macrocycle basicity. Specifically, the eight electron-donating ethyl groups of (OEP)Ru(CO) should lead to an increased electron density on the porphyrin π-ring system, thus making electron addition to the central Ru metal relatively easier than electron addition to the porphyrin π-ring system. This is only a qualitative description. Other factors such as the donicity of the solvent may play some role in influencing the site of electron transfer. The Gutmann donor number increases from 11.9 to 16.6 upon going from PhCN to PrCN and from 20.0 to 33.1 upon going from THF to py.[24] An increase in donor number should result in more electron density on the central metal if the ligand is axially coordinated. Iterative extended Hückel calculations[1] show that the empty $d_{x^2-y^2}$ and d_{z^2} orbitals of the Ru ion in (OEP)Ru(CO)(py) have higher energy than that of the $e_g(\pi^*)$ orbital. Thus, the addition of one electron to the porphyrin π-ring system might be more favorable in this case.

Acknowledgment. The support of the National Science Foundation (Grant CHE-8822881) is gratefully acknowledged. We also acknowledge the help of Dr. John Bear with the thermogravimetric analysis experiments.

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Registry No. TBAP, 1923-70-2; THF, 109-99-9; DMSO, 67-68-5; py, 110-86-1; (OEP)Ru(CO)(PhCN), 135228-22-7; (OEP)Ru(CO)(CH_3CN), 135256-26-7; (OEP)Ru(CO)(PrCN), 135228-23-8; (OEP)Ru(CO)(THF), 55059-68-2; (OEP)Ru(CO)(DMSO), 112374-62-6; (OEP)Ru(CO)(py), 38478-17-0; [(OEP)Ru(CO)(PhCN)]$^-$, 135256-27-8; [(OEP)Ru(CO)(CH_3CN)]$^-$, 135228-24-9; [(OEP)Ru(CO)(PrCN)]$^-$, 135228-25-0; [(OEP)Ru(CO)(THF)]$^-$, 135228-26-1; [(OEP)Ru(CO)(DMSO)]$^-$, 135228-27-2; [(OEP)Ru(CO)(py)]$^-$, 135228-28-3; [(OEP)Ru(CO)]$^+$, 43145-33-1; [(OEP)Ru(CO)(PhCN)]$^+$, 135228-29-4; [(OEP)Ru(CO)(CH_3CN)]$^+$, 135228-30-7; [(OEP)Ru(CO)(PrCN)]$^+$, 135228-31-8; [(OEP)Ru(CO)(THF)]$^+$, 135228-32-9; [(OEP)Ru(CO)(DMSO)]$^+$, 135228-33-0; [(OEP)Ru(CO)(py)]$^+$, 80675-23-6; [(OEP)Ru(CO)(PhCN)]$^{2+}$, 135228-34-1; [(OEP)Ru(CO)(CH_3CN)]$^{2+}$, 135228-35-2; [(OEP)Ru(CO)(PrCN)]$^{2+}$, 135228-36-3; [(OEP)Ru(CO)(THF)]$^{2+}$, 135228-37-4; [(OEP)Ru(CO)(py)]$^{2+}$, 135228-38-5; [(OEP)Ru(CO)(py)]$^{2-}$, 135228-39-6; [(OEP)Ru(CO)]$^{2-}$, 135228-40-9; [(OEP)Ru(CO)(THF)]$^{2-}$, 135228-41-0; [(OEP)Ru(CO)(PrCN)]$^{2-}$, 135228-42-1; CH_2Cl_2, 75-09-2; PhCN, 100-47-0; CH_3CN, 75-05-8; PrCN, 109-74-0; (OEP)Ru(CO), 41636-35-5; (OEP)Ru(CO)(CH_3OH), 89530-39-2; [(OEP)Ru(CO)(CH_3OH)]$^-$, 135228-43-2.

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Gold(I) Phosphine Complexes: Mercaptooxopurine Base Interactions. Molecular and Crystal Structure of (8-Mercaptotheophyllinato-*S*)(triphenylphosphine)gold(I)

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The interaction of chloro(triphenylphosphine)gold(I) and [μ-1,2-bis(diphenylphosphino)ethane]bis[bromogold(I)] with mercaptooxopurine derivatives (8-mercaptotheophylline, 8-mercapto-2-thiotheophylline, and 8-(methylthio)theophylline) under basic conditions yields complexes of the type [Au(PPh_3)L], [{Au(PPh_3)}$_2$(μ-L)], [Au(μ-dppe)(μ-L)Au], and [LAu(μ-dppe)AuL] [L = mercaptooxopurine anion, dppe = 1,2-bis(diphenylphosphino)ethane], which contain either one S8-bonded or two N7,S8-bonded gold(I) phosphine groups. These complexes were characterized by means of ^{1}H, ^{13}C, and ^{31}P NMR and IR spectroscopy. Besides this, the crystal structure of the complex (8-mercaptotheophyllinato)(triphenylphosphine)gold(I) was determined from X-ray diffraction data. The compound crystallizes in triclinic space group $P\bar{1}$ with a = 8.035 (1) Å, b = 12.749 (5) Å, c = 13.172 (4) Å, α = 102.89 (5)°, β = 103.03 (2)°, γ = 103.77 (5)°, V = 1221.0 (8) Å^3, Z = 2, R = 0.037, and R_w = 0.039. The structure consists of neutral [Au(PPh_3)(HL^1)] (HL^1 = 8-mercaptotheophyllinato anion) held together in pairs by two N7-H---O6 hydrogen bonds and related by a crystallographic center of inversion. The coordination of the gold atom is almost linear, P-Au-S8 = 178.6 (2)°, with Au-S and Au-P bond distances of 2.308 (2) and 2.256 (2) Å, respectively. The substitution reaction between [Au(PPh_3)(HL^1)] and [($AuBr)_2$(μ-dppe)] to give the complex [Au(μ-dppe)(μ-L^1)Au] was studied. It seems that the reaction takes place through the intermediate complexes K[(L^1)Au(μ-dppe)AuBr]·4H_2O and [{Au(PPh_3)}$_2$(μ-L^1)].

Introduction

The current interest in the characterization of gold(I) phosphine complexes owes much to the successful use of the "auranofin", a gold(I) compound containing triethylphosphine and tetraacetylthioglucose ligands, for the treatment of rheumatoid arthritis.[1,2] In addition, auranofin and a number of Au(I) complexes of PPh_3 have been reported to have anticancer activity.[3-6] Likewise, 1,2-bis(diphenylphosphino)ethane (dppe) and some of its analogues have also been shown to have antitumor activity, and their activity is enhanced on coordination to gold(I).[7-11] In view of all this, the biological importance of purine bases and the possibility that gold binding to DNA bases could occur,[12,13] the study of (purine)gold(I) phosphine complexes is of interest. In a previous work[14] we have investigated the interaction of chloro(triphenylphosphine)gold(I) and [μ-1,2-bis(diphenylphosphino)ethane]bis[bromogold(I)] with a number of oxopurine bases and found the involvement of the deprotonated N-H groups in the complex formation, the N7 atom being the first binding

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site to gold(I). Owing to the pharmacological interest in sulfur-containing purine bases and in view of the existence of many tautomers of the 8-mercaptopurine bases involving N7, N9, and S8 atoms, each of which may give rise to a different gold(I) complex, we decide to extent our investigations to the preparation of gold(I) phosphine complexes of 8-mercaptotheophylline (H_2L^1), 8-mercapto-2-thiotheophylline (H_2L^2), and 8-(methylthio)theophylline (HL^3). Because some of these gold(I) compound display a high degree of cytotoxic potency "in vitro",[15] they are being tested for "in vivo" antitumor activity.

