delta_{\rm B}$ = 0.62 (2d, ¹*J*_{P,Ag} = 602.4 and 522.3 Hz). - MS (FAB), *m/z* (%):626 (90) [(L)¹⁰⁹Ag]⁺, 624 (94) [(L)¹⁰⁷Ag]⁺, 367 (86) [(L)¹⁰⁹Ag]⁺, 365 (100) [(L)¹⁰⁷Ag]⁺.

Crystal structure determinations

Specimens of suitable quality and size of the compounds 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, 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 direct ((L)PAuBr) and Patterson ((L)PAuCl) methods, respectively (SHELXS-86) and completed by full-matrix least squares techniques against F² (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), whereas the O-H atoms were located and refined with isotropic contributions. Further information on

	[Ph ₂ (C ₄ H ₈ OH)P]AuC]	$[Dh_{(C, U, OU)}]A_{U}P_{r}$	Table I. Crystal data, data col
	t=2(- +0)- j	[FII2(C4H8OH)F]AuBI	lection, and structure refinemen
Crystal data			for compounds (L)AuCl and
Formula	C ₁₆ H ₁₉ AuClOP	C ₁₆ H ₁₉ AuBrOP	(L)AuBr.
Mr	490.70	535.16	
Crystal system	monoclinic	monoclinic	$\sum_{(h)}^{[a]} R = \Sigma(F_{o} - F_{c})/\Sigma F_{o} ;$
Space group	$P 2_1/c$	$P 2_1/c$	$^{[b]} wR2 =$
a (Å)	11.935(1)	12.129(2)	$\{[\Sigma w(F_0^2 - F_c^2)^2]/\Sigma [w(F_0^2)^2]\}^{1/2};$
$b(\mathbf{A})$	11.416(1)	11.574(1)	$w = 1/[\sigma^2 (F_o^2) + (ap)^2 + bp];$
c(Å)	11.909(1)	11.808(2)	$p = (F_0^2 + 2F_c^2)/3;$
α (°)	90	90	a = 0.0361 ((L)AuCl), 0.0940
β (°)	95.24(1)	95.02(1)	((L)AuBr);
γ (°)	90	90	b = 5.313 ((L)AuCl), 5.33
$V(Å^3)$	1602.1(2)	1651.3(4)	((L)AuBr).
$\rho_{\rm calc} ({\rm gcm}^{-3})$	2.034	2.153	
Ζ	4	4	
<i>F</i> (000)	936	1008	
$\mu(\text{Mo } K_{\alpha}) (\text{cm}^{-1})$	94.42	114.19	
Data collection			
$T(^{\circ}C)$	-74	-68	
Scan mode	ω	ω	
hkl range	$-15 \rightarrow 0, 0 \rightarrow 14, -14 \rightarrow 15$	$-15 \rightarrow 0, 0 \rightarrow 14, -14 \rightarrow 14$	
$\sin(\theta/\lambda)_{\rm max}$ (Å ⁻¹)	0.64	0.64	
Measured reflections	3424	3464	
Unique reflections	$3297 [R_{int} = 0.0123]$	$3322 [R_{int} = 0.0130]$	
Refls. used for refinement	3297	3322	
Absorption correction	spi-scans	spi-scans	
$T_{\rm min}/\dot{T}_{\rm max}$	0.43/0.99	0.17/0.99	
Refinement			
Refined parameters	184	185	
H Atoms (found/calcd)	1/18	1/18	
Final R values $[I > 2\sigma(I)]$			
$R 1^{[a]}$	0.0280	0.0436	
$wR2^{[b]}$	0.0681	0 1187	
(shift/error)max	<0.001	<0.001	
$\rho_{\rm fm}({\rm max/min})$ (eÅ ⁻³)	1.485/-2.121	2.206/-2.132	

crystal data, data collection and structure refinement are summarized in Table I. Important interatomic distances and angles are shown in the corresponding Figure Caption. Anisotropic thermal parameters, tables of distances and angles, and atomic coordinates have been deposited with Fachinformationszentrum Karlruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen. The data are available on request on quoting CSD No. 407794 and 407795.

- R. J. Puddephatt, The Chemistry of Gold, p. 51, Elsevier, Amsterdam (1978).
- [2] a) H. Schmidbaur, Gold Bull. 23, 11 (1990);
 b) H. Schmidbaur, Chem. Soc. Rev. 24, 391 (1995);

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- [3] a) P. Pyykkö, Chem. Rev. 88, 563 (1988);
 b) N. Kaltsoyannis, J. Chem. Soc., Dalton Trans. 1997, 1.
- [4] H. Schmidbaur, W. Graf, G. Müller, Angew. Chem., Int. Ed. Engl. 27, 417 (1988).

- [5] a) K. Angermaier, A. Sladek. H. Schmidbaur, Z. Naturforsch. 51 b, 1671 (1996);
 b) J.-C. Shi, X.-Y. Huang, D.-X. Wu, Q.-T. Liu, Inorg. Chem. 35, 2747 (1996);
 c) J.-C. Shi, B.-S. Kang, T. C. W. Mak, J. Chem. Soc., Dalton Trans. 1997, 2171.
- [6] A. Bayler, G. A. Bowmaker, H. Schmidbaur, Inorg. Chem. 35, 5959 (1996).
- [7] a) W. Schneider, A. Bauer, H. Schmidbaur, Organometallics 15, 5445 (1996);
 b) C. Hollatz, A. Schier, H. Schmidbaur, J. Am. Chem. Soc. 119, 8115 (1997).
- [8] E. N. Tsvetkov, N. A. Bondarenko, I. G. Malakhova, M. I. Kabachnik, Synthesis 1986, 198.
- [9] R. J. Lancashire, in G. Wilkinson (ed.): Comprehensive Coordination Chemistry, Vol. 5, p. 798, Pergamon: Oxford (1987).
- [10] a) P. G. Jones, G. M. Sheldrick, Acta Crystallogr. B36, 1486 (1980);

b) R. Uson, A. Laguna, M. V. Castrillo, Synth. React. Inorg. Met.-Org. Chem. 9, 317 (1979);

c) A. Bayler, A. Bauer, H. Schmidbaur, Chem. Ber. **130**, 115 (1997).