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Hydroxymethyl Functionalized Phosphanes as Building Blocks to New Water-Soluble Gold(I) Complexes – Synthesis,Characterization, and X-ray Crystal Structures of Novel Tetrahedral $[Au\{P(CH_2OH)_3\}_4]^+$ and Trigonal Planar $[Au(Ph_2PCH_2OH)_3]^+$ Gold(I) Complexes

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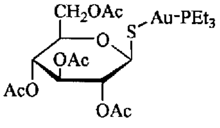
The reactions of water-soluble phosphanes $P(CH_2OH)_3$ (**1**) and Ph_2PCH_2OH (**2**) with $NaAuCl_4$ in aqueous or alcoholic media, produced the water/alcoholic-soluble Au^I complexes $[Au\{P(CH_2OH)_3\}_4]^+$ (**3**) and $[Au(Ph_2PCH_2OH)_3]^+$ (**4**) in near quantitative yields. The X-ray structures of **3** and **4**, reported in this paper, confirm the structures of these new generation of water-soluble transition metal complexes. All compounds were characterized by ^1H-, ^{13}C-, ^{31}P-NMR spectroscopy and mass spectrometry. The structures of **3** and **4** were determined by X-ray crystallography.

The coordination chemistry of gold with a wide variety of ligands continues to be an important area of chemical research because of the potential utility of functionalized complexes of gold in therapeutic applications. For example, several studies have demonstrated that auranofin, [(2,3,4,6,-tetra-*O*-acetyl-1-thio-β-D-glucopyranosato-*S*)(triethylphosphane)]gold(I) (Figure 1) inhibits human lymphocyte responsiveness both in vivo and in vitro[2–3]. It has also shown properties characteristic of in vivo antitumor activity against interperitoneal P388 leukemia[4–5]. Studies have also shown that gold(I) complexes derived from [1,2-bis(diphenylphosphane)ethane] (DPPE) exhibit significant antitumor activity in a broad spectrum of murine tumor models and potent cytotoxic activity to tumor cells in vitro[2,6].

Figure 1. Structure of Auranofin



It is clear from the investigations by several research groups that the phosphane ligands play an important role in the design and development of gold complexes for use in biomedical applications[6–9]. Therefore, coordination chemistry of functionalized phosphane ligands with gold will be important in terms of understanding the structure-biological activity relationships of gold-containing therapeutic agents. Despite significant medical applications of gold-containing compounds, the development of specific ligand systems to produce water-soluble, kinetically inert, and in vivo stable gold complexes of optimum toxicities is still in infancy[10]. In this context, we have reasoned to explore the utility of tris(hydroxymethyl)phosphane [$P(CH_2OH)_3$, **1**, THP] and diphenylhydroxymethylphosphane (Ph_2PCH_2OH, **2**) as complexing agents toward gold precursors. In fact, recent studies have shown that THP and its derivatives produce water-soluble and kinetically inert complexes with several transition metal precursors that include rhenium, palladium, and platinum[11–17]. Our studies have also demonstrated that THP produces a complex with technetium-99m that is not only highly stable in vivo but also clears, primarily, via the kidneys as the undecomposed complex[18].

As part of our ongoing studies on the coordination chemistry of functionalized phosphanes, we herein report the formation of novel water-soluble mononuclear gold(I) complexes derived from the hydroxymethyl phosphane frameworks **1** and **2**. X-ray crystallographic investigations

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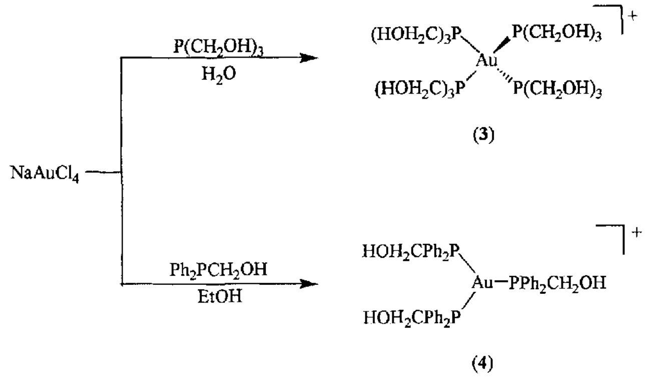
to confirm the molecular constitutions of the mononuclear tetrahedral $[Au\{P(CH_2OH)_3\}_4]^+$ (**3**) and trigonal planar $[Au(Ph_2PCH_2OH)_3]^+$ (**4**) complexes are also described.