Experimental Section

The ligands 8-mercaptotheophylline, theophylline, and 8-(methylthio)theophylline were prepared as described in the literature.[16] Triphenylphosphine and 1,2-bis(diphenylphosphino)ethane were purchased from Aldrich. The $[(AuBr)^2(\mu\text{-dppe})]$ complex was prepared from $Na[AuCl_4]\cdot 2H_2O$, NaBr, and acetone, as we previously described.[14]

Microanalyses were performed with a Perkin-Elmer 240C analyzer. Gold was determined thermogravimetrically with a Mettler TG-50 thermobalance by using samples varying in weight from 9 to 10 mg and a heating rate of 5 °C·min^{-1} in an air atmosphere. In all cases, at 850 °C the weight of the residue (metallic gold) was stable. Infrared spectra were recorded in the 4000–200-cm^{-1} range on a Perkin-Elmer 983G spectrophotometer, using KBr and polyethylene pellets. ^1H, ^{13}C, and ^{31}P NMR spectra of the compounds dissolved in $(CD_3)_2SO$ were recorded on a Bruker AM300 spectrometer. ^1H NMR spectra were referenced to $SiMe_4$, whereas for ^{13}C NMR spectra the center peak of $(CD_3)_2SO$ was used as an internal reference and converted to the $SiMe_4$ scale by addition of 39.4 ppm. For ^{31}P NMR spectra H_3PO_4/D_2O (85:15 v/v) was used as an external shift reference. The molar masses were determined by using a Knauer Model 1974 vapor-pressure osmometer (VPO) equipped with an universal probe that was able to operate between 293 and 400 K. The VPO apparatus has been calibrated by using 1,1′-biphenyl samples in 1,2-dichloromethane and chloroform.

Preparation of [Au(PPh$_3$)L] (HL = H$_2$L^1, H$_2$L^2, HL^3). The general procedure for the synthesis of $[Au(PPh_3)L]$ was as follows: A solution of $[Au(PPh_3)Cl]$ (0.26 g, 1 mmol in 30 mL of acetone) was added to one of the purine derivatives (1 mmol) in water containing 1 mol equiv of KOH. The resulting solution was refluxed for 15 min and then allowed to stand at room temperature for several hours, whereupon the white compound precipitated. The complex was filtered off, washed with water, acetone and diethyl ether, and dried in vacuo. Crystals of $[Au(PPh_3)L^1]$ suitable for X-ray analysis were obtained by slow evaporation of a solution of the complex in methanol at 4 °C.

[Au(PPh$_3$)(HL^1)] (1). Anal. Calcd for $C_{25}H_{22}AuN_4O_2PS$: C, 44.79; H, 3.31; N, 8.36; Au, 29.38. Found: C, 44.92; H, 3.46; N, 8.27; Au, 28.90. Mp: 253–258 °C dec. IR (KBr, cm^{-1}): 1689, ν(C6=O); 1647, ν(C2=O); 1531, thioamide I, 1218, thioamide II.

[Au(PPh$_3$)(HL^2)] (2). Anal. Calcd for $C_{25}H_{22}AuN_4OPS_2$: C, 43.74; H, 3.23; N, 8.16, Au, 28.69. Found: C, 44.01; H, 3.31; N, 8.10; Au, 28.68. Mp: 268–273 °C dec. IR (KBr, cm^{-1}): 1676, ν(C6=O); 1522, thioamide I; 1210, thioamide II.

[Au(PPh$_3$)L^3] (8). Anal. Calcd for $C_{26}H_{24}AuN_4O_2PS$: C, 45.62, H, 3.53; N, 8.18; Au, 28.77. Found: C, 45.38; H, 3.48; N, 8.55; Au, 28.95. Mp: 195–200 °C dec. IR (KBr, cm^{-1}): 1687, ν(C6=O); 1643, ν(C2=O); 1585, ν(C=C), 1522, ν(C=N).

Preparation of [{Au(PPh$_3$)}$_2$(μ-L)] (H$_2$L = H$_2$L^1, H$_2$L^2). These complexes were prepared by using the above method for $[Au(PPh_3)L]$ but with a purine derivative: $[Au(PPh_3)Cl]$:KOH ratio of 1:2:2. These compounds were also prepared by adding a solution of $[Au(PPh_3)Cl]$ (1 mmol in 30 mL of acetone) to one of the corresponding $[Au(PPh_3)L]$ complex (1 mmol) in 30 mL of water/acetone (5:1) containing KOH (1 mmol).

[{Au(PPh$_3$)}$_2$(μ-L^1)] (3). Anal. Calcd for $C_{43}H_{36}Au_2N_4O_2P_2S$: C, 45.76; H, 3.21; N, 4.96; Au, 34.93. Found: C, 45.55; H, 3.41; N, 5.26; Au, 34.71. Mp: 265–270 °C dec. IR (KBr, cm^{-1}): 1686, ν(C6=O); 1641, ν(C2=O); 1522, thioamide I; 1296, thioamide II.

[{Au(PPh$_3$)}$_2$(μ-L^2)] (4). Anal. Calcd for $C_{43}H_{36}Au_2N_4OP_2S_2$: C, 45.12; H, 3.17; N, 4.89; Au, 34.41. Found: C, 45.30; H, 3.27; N, 5.02; Au, 34.70. Mp: 270–275 °C dec. IR (KBr, cm^{-1}): 1676, ν(C6=O); 1500, thioamide I; 1296, thioamide II.

Preparation of [Au(μ-dppe)(μ-L)Au] (H$_2$L = H$_2$L^1, H$_2$L^2). A solution of $[(AuBr)_2(\mu\text{-dppe})]$ (1 mmol in 30 mL of ethanol) was added to a solution of purine derivative (1 mmol in 5 mL of water) containing 1 mol equiv of KOH. The resulting solution was refluxed for 30 min, and a white product formed, which was filtered off, washed with water and ethanol, and dried with diethyl ether.

[Au(μ-dppe)(μ-L^1)Au]·H$_2$O (5). Anal. Calcd for $C_{33}H_{32}Au_2N_4O_3P_2S$: C, 38.84; H, 3.16; N, 5.49; Au, 38.63. Found: C, 38.72; H, 3.21; N, 5.17; Au, 39.10. Mp: 245–250 °C dec. IR (KBr, cm^{-1}): 1676, ν(C6=O); 1638, ν(C2=O); 1521, thioamide I; 1299, thioamide II.

[Au(μ-dppe)(μ-L^2)Au]·H$_2$O (6). Anal. Calcd for $C_{33}H_{32}Au_2N_4O_2P_2S_2$: C, 38.24; H, 3.11; N, 5.41; Au, 38.03. Found: C, 37.83, H, 2.98; N, 5.49; Au, 38.50. Mp: 260–265 °C dec. IR (KBr, cm^{-1}): 1667, ν(C6=O); 1501, thioamide I; 1299, thioamide II.

[L^{3}Au(μ-dppe)AuL^3] (9). This product was prepared by the same method as for **5**, using a 1:2 $[(AuBr)_2(dppe)]$:HL^3 molar ratio. Anal. Calcd for $C_{42}H_{42}Au_2N_8O_4P_2S_2$: C, 40.59; H, 3.41; N, 9.02; Au, 31.70. Found: C, 40.38; H, 3.37; N, 8.90; Au, 32.10. Mp: 260–265 °C dec. IR (KBr, cm^{-1}): 1686, ν(C6=O); 1639, ν(C2=O); 1588, ν(C=C); 1523, ν(C=N).

Reaction of 1 with [(AuBr)$_2$(dppe)]. KOH (1 mmol) was added to a suspension of **1** (1 mmol) and $[AuBr)_2(\mu\text{-dppe})]$ (1 mmol in 50 mL of ethanol/water (20:1 v/v)). The mixture was stirred and heated at 60 °C until an almost clear solution was obtained (ca. 5 min). After filtration of a small amount of **5**, the resulting solution was allowed to stand at room temperature for 1 day, whereupon colorless plates of complex **7** precipitated. From the filtrate after 2 additional days colorless needless of complex **3** were isolated, which were filtered off, washed with ethanol and diethyl ether, and dried in vacuo. On the other hand, when the reaction mixture was heated for 30 min, a white precipitate of complex **5** was obtained.

Table I. Summary of Crystal and Data Collection Parameters of Compound **1**

chem formula	$C_{25}H_{22}AuN_4O_2PS$
cryst system	triclinic
space group	$P\bar{1}$
M_r	670.48
cryst dimens, mm	0.10 × 0.30 × 0.40
a, Å	8.035 (1)
b, Å	12.749 (5)
c, Å	13.172 (4)
α, deg	102.89 (5)
β, deg	103.03 (2)
γ, deg	103.77 (5)
V, Å^3	1221.0 (8)
Z	2
μ, cm^{-1}	63.9
ρ_{calc}, g·cm^{-3}	1.823
ρ_{obs}, g·cm^{-3}	1.84 (2)[a]
$F(000)$	652
four-circle diffractometer	CAD4
radiation (λ, Å)	Mo Kα (0.71069) (graphite monochromated)
temp, K	295 (1)
scan limits, deg	$4 \le 2\theta \le 60$
scan width	$\Delta\theta = 2.0 + 0.34 \tan\theta$
scan technique	ω–2θ
range of hkl	$0 \le h \le 11$; $-17 \le k \le 17$; $-18 \le l \le 17$
no. of reflcns collcd	7403
no. of unique data	7021
no. of obsd reflcns	5945 [$I \ge 2\sigma(I)$]
no. of variables	373
abs corr	empirical, DIFABS[18]
min and max transm factors	0.76 and 1.42
R	0.037
R_w	0.039

[a] By flotation.

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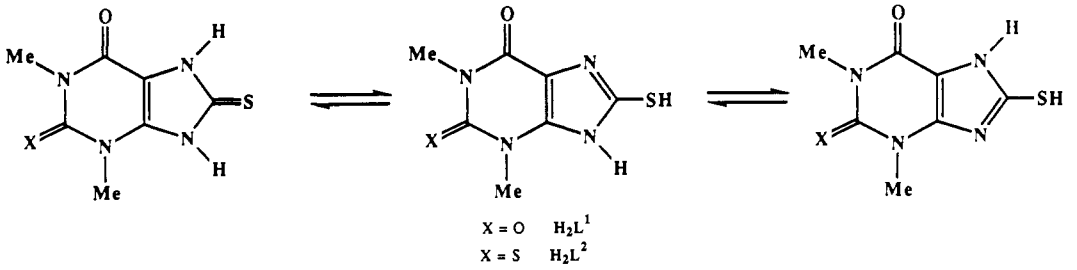
Scheme I



K[(L¹)Au(μ-dppe)AuBr]·4H₂O (7). Anal. Calcd for $C_{33}H_{38}Au_2BrKN_4O_6P_2S$: C, 33.21; H, 3.21; N, 4.69; Au, 33.00. Found: C, 33.36; H, 2.94; N, 4.56; Au, 33.10. Mp: 235–240 °C dec. Experimental water percentage by thermogravimetric analysis: 6.18 (calcd, 6.03). Λ_M (5×10^{-4} M), DMF: 128 Ω^{-1} cm² mol⁻¹. IR (KBr, cm⁻¹): 1676, ν(C6=O); 1639, ν(C2=O); 1522, thioamide I; 1298, thioamide II.

X-ray Crystal Structure of [Au(PPh₃)(HL¹)] (1). Single crystals of complex **1** were obtained as described above. Details of the intensity data collection and structure determination are summarized in Table I.

Structure Solution and Refinement. The Au position was determined by Patterson techniques. A succession of difference Fourier syntheses and least-squares refinements revealed the position of all atoms including hydrogens. All non-hydrogen atoms were refined anisotropically. The positional parameters of all hydrogen atoms were refined with isotropic thermal parameters set to U_{eq} of the bonded atom. The atomic scattering factors and anomalous dispersion factors were taken from the literature.[17] The final full-matrix least-squares refinement, minimizing $\sum w(|F_o| - |F_c|)^2$, converged to $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.037$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum|F_o|^2]^{1/2} = 0.039$ with a weighting scheme $w = 1$. The goodness of fit was 1.65 with 5945 observations and 373 variables.

Positional parameters are listed in Table II. Most calculations were carried out on a VAX 11/750 computer using the XRAY80 system.[19]

Complete crystal data, components of the anisotropic temperature factor, deviations of atoms from their least-squares planes, and observed and calculated structure factor amplitudes have been deposited as supplementary material.

Results and Discussion

Complexes of 8-Mercaptotheophylline and 8-Mercapto-2-thiotheophylline. Both H_2L^1 and H_2L^2 have two ionizable protons in the imidazole ring that are involved in two types of tautomerism: prototropic N7–H ⇌ N9–H and imino thio–thioamide NH–C8=S ⇌ N=C8–SH (Scheme I).

The IR spectra of H_2L^1 and H_2L^2 show the presence of strong ν(N–H) bands in the 3200–3000-cm⁻¹ region as well as very weak ν(S–H) bands in the 2700–2500-cm⁻¹ region, indicating that the thioamide tautomer dominates in the solid. In solution, the position of the imino thio–thioamide tautomeric equilibrium can be determined by ^{13}C NMR spectroscopy by studying suitable model compounds in which the tautomerism is hindered, for instance *S*-methyl and *N*-methyl derivatives of the imino thiol and thioamide tautomers, respectively.[20,21]

The molar fraction of the thioamide tautomer, $X(S)$, can be estimated by using the following equation:

$$X(S) = \frac{\delta_{obs} - [\delta(SCH_3) + \Delta(SH)]}{[\delta(NCH_3) + \Delta(NH)] - [\delta(SCH_3) + \Delta(SH)]}$$

Here $\delta(SCH_3)$ and $\delta(NCH_3)$ are the chemical shifts for the *S*-methyl and *N*-methyl derivatives of the imino thiol and thioamide tautomers, respectively, and Δ(NH) and Δ(SH) are the respective correction parameters for the effects of methyl substitution, indicating the chemical shift difference on going from NCH_3 to NH and from SCH_3 to SH.