Results and Discussion

Interaction of an aqueous solution of sodium tetrachloroaurate with six equivalents of the monophosphanes (**1**) and (**2**) afforded the new gold(I) complexes $[Au\{P(CH_2OH)_3\}_4]Cl$ (**3**) and $[Au(Ph_2PCH_2OH)_3]Cl$ (**4**) (Scheme 1), respectively, in near quantitative yields. The use of excess ligand for these reactions becomes apparent as the phosphanes reduce sodium tetrachloroaurate from gold(III) to gold(I) oxidation state.

Scheme 1

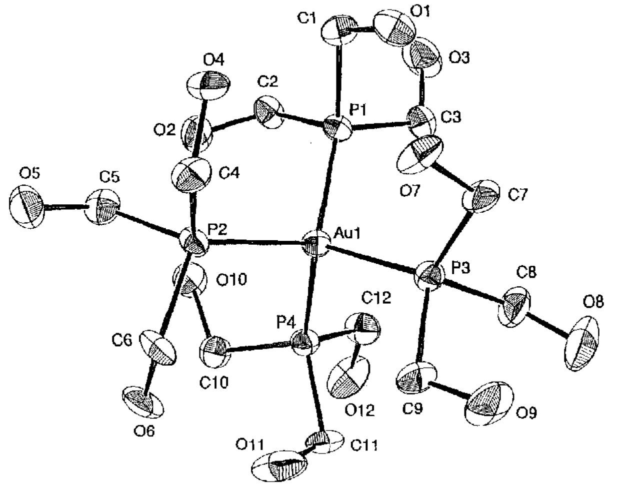


The molecular constitutions of **3** and **4** were confirmed by fast atom bombardment mass spectra ($[M]^+$, m/z = 693.0825 for **3**; $[M - Ph_2PCH_2OH]^+$, m/z = 629.1055 for **4**). The ^{31}P-NMR spectra of **3** and **4** consisted of singlets at δ = 9.4 and 31.4, respectively, indicating a pronounced downfield shift compared to the parent ligands **1** and **2** ($\Delta\delta$ = 32.8 for **3** and 51.8 for **4**). In the ^{1}H-NMR spectra, the methylene protons for **3** and **4** consisted of singlets at δ = 4.12 and 4.70, respectively. The final confirmation of the structures of **3** and **4** has come from X-ray crystallographic investigations of the single crystals as outlined in the following sections.

X-ray Crystallographic Investigations of $[Au\{P(CH_2OH)_3\}_4]Cl$ (3) and $[Au(Ph_2PCH_2OH)_3]Cl$ (4)

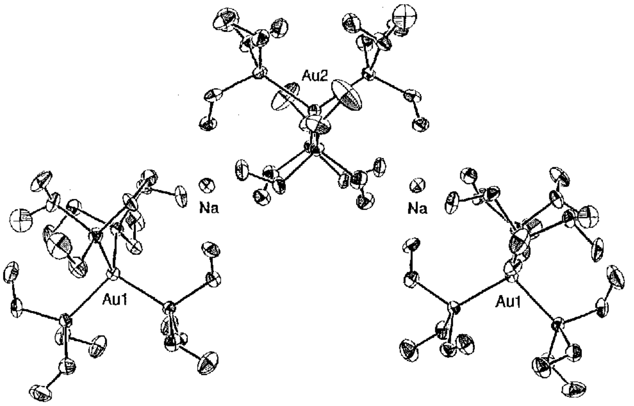
Complex **3** crystallizes as a NaCl inclusion complex, with a ratio of 3:2 $[Au\{P(CH_2OH)_3\}_4]^+$/NaCl. One of the $[Au\{P(CH_2OH)_3\}_4]^+$ cations lies on a twofold axis while the other is in a general position. The crystallographic independent cations are very similar in geometry. Figure 2 is an ORTEP drawing of the cation which lies in a crystallographic general position. The inclusion of NaCl leads to an interesting solid state packing which can be described as trimers of the $[Au\{P(CH_2OH)_3\}_4]^+$ cations in which the three cations are linked by two sodium cations which are complexed by an octahedral array of –OH groups from the central and terminal $[Au\{P(CH_2OH)_3\}_4]^+$ cations, as shown in Figure 3. As the central $[Au\{P(CH_2OH)_3\}_4]^+$ cation lies on a twofold axis, there are four of these complexes in the unit cell. The structure is completed, and the charge balanced, by two chloride ions in general positions and one chloride ion on a twofold axis, for twenty chloride ions in the unit cell.