From the ^{13}C chemical shift values for C8 in H_2L^1 and H_2L^2 and their 8-methylthio derivatives of 163.78, 164.89, 153.04, and 151.60 ppm, respectively, the chemical shift of C2, δ = 169 ppm, in 1,3-dimethyl-1,3-dihydro-3*H*-benzimidazole-2-thione,[22] which was used as model compound for the thioamide tautomer, and Δ(NH) and Δ(SH) values of −2 and −7 ppm, respectively,[20] the equilibrium thioamide molar fractions estimated for H_2L^1 and H_2L^2 were 0.85 and 0.90, respectively. These values indicate that both compounds, in DMSO solution, exist predominantly as the thioamide tautomer. Moreover, the nature of the substituent at the 2-position of the pyrimidine ring seems not to have an important effect on the position of the imino thio–thioamide equilibrium. However, these are only qualitative results, since a small modification in either the correction parameters or $\delta(SCH_3)$ and $\delta(NCH_3)$ chemical shifts, which are approximate values, leads to a relatively important change of the molar fraction value.

The dominance of the thioamide tautomer for H_2L^1 and H_2L^2, in solution and solid state, is in good agreement with IR, NMR,

Table II. Atomic Coordinates for Compound **1**

atom[a]	x	y	z	U_{eq}[b]
Au	0.12979 (3)	0.21756 (6)	0.00117 (2)	391 (1)
P	0.1187 (2)	0.0900 (1)	−0.1515 (1)	356 (5)
S8	0.1371 (2)	0.3446 (1)	0.1585 (1)	433 (5)
N1	0.9266 (7)	0.6038 (5)	0.4139 (5)	52 (2)
C1	1.0833 (11)	0.6723 (8)	0.5073 (8)	77 (4)
C2	0.9513 (8)	0.5960 (5)	0.3112 (6)	54 (3)
O2	1.0967 (6)	0.6435 (4)	0.3023 (5)	72 (2)
N3	0.8068 (7)	0.5322 (4)	0.2226 (5)	49 (2)
C3	0.8219 (11)	0.5252 (7)	0.1120 (7)	63 (3)
C4	0.6436 (7)	0.4867 (4)	0.2377 (5)	40 (2)
C5	0.6250 (7)	0.4994 (5)	0.3398 (5)	41 (2)
C6	0.7648 (8)	0.5619 (5)	0.4364 (5)	46 (2)
O6	0.7558 (6)	0.5819 (5)	0.5304 (4)	65 (2)
N7	0.4431 (6)	0.4503 (4)	0.3228 (4)	40 (2)
C8	0.3665 (7)	0.4100 (4)	0.2133 (5)	39 (2)
N9	0.4874 (6)	0.4300 (4)	0.1575 (4)	42 (2)
C11	0.2374 (7)	0.1547 (5)	−0.2352 (5)	40 (2)
C12	0.3997 (9)	0.2394 (5)	−0.1840 (6)	51 (3)
C13	0.4980 (9)	0.2874 (6)	−0.2463 (7)	61 (3)
C14	0.4320 (11)	0.2541 (6)	−0.3579 (7)	63 (4)
C15	0.2699 (11)	0.1735 (7)	−0.4104 (7)	64 (4)
C16	0.1724 (8)	0.1217 (6)	−0.3480 (5)	52 (3)
C21	0.2156 (6)	−0.0193 (5)	−0.1241 (4)	36 (2)
C22	0.2547 (9)	−0.0908 (6)	−0.2065 (5)	51 (3)
C23	0.3210 (9)	−0.1781 (6)	−0.1842 (6)	53 (3)
C24	0.3484 (8)	−0.1931 (6)	−0.0827 (6)	52 (3)
C25	0.3124 (8)	−0.1205 (6)	0.0009 (5)	47 (2)
C26	0.2452 (7)	−0.0341 (5)	−0.0202 (5)	40 (2)
C31	−0.1085 (7)	0.0159 (5)	−0.2404 (4)	36 (2)
C32	−0.2129 (8)	0.0801 (5)	−0.2790 (5)	47 (2)
C33	−0.3851 (9)	0.0266 (6)	−0.3480 (6)	57 (3)
C34	−0.4569 (8)	−0.0895 (6)	−0.3761 (6)	54 (3)
C35	−0.3565 (9)	−0.1536 (6)	−0.3371 (6)	51 (3)
C36	−0.1810 (8)	−0.1005 (5)	−0.2688 (5)	41 (2)

[a] Atoms are labeled in agreement with Figure 1. [b] $U_{eq} = {}^1/_3\sum[U_{ij}a_i^*a_j^*a_ia_j\cos(a_i{\cdot}a_j)] \times 10^3$ (×10⁴ for Au, P, S).