Figure 2. Molecular structure of **3**[a]



[a] Selected bond lengths [Å] and angles [°]: Au1–P1 2.389(2), Au1–P2 2.409(2), Au1–P3 2.403(2), Au1–P4 2.392(2), Au2–P5 2.403(2), Au2–P5a 2.403(2), Au2–P6 2.416(2), Au2–P6a 2.416(2); P1–Au1–P2 113.33(7), P1–Au1–P3 110.86(7), P1–Au1–P4 106.73(7), P2–Au1–P3 106.92(7), P2–Au1–P4 109.81(7), P3–Au1–P4 109.15(7), P5–Au2–P5a 110.32(7), P5–Au2–P6 106.68(7), P5–Au2–P6a 110.61(7), P5a–Au2–P6 110.61(7), P5a–Au2–P6a 106.68(7), P6–Au2–P6a 106.68(7).

Figure 3. Molecular structure of **3** showing packing arrangement

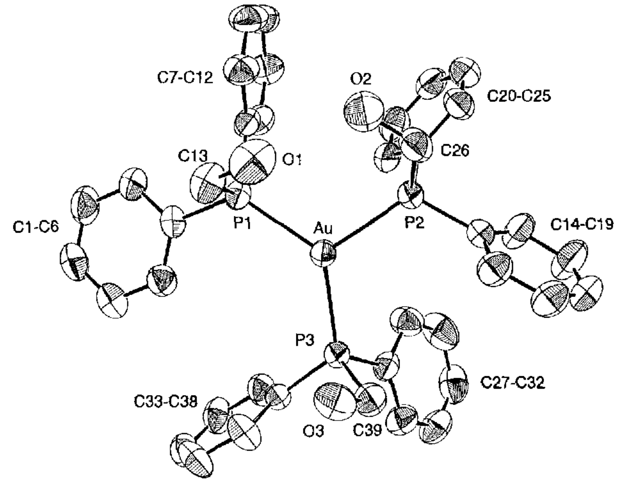


The structure was solved by direct methods. One –OH group on each $[Au\{P(CH_2OH)_3\}_4]^+$ cation was found to be disordered, in each case to two orientations. The disordered oxygen atoms were refined with anisotropic thermal parameters, and all other nonhydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atom positions were calculated or, in the case of hydroxyl hydrogen atoms, were located from difference Fourier maps and included in the refinement using a riding model, with fixed isotropic thermal parameter equal to 1.3 times the isotropic equivalent thermal parameter of the atom attached. The hydrogen atoms of the disordered –CH$_2$OH units were omitted from the final model.

The gold atoms is coordinated by four phosphorus atoms in a tetrahedral environment where the P–Au–P angles range from 106.7 to 113.3° with an average of 109.0°. The Au−P distances range from 2.389 to 2.416 Å with an average of 2.404 Å and are consistent with previously reported values for Au−P bonds in similar environments[19−20].

Crystals of **4** suitable for X-ray diffraction analysis were produced from a methanol/diethyl ether solution at −20°C. The asymmetric unit is comprised of the cationic complex $[Au(Ph_2PCH_2OH)_3]^+$ with one chloride counter ion per molecule. The structure was solved by direct methods. All non-hydrogen atoms were defined with anisotropic parameters. Hydrogen atom positions were calculated or, in the case of hydroxyl hydrogen atoms, were located from difference Fourier maps and included in the refinement using a riding model, with fixed isotropic thermal parameters equal to 1.3 times the isotropic equivalent thermal parameter of the atom attached. An ORTEP drawing is shown in Figure 4.

Figure 4. Molecular structure of **4**[a]



[a] Selected bond lengths [Å] and angles [°]: Au−P1 2.3704(12), Au−P3 2.3690(11), Au−P2 2.4252(12); P1−Au−P2 112.25(4), P2−Au−P3 115.20(4), P1−Au−P3 132.33(4).

The gold atom is coordinated by three phosphorus atoms in a distorted trigonal planar environment. The sum of the P−Au−P angles is 359.8°, indicating very near planarity, with individual P−Au−P angles of 112.25(4), 132.33(4), and 115.20(4)°. the average Au−P bond distance is 2.3882 Å and is consistent with previously reported Au−P bond lengths for similar compounds[21−25].