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Scheme II

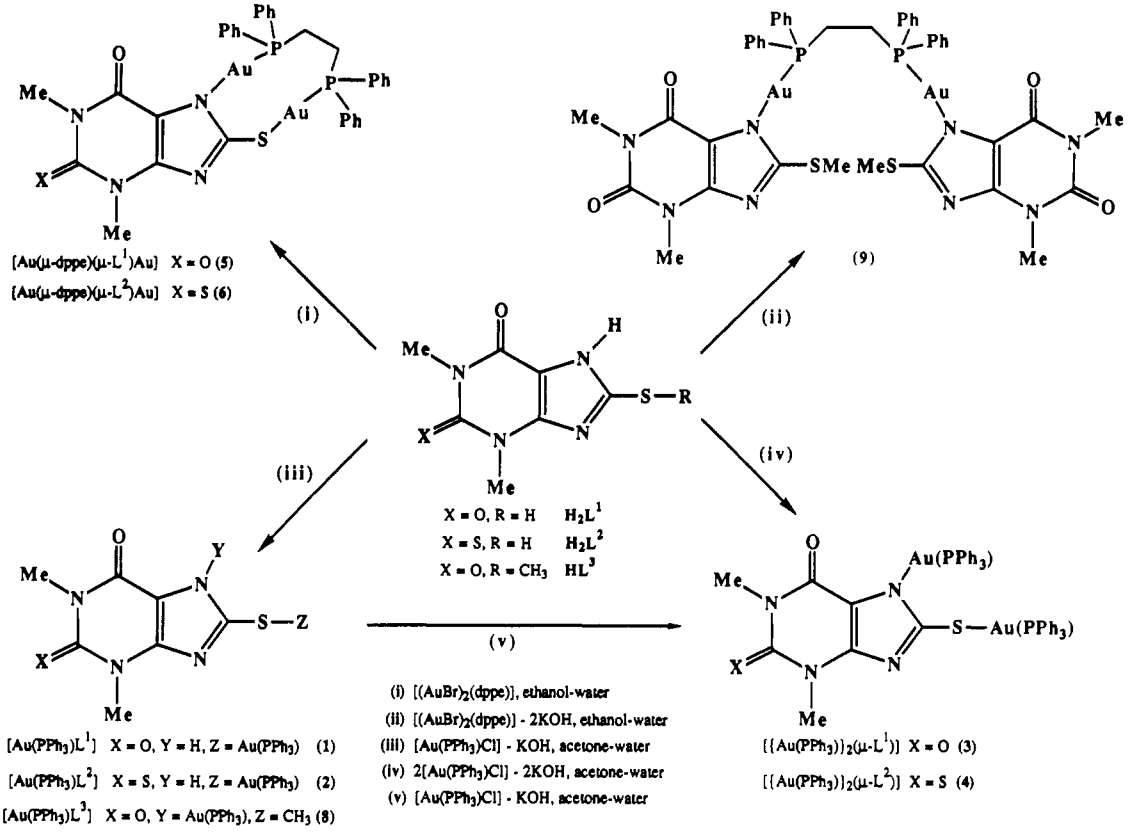

Table III. ^1H and ^{31}P NMR Data for the Isolated Complexes (δ, ppm)

compd	^1H NMR[a] N1–CH_3	N3–CH_3	N7–H	N9–H	S8–CH_3	phenyl protons[c]	^{31}P NMR[b]
H_2L^1	3.15	3.34	13.36	12.95			
$[Au(PPh_3)(HL^1)]$ (1)	3.19	3.37	12.89			7.61	38.66
$[\{Au(PPh_3)\}_2(\mu\text{-}L^1)]$ (3)							29.80, 36.46
$[Au(\mu\text{-dppe})(\mu\text{-}L^1)Au]\cdot H_2O$ (5)							29.81, 36.42
$K[(L^1)Au(\mu\text{-dppe})AuBr]\cdot 4H_2O$ (7)[d]	3.11	3.27				7.45, 7.70, 7.92	29.83, 36.44
H_2L^2	3.55	3.71	13.50	13.19			
$[Au(PPh_3)(HL^2)]$ (2)	3.64	3.80	13.19			7.61	37.88
$[\{Au(PPh_3)\}_2(\mu\text{-}L^2)]$ (4)							29.72, 36.29
HL^3	3.18	3.37	13.38		2.63		
$[Au(PPh_3)(L^3)]$ (8)	3.21	3.42			2.62	7.65	31.90

[a] Relative to $SiMe_4$; solvent Me_2SO. [b] Relative to external 85% H_3PO_4; solvent Me_2SO. [c] Multiplets. [d] Bridge CH_2 protons appear as multiplet at 2.87 ppm.

and X-ray crystallographic studies on analogous compounds containing the imino thiol–thioamide tautomerism.[23] Although thioamide dominates in solution, just prior to complexation the tautomeric equilibrium may be modified by the nature of the solvent, the presence of base, or the nature of the metal cation, and therefore, a potentially rich coordination chemistry is available. Thus, monodeprotonation of H_2L^1 and H_2L^2 in basic medium yields a thiolate anion that may be involved in monodentate, bidentate, or bridging coordination with sulfur and/or nitrogen atoms.

The complexes obtained from the interaction of H_2L^2 and H_2L^1 with $[Au(PPh_3)Cl]$ and $[(AuBr)_2(\mu\text{-dppe})]$ are given in Scheme II.

Information about the structure of the complexes was obtained in the first instance from ^1H, ^{31}P NMR (Table III), and IR spectroscopy (supplementary material). The ^{13}C NMR spectra could not be obtained because of the low solubility of the complexes in DMSO. Besides this, the X-ray crystal structure of $[Au(PPh_3)(HL^1)]$ was determined to check the conclusion based on the spectroscopic results. This complex will be discussed first, since it provides a reference point against which the structures of the other compounds can be discussed.

$[Au(PPh_3)L]$ Complexes. Complex **1** is found by microanalysis to correspond to the formula $[Au(PPh_3)(HL^1)]$. Integration of the ^1H NMR spectrum confirmed the 1:1 stoichiometry of the complex, while the lack of one of the low-field signals due to N7–H and N9–H in the spectrum of the ligand is consistent with the presence of $(HL^1)^-$ thiolate anion in compound **1**. In view of the above discussion concerning tautomerism in H_2L^1, the thiolate anion may coordinate to gold(I) through either N7 or N9 or S8. Nevertheless, the sulfur atom must be the most probable $Au(PPh_3)$ binding site, since a soft (class b) polarizable metal such as gold(I) shows preference for the softer S donor over the less polarizable nitrogen donor atoms.[24] Evidence of S bonding in **1** can be derived from the ^{31}P NMR spectrum, since the position of the signal due to the X–Au–PPh_3 arrangement depends of the donor atom opposite to the phosphorus one. For **1** this signal appears at 38.66

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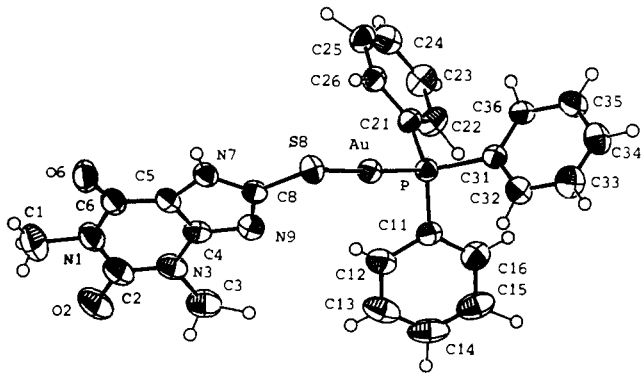

Figure 1. ORTEP view of the $[Au(PPh_3)(HL^1)]$ molecule with atom labeling.

ppm, a typical position for a S–Au–PPh_3 but not for a N–Au–PPh_3 arrangement.[25]

The infrared spectrum of **1** shows bands associated with the $Au(PPh_3)$ group and HL^1 ligand. Although the parent complex, $[Au(PPh_3)Cl]$, exhibits a strong ν(Au–Cl) band at 326 cm^{-1}, no bands are observed in this region for **1**, supporting that the chloride is not coordinated to gold(I). Assignment of either S or N bonding in **1** by noting changes in intensities and positions of some bands with respect to the spectrum of the ligand is very difficult because of the simultaneous iminothio–thioamide ring reordering, and certain ligands bands are masked by those of the $Au(PPh_3)$ group. Furthermore, the most important vibrations for the analysis of the complex ν(CN) and ν(CS) are not pure but just two of the contributions to the characteristic thiamide bands I–IV, which are produced by extensive coupling of NH, CN, and CS vibrational activity.[23] In spite of this, a tentative assignment of the binding mode can be made from IR data. The thioamide I band at 1551 cm^{-1} for uncomplexed H_2L^1 is decreased to 1531 cm^{-1}, while thioamide II band at 1175 cm^{-1} increases to 1218 cm^{-1}. The shift of these bands might also indicate, according to the IR results reported for the complex (2-mercapto-1-methylimidazolato-*S*)-methylmercury(II),[26] S bonding in **1**. This is supported by the presence of a new band at 365 cm^{-1} assigned to ν(Au–S). This assignment is reasonable in view of the reported ν(Au–S) at 342 cm^{-1} for the anionic complex $[Au(SMe)_2]^-$[27] and 350–362 cm^{-1} for the dinuclear complex $[\{(Et_3P)Au\}_2(\mu\text{-}S)]$.[28]

Crystal Structure of $[Au(PPh_3)(HL^1)]$. The results of the crystal structure determination confirm the above proposed coordination for H_2L^1. The crystal contains neutral $[Au(PPh_3)(HL^1)]$ molecules, held together in pairs by two N–H···O hydrogen bonds and related by a crystallographic center of inversion. In these molecules, the ligand coordinates to gold(I) via the deprotonated 8-thiol group. A perspective drawing of the molecule is shown in Figure 1 together with the atom labeling. Selected interatomic distances and bond angles are listed in Table IV.