Literature on the coordination chemistry of gold reveals that the preferred geometry for gold(I) complexes is linear, two-coordinate although the existance of trigonal planar and tetrahedral coordination have been reported[26−27]. To date, the majority of the three- and four-coordinate complexes are with coordinating anions ($[Au(L)_2X]$ or $[Au(L)_3X]$) (L = phosphane) or bidentate phosphanes ($[Au(L-L)_2]^+$)[26−33]. However, relatively few three- and four-coordinate complexes of the type $[Au(L)_3]^+$ and $[Au(L)_4]^+$ have been isolated and characterized[20,34−35]. The $[Au(L)_3]^+$ complexes are dominated by aryl phosphanes or a mixture of aryl/alkyl phosphanes. Two such structurally characterized examples are $[Au\{PPh(c\text{-}C_6H_{11})_2\}_3]^+$ and $[Au(PPh_3)_3]^+$ (with various anions)[21−25]. Furthermore, $[AuL_4]^+$ complexes were predicted to be unattainable until $[Au(Ph_2Me)_4][PF_6]$ was characterized[19−20]. Since then, a few other tetrahedral complexes have been reported. These complexes are derived from 1,3,5-triaza-7-phosphaadamantane (TPA) and its protonated and methylated derivaties[20]. As expected, the magnitude of the cone angle plays a large role in determining the coordination geometry around the metal center. With large phosphanes such as triphenylphosphane, the complexes tend to be trigonal planar however, ligands with smaller cone angles such as TPA and mixed alkyl/aryl phosphanes have the capability of forming tetrahedral complexes. In this context complexes **3** and **4** provide examples of tetrahedral $[AuL_4]^+$ and trigonal planar $[AuL_3]^+$ gold(I) complexes that display unusual kinetic inertness and aqueous/alcoholic stability.

Conclusions

The coordination chemistry of the hydroxymethyl phosphanes **1** and **2** with sodium tetrachloroaurate and, as reported in this paper, offers opportunities for the development of gold complexes with diversity in solution chemistry and solid state structural features. The hydroxymethyl phosphane **1** forms a tetrahedral gold complex (**3**), that is water-soluble, upon interaction with sodium tetrachloroaurate. In contrast, the hydroxymethyl phosphane **2** forms a trigonal planar gold complex (**4**), that is soluble in higher molecular weight alcohols and non-polar organic solvents, illustrating the systematic control of the phosphane cone angle on the overall geometry around the gold(I) center. Preliminary studies on the radiochemical investigation with Au-198 have indicated that ligand **1** produces a complex in high yields. Furthermore, the Au-198 complex of **1** has demonstrated moderate in vitro and in vivo stability. Details on the results of the radiochemical investigations of **1** with Au-198 and its in vivo properties will be reported elsewhere[36].

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Experimental Section

All reactions were carried out under purified nitrogen by standard Schlenk techniques. Solvents were purified and dried by standard methods and distilled under nitrogen prior to use. $NaAuCl_4$ was purchased from Alfa used without further purification. The synthesis of $P(CH_2OH)_3$[16−17] has been reported earlier. Ph_2PCH_2OH[37] was synthesized by a modified procedure. − Nuclear magnetic resonance spectra were recorded on a Bruker ARX-300 spectrometer using D_2O or $CDCl_3$ as a solvent. The ^{1}H-NMR chemical shifts are reported in parts per million, downfield from external standard $SiMe_4$. The ^{31}P-NMR (121.5 MHz) spectra were recorded with 85% H_3PO_4 as an external standard, and positive chemical shifts lie downfield of the standard. − Mass spectra were performed by Washington University, St. Louis, MO.

Synthesis of $[Au\{P(CH_2OH)_3\}_4]Cl$ (**3**): An aqueous solution (5 ml) of sodium tetrachloroaurate (0.26 g, 0.65 mmol) was added dropwise to tris(hydroxymethyl)phosphane (0.50 g, 4.0 mmol) in water (5 ml) at 25°C with constant stirring. The stirring was continued for thirty minutes upon which the solvent was removed under reduced pressure and the residue crystallized twice from methanol/diethyl ether at −20°C to give compound **3** in 80% yield (0.38 g, 0.52 mmol). $C_{12}H_{36}O_{12}P_4Au$: calcd. 693.0822, found 693.0825 (FABMS): − M.p. = 160−162°C (dec.). − ^1H NMR (D_2O): δ = 4.12 (s, 8H, PCH_2OH). − ^{13}C NMR (D_2O): δ = 57.7 (d, $^1J_{PC}$ = 21.6 Hz, PCH_2OH). − ^{31}P NMR (D_2O): δ = 9.4 (br. s).