The gold atom exists in the expected linear coordination geometry [P–Au–S8 = 178.6 (2)°]. The Au–P and Au–S bond lengths, 2.256 (2) and 2.308 (2) Å, are similar to those reported for other compounds containing a P–Au–S linkage (Table V).

Table IV. Selected Interatomic Distances (Å) and Angles (deg) for Compound **1**

Au–P	2.256 (2)	C2–N3	1.374 (7)
Au–S8	2.308 (2)	N3–C3	1.473 (12)
P–C11	1.819 (7)	N3–C4	1.379 (8)
P–C21	1.815 (7)	C4–C5	1.365 (9)
P–C31	1.822 (5)	C4–N9	1.358 (6)
S8–C8	1.735 (5)	C5–C6	1.412 (7)
N1–C1	1.470 (9)	C5–N7	1.390 (7)
N1–C2	1.397 (11)	C6–O6	1.229 (9)
N1–C6	1.406 (9)	N7–C8	1.358 (7)
C2–O2	1.226 (9)	C8–N9	1.355 (9)
P–Au–S	178.6 (2)	C3–N3–C4	120.4 (6)
Au–P–C11	112.3 (3)	N3–C4–C5	121.0 (6)
Au–P–C21	113.2 (2)	N3–C4–N9	125.9 (6)
Au–P–C31	113.3 (2)	C5–C4–N9	113.1 (6)
C11–P–C21	106.4 (3)	C4–C5–C6	123.9 (6)
C11–P–C31	105.3 (3)	C4–C5–N7	104.7 (5)
C21–P–C31	105.7 (3)	C6–C5–N7	131.0 (6)
Au–S8–C8	100.3 (3)	N1–C6–C5	111.3 (6)
C1–N1–C2	115.8 (7)	N1–C6–O6	121.1 (6)
C1–N1–C6	117.1 (6)	C5–C6–O6	127.6 (7)
C2–N1–C6	126.8 (6)	C5–N7–C8	106.6 (5)
N1–C2–O2	120.6 (7)	N7–C8–S8	120.8 (5)
N1–C2–N3	116.9 (7)	N7–C8–N9	112.3 (6)
O2–C2–N3	122.5 (7)	S8–C8–N9	126.9 (5)
C2–N3–C3	119.4 (7)	C4–N9–C8	103.2 (5)
C2–N3–C4	119.8 (6)		

In the phosphine ligand, bond lengths and angles involving gold, phosphorus, and the phenyl rings are quite normal and comparable to those determined for other gold triphenylphosphine complexes.[14] In the present compound, H_2L^1 displays the remaining imidazolic proton bonded to the N7 atom, having bond angles similar to those average values reported for neutral theophylline compounds containing either a N7–H or N7–C bond and significantly different from those for N7–M compounds, in which a theophylline monoanion is bonded to the metal atom via N7 in a monodentate manner.[14,38] The bond lengths are slightly affected upon coordination, but a significant change is detected in the N7–C8–N9 region. The N7–C8 and C8–N9 distances, which are respectively 1.346 (18) and 1.337 (12) Å in the neutral theophylline compounds, are somewhat larger in the present compound (1.358 (7) and 1.355 (9) Å, respectively), indicating that a significant degree of conjugation exists between the C–S bond and the imidazole ring. According to this, the C8–S8 distance of 1.735 (6) Å is rather shorter than the theoretical value for a single C–S bond (1.78 Å).

The Au–S8–C8 angle of 100.3 (3)° is in the lower end of the range previously observed for similar compounds also containing a S-coordinated ligand in its anionic form.[25,29-37] This may be because of the existence of an interaction between the Au and N9 atoms, since the ligand is oriented so that the N9 atom is directed toward the gold atom. However, the Au···N9 distance of 3.312 (4) Å is larger than 3.2 Å, the sum of the van der Waals radii for gold and nitrogen,[39] indicating that there is no significant interaction between these atoms. The values of the Au–S8–C8 angle probably reflects a combination of factors including the electron distribution at the coordinated sulfur as well as the steric requirements of the ligands. This latter factor might also be responsible for the noncoplanarity of the metal–sulfur bond and the imidazolic ring, as revealed by the Au–S8–C8–N9 torsion angle of 33.1 (6)°.

The nine atoms of the purine system are coplanar as expected, but the exocyclic atoms O2, O6, C1, and C2 are distant from this plane by 0.151 (7), 0.062 (7), 0.08 (1), and 0.09 (1) Å, respec-

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Table V. Comparison of Distances (Å) and Angles (deg) in the Gold Atom Coordination Sphere

compd	Au-P	Au-S	P-Au-S	C-S-Au	ref
$[Au(PPh_3)(S_2CNEt_2)]$	2.252 (3)	2.339 (3)	175.7 (1)	96.8 (2)	29
$[Au(PPh_3)(S_2COMe)]$	2.261 (1)	2.310 (1)	174.1 (1)	103.2 (2)	30
Auranofin	2.259 (3)	2.293 (3)	173.6 (1)	105.6 (3)	31
$[Au(PPh_3)(C_4H_3N_2OS)]$	2.248 (2)	2.296 (2)	175.4 (2)	103.8 (3)	32
	2.248 (2)	2.300 (2)	177.0 (2)	100.8 (2)	
$[Au(PCy_3)(C_4H_5N_2S)\cdot 2C_7H_6N_2$	2.292 (2)	2.331 (3)	172.0 (1)	106.6 (3)	25
$[Au(PPr^i_3)(C_{10}H_{15}CS_2)]$	2.251 (3)	2.317 (3)	174.3 (1)	105.0 (3)	33
$[Au(PPh_3)(SCN)]$	2.252 (7)	2.305 (7)	176.6 (3)	103 (1)	34
$[Au(PPh_3)(S_2C_2[CN]_2)]$	2.257 (2)	2.313 (2)	172.1 (1)	102.9 (3)	35
$[Au(PPh_3)(C_7H_4NOS)]$	2.258 (2)	2.299 (2)	176.4 (1)	103.1 (3)	36
$[\{Au(PPh_2Me)\}_2(S_4C_4)]$	2.270 (3)	2.365 (3)	162.4 (2)	101.9 (4)	37
$[Au(PPh_3)(C_7H_7N_4O_2S)]$ (**1**)	2.256 (2)	2.308 (2)	178.6 (2)	100.3 (3)	this work

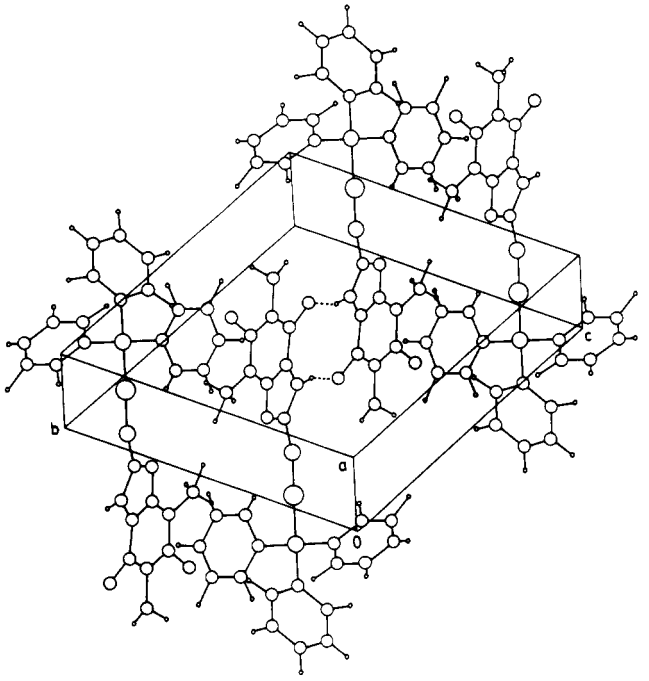

Figure 2. Cell packing of $[Au(PPh_3)(HL^1)]$, where dashed lines indicate hydrogen bonding.

tively. These deviations are somewhat larger than those found in the complex $[Au(PPh_3)L]$ (where HL = theophylline) and might be due to the steric interactions between the methyl groups at N1 and N3 and the oxygen atoms O2 and O6.[14] Nevertheless, the larger departure from this plane of 0.173 (4) Å involves the S8 atom.

Figure 2 illustrates the packing diagram for $[Au(PPh_3)(HL^1)]$. It shows that centrosymmetrically related molecules are linked by a pair of complementary N7-H7···O6 hydrogen bonds [N7···O6^i = 2.810 (8) Å and N7-H71···O6^i = 163 (7)°; i indicates the equivalent coordinates $-x + 1, -y + 1, -z + 1$]. Formation of relatively strong hydrogen bonds is consistent with the IR spectrum of $[Au(PPh_3)(HL^1)]$, showing a characteristic broad N-H stretching band in the 3200–3000-cm^{-1} region. Besides these two hydrogen bonds, there are no other significantly short contacts between the molecules.

The IR spectrum of **2** is very similar to that of **1**, showing ligand bands at 3200–3000 [ν(N-H)], 1676 [ν(C6=O)], 1522 (thioamide I), 1210 (thioamide II), and 360 cm^{-1} [ν(Au-S)]. This, together with the similarity of the ^{1}H NMR spectra (Table II), suggests an analogous structure for both complexes, with the thiolate anion S8-bonded to the $Au(PPh_3)$ group. In good accord with this, the ^{31}P NMR spectrum shows a single signal at 37.88 ppm near to that for **1**.

$[\{Au(PPh_3)\}_2(\mu$-L)] Complexes. The reaction of H_2L^1 and H_2L^2 with $[Au(PPh_3)Cl]$ and KOH under 1:2:2 stoichiometry yielded complexes **3** and **4**. These complexes were also obtained by reactions of **1** and **2**, which still contain an acidic proton, with an additional 1 molar equiv of $[Au(PPh_3)Cl]$. Analogous complexes have also been reported for hypoxanthine and 3-methyl-8-ethylxanthine.[14] The evidence concerning the structures of **3** and **4** has been derived from IR and ^{31}P NMR results, since ^{1}H and ^{13}C NMR spectra of good enough quality could not be obtained because of the low solubility of the complexes in DMSO.

In the IR spectra of **3** and **4** the absence of N-H stretching vibrations provides good evidence for $Au(PPh_3)$ coordination at S8 and either the N7 or N9 atom of the imidazole ring. The ^{31}P NMR spectra for these complexes show only two single signals (36.46 and 29.80 ppm for **3** and 36.29 and 29.72 ppm for **4**). The signal near to 36 ppm is due to the atom trans to S8, whereas that at about 30 ppm corresponds to the atom trans to either N7 or N9. The position of this latter signal is comparable with those found in the range 30.98–32.84 ppm for other gold(I) complexes also containing a N-Au-PPh_3 arrangement.[25,40-42] In view of the steric hindrance from the N3-CH_3 group, N7 seems to be favored over N9 for the binding of the second $Au(PPh_3)$ group. This is consistent with the N7 coordination observed in all metal complexes containing the theophyllinato anion for which crystallographic results are available.[38] At this point, it would be necessary to point out that even though the neutral 2-thione group of H_2L^2 might acts as binding site to the gold(I) phosphine group, as it has been demonstrated to occur in other thione-containing gold(I) triethylphosphine complexes;[43] because under basic conditions the H_2L^2 ligand is deprotonated, only the most stable complex **4**, containing the second $Au(PPh_3)$ group bonded to N7 atom, is obtained. Therefore, the proposed structure for **3** and **4** is as depicted in Scheme II.

[Au(μ-dppe)(μ-L)Au] Complexes. These complexes were prepared in good yield from the reaction of $[(AuBr)_2(\mu$-dppe)] and the corresponding ligand under 1:1 stoichiometry (Scheme II). The IR spectra of **5** and **6** do not show significant differences in the position and intensity of the ligand bands with respect to those in **3** and **4**, respectively. This together with the appearance in the ^{31}P NMR spectrum of **5** of two single signals at 29.81 and 36.42 ppm suggests S8,N7 coordination of the ligand in both complexes. The molar mass measurements indicate that both compounds present a dinuclear structure.

Substitution Reaction between 1 and $[(AuBr)_2$(dppe)]. $[(AuBr)_2(\mu$-dppe)] reacts with **1** and KOH under 1:1 stoichiometry in boiling ethanol affording different complexes depending on the heating time. Thus, when the heating time was of 5 min, after filtration of a small amount of complex **5**, from the resulting clear solution consecutively crystallized the complexes $K[(L^1)$-$Au(\mu$-dppe)$AuBr]\cdot 4H_2O$ (**7**) and $[\{Au(PPh_3)\}_2(\mu$-$L^1]$ (**3**). However, if the heating time is increased to 30 min, complex **5** can be isolated almost quantitatively. The IR spectra of **3** and **5** obtained in these substitution reactions are identical with those of these complexes prepared by direct reaction of H_2L^1 with $[Au(PPh_3)Cl]$ and $[(AuBr)_2(dppe)]$, respectively. The integration