Synthesis of [Au(Ph₂PCH₂OH)₃]Cl (**4**): Sodium tetrachloroaurate (0.26 g, 0.65 mmol) in ethanol (5 ml) was added dropwise to diphenylhydroxymethylphosphane (0.84 g, 3.9 mmol) in ethanol (5 ml) at 25°C with constant stirring. The stirring was continued for thirty minutes upon which the solvent was removed under reduced pressure to afford the complex **4** in 83% (0.46 g, 0.54 mmol) yield. Crystals were obtained from methanol/diethyl ether at −20°C. − $C_{39}H_{39}O_3P_3Au$: calcd. 845.1778, found $[M - Ph_2PCH_2OH]^+$, 629.1055 (FABMS). − M.p. = 153−156°C. − ^1H NMR ($CDCl_3$): δ = 4.70 (s, 6H, PCH_2OH), 7.12 (t, 12H, $m\text{-}C_6H_5$), 7.24−7.35 (m, 18H, $o,p\text{-}C_6H_5$). − ^{13}C NMR ($CDCl_3$): δ = 63.1 (d, $^1J_{PC}$ = 27.2 Hz, PCH_2OH), 128.5 (d, $^3J_{PC}$ = 7.6 Hz, $m\text{-}C_6H_5$), 130.08 (s, $p\text{-}C_6H_5$), 131.5 (d, $^2J_{PC}$ = 33.2 Hz, $o\text{-}C_6H_5$), 132.5 (d, $^1J_{PC}$ = 10.6 Hz, $m\text{-}C_6H_5$). − ^{31}P NMR ($CDCl_3$): δ = 31.4 (s).

X-ray Data Collection and Processing: The crystal data and details of data collection for complexes **3** and **4** are given in Table 1. Clear colorless crystals of **3** and **4** suitable for X-ray diffraction were obtained from methanol/diethyl ether at −20°C. Intensity data were collected on a Siemens SMART CCD system using the omega scan mode. Data were corrected for absorption using the program SADABS which is based on the method of Blessing[38]. Crystal decay was less than one percent and a correction deemed unnecessary. The programs used for the crystallographic computations are reported in ref.[39]. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100089. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: int. code +44(1223)336-033, e-mail: deposit@chemcrys.cam.ak.uk].

Table 1. Crystal data for compounds **3** and **4**[a]

	3	**4**
formula	$[C_{12}H_{36}O_{12}P_4Au]_3Cl_3 \cdot 2NaCl$	$[C_{39}H_{39}O_3P_3Au]Cl$
crystal system	orthorhombic	monoclinic
space group	*Pbcn*	$P2_1/n$
formula weight	2303.07	881.07
crystal size [mm]	0.15 × 0.25 × 0.50	0.20 × 0.35 × 0.40
a [Å]	10.6927(6)	12.0940(7)
b [Å]	17.0356(9)	14.9895(8)
c [Å]	42.948(2)	20.0770(11)
β [°]	90	90.5832(10)
T [K]	295(2)	295(2)
λ [Å]	0.71073	0.71073
Z	4	4
F(000)	4544	1752
V [Å^3]	7823.3(7)	3639.4(3)
$\rho_{calcd.}$ [g/cm^3]	1.955	1.608
μ [mm^{-1}]	6.10	4.27
2θ range [°]	10–50	10–50
T_{min}–T_{max}	0.58–1.00	0.59–0.91
no. of unique rflns.	8537	7900
no. of rflns with $I > 2\sigma$	7715	6752
no. of variables	433	424
R_f, R_w[a]	0.045, 0.085	0.033, 0.051
GOF	1.78	1.29
shift/σ	0.012	0.014

[a] $R_f = \Sigma (||F_o| - |F_c*)/\Sigma(|F_o|)$; $R_w = [\Sigma s\{(|F_o| - |F_c|)^2\}/\Sigma w(|F_o|)^2]^{1/2}$.

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