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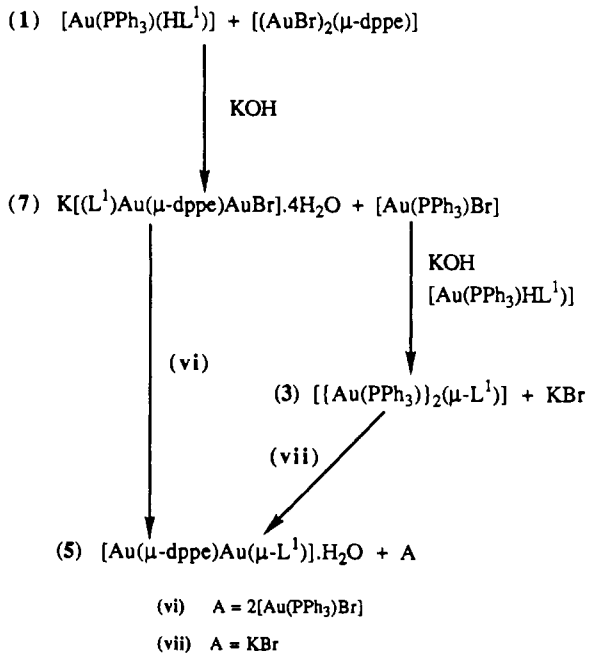
Scheme III



of the ^{1}H NMR spectrum of **7** confirmed a 1:1 (phosphine)-gold(I):8-mercaptotheophylline stoichiometry of the complex. This spectrum is devoid of any signal due to either N7–H or N9–H protons, and the IR spectrum shows no ν(N–H) bands in the 3200–2800-cm^{-1} region, which is consistent with the presence of an $(L^1)^{2-}$ dianion in the complex. The ^{31}P NMR spectrum of **7** displays two single signals at 29.83 and 36.44 ppm. The position of the first one suggests N7 coordination of the ligand to gold(I), whereas the second one might correspond to the atom trans to the bromine atom. In good accord with this, the ^{31}P NMR spectrum of the complex $[(AuBr)_2(\mu\text{-dppe})]$ shows only a single signal at 37.16 ppm.

In view of the complexes produced in the substitution reaction, it seems to occur through the intermediate complex **7** (Scheme III), probably by attack of the deprotonated N7–H group of **1** on one of the gold(I) atoms of $[(AuBr)_2(\mu\text{-dppe})]$ with further displacement of the $Au(PPh_3)$ group bonded to S8. Complex **7** can further undergoes a rearrangement with S8 coordination of the ligand to a second gold(I) atom of $[(AuBr)_2(dppe)]$ to give complex **5**. This complex can also be obtained by a parallel way. The $[Au(PPh_3)Br]$ produced in the first reaction might react with the unreacted **1** leading to complex **3**, as was indicated above. Finally, the reaction between **3** and $[(AuBr)_2(\mu\text{-dppe})]$ could give **5**. This was further supported by the reaction of complex **3** with $[(AuBr)_2(\mu\text{-dppe})]$ under 1:1 stoichiometry in boiling ethanol during 30 min, which led almost quantitatively to complex **5**. In light of the above discussion, it seems to be clear that by increasing the heating time the system progresses to the most stable complex **5**.

Complexes of HL^3. Like theophylline, its 8-methylthio derivative presents a weakly acidic proton in the imidazole ring, which is involved in the tautomeric equilibrium N7–H $\rightleftharpoons$ N9–H. After deprotonation in basic medium either N7 or N9 might act as the coordination site to gold(I). However, N7 must be favored over N9 due to the steric hindrance from N3–CH_3. Supporting this, the only metal complex of HL^3 for which crystallographic results are available, $[Zn(L^3)_2(H_2O)_2]$,[44] contains the $(L^3)^-$ anion bonded to Zn(II) via N7.

$[Au(PPh_3)L^3]$ (8). Our results are in accord with the above considerations. Reacting HL^3 with $[Au(PPh_3)Cl]$ in basic medium yields the neutral 1:1 complex, in which the imidazolic proton is displaced by an $Au(PPh_3)$ group. The low-field signal for this proton is absent from the ^{1}H NMR spectrum of the complex (Table III), and the IR spectrum shows no ν(N–H) bands in the 3200–2800-cm^{-1} region. In addition, the IR spectrum is similar to that of the analogous N7-bonded complex of 8-ethyltheophylline,[14] showing that the bands for the ligand assigned to ν(C=O), ν(C=C), and ν(C=N) at 1701, 1602, and 1546 cm^{-1}, respectively, are shifted to 1687, 1585, and 1522 cm^{-1}, respectively. These bands occur practically at the same position in all theophyllinato complexes, being indicative of N7 coordination.[39] According to this, the ^{31}P NMR spectrum displays only a single signal at 31.90 ppm, a typical position for a N–Au–PPh_3 arrangement.[25,40-42]

$[L^3Au(\mu\text{-dppe})AuL^3]$ (9). The complex was prepared in good yield from the reaction of $[(AuBr)_2(\mu\text{-dppe})]$ and HL^3 under 1:2 stoichiometry. The IR spectrum of **9** does not show significant differences in the position of the ligand bands with respect to those in **8**, suggesting also N7 coordination of the $(L^3)^-$ anion in this complex. In view of this, the proposed structure for **9** is as depicted in Scheme II. Finally, is necessary to point out that all attempts to obtain the complex $[L^3Au(\mu\text{-dppe})AuBr]$ under 1:1 stoichiometry were unsuccessful.

Conclusions

H_2L^1 and H_2L^2, purine bases containing both NH and SH groups at the imidazole ring, react with $[Au(PPh_3)Cl]$ under basic conditions at 1:1 and 1:2 stoichiometries affording the $[Au(PPh_3)(HL)]$ and $[\{Au(PPh_3)\}_2(\mu\text{-L})]$ complexes, respectively, in which the S8 atom is the first binding site for the $Au(PPh_3)$ group. In $[\{Au(PPh_3)\}_2(\mu\text{-L})]$ both the S8 and N7 atoms are involved in the coordination. These atoms also are the binding sites to gold(I) in the complexes $[Au(\mu\text{-dppe})(\mu\text{-L})Au]$, which are obtained by reaction of either H_2L^1 or H_2L^2 with $[(AuBr)_2(dppe)]$, the reaction being independent of the stoichiometry of the reactants. The S2 atom of H_2L^2 does not act as a coordination site for metals under the condition used here.

Reactions of $[Au(PPh_3)Cl]$ and $[(AuBr)_2(\mu\text{-dppe})]$ with HL^3 affords the $[Au(PPh_3)L^3]$ and $[L^3Au(\mu\text{-dppe})AuL^3]$ complexes, respectively, in which the binding of gold(I) phosphine occurs at the N7 atom. The substitution reaction between **1** and $[(AuBr)_2(\mu\text{-dppe})]$ depends on the heating time. This reaction seems to occur through the intermediate complexes **7** and **3** to give the most stable complex **5**.

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Supplementary Material Available: For the complexes a table of analytical and physical data and for **1** tables listing atomic coordinates for the H atoms, least-squares planes with atomic displacements, and the final output from the PARST program (8 pages); a listing of observed and calculated structure factors (28 pages). Ordering information is given on any current masthead page.

(44) Colacio, E. Unpublished results.