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Synthesis, Structure and Bactericide Activity of (Aminophosphane)gold(I) Thiolate Complexes

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Reaction of the aminophosphane ligands 2-(diphenylphosphanylamino)pyridine (Ph_2PNHpy, **1**) and 3-(diphenylphosphanylamino)-1,2,4-triazole [$Ph_2PNH(Htrz)$, **2**] with the gold(I) compound [AuCl(tht)] (tht = tetrahydrothiophene) gave the complexes [$AuCl(Ph_2PNHpy)$] (**3**) and [$AuCl\{Ph_2PNH(Htrz)\}$] (**4**), respectively. A series of new gold(I) thiolate derivatives were synthesized from the reactions of complex **3** or **4** with 1 equiv. of a deprotonated thiol ligand. Complexes [$Au(SR)(PPh_2NHpy)$] (**5**–**8**) were prepared by reaction of complex **3** with the corresponding thiol HSR [HSR = 2-mercaptopyridine (2-HSpy), 2-mercaptonicotinic acid (2-H_2-mna), 2-thiouracil (2-HTU) or 2-thiocytosine (2-HTC)] in the presence of sodium carbonate or triethylamine. Complexes [$Au(SR)\{PPh_2NH(Htrz)\}$] (**9**–**11**) were prepared by the treatment of complex **4** with triethylamine and the respective thiol HSR [HSR = 2-mercaptopyridine (2-HSpy), 2-thiocytosine (2-HTC) or 6-thioguanine (6-HTG)]. The susceptibility of *Enterococcus faecalis* ATCC25923, *Staphylococcus aureus* ATCC29213 and *Escherichia coli* TG1 towards the synthesized gold(I) complexes was evaluated. Some of them exhibit powerful anti-bacterial activity, being more efficient against Gram-positive microorganisms. Complexes **7**–**9** and **11** present excellent activity against *E. faecalis*, whereas the highest sensitivity of *S. aureus* was against complexes **7** and **8**. The structures of complexes **4**, **5**, **8** and **9** were determined by X-ray structural analysis. None of the four compounds shows aurophilic interactions between the gold(I) centres in the crystals. The four complexes possess intermolecular hydrogen bonds that lead to supramolecular arrangements.

Introduction

The chemistry community has shown growing interest in the synthesis of gold(I) complexes that display biological properties, mainly anticancer and antibacterial activity, and in the understanding of their mechanisms of action, as shown in recent reviews.[1] Among them, derivatives containing the P–Au–S unit have gained considerable attention in part because they are structurally related to Auranofin (2,3,4,6-tetra-*O*-acetyl-β-1-thio-D-glucopyranosato-S)(triethylphosphane)gold(I), a drug used for the treatment of rheumatoid arthritis, the antitumour and antimicrobial activities of which have been investigated.[1b,1c,2,3] Although the antimicrobial properties of gold(I) derivatives have been less investigated than their cytotoxic activities,[3b,3c,3f,4] the increasing multidrug resistance exhibited by many ubiquitous pathogens points to these compounds as promising alternatives to antibiotic chemotherapy. Some recent articles have reported important results, for example, the review by Navarro[5] on antiparasitic agents shows the efforts, some of them very recent and encouraging, made in the fight against malaria, leishmaniasis and other parasitic diseases with gold(I) complexes. The article of Jackson-Rosario et al.[6] reports that Auranofin inhibits the growth of *Clostridium difficile* through the formation of auranofin–selenium, thus interfering in the selenium metabolism and the production of selenoproteins, and Eiter et al.[7] have reported the strong activity against *Mycobacterium tuberculosis* of gold(I) analogues of a platinum antitumour agent.

Herein we report on the synthesis and characterization of a series of gold(I) thiolate derivatives with two different aminophosphanes: 2-(diphenylphosphanylamino)pyridine[8] (Ph_2PNHpy) and 3-(diphenylphosphanylamino)-1,2,4-triazole [$Ph_2PNH(Htrz)$]. Aminophosphanes are an important type of compounds because of the interest in hemilabile ligands in coordination chemistry and catalysis, and they are also suitable for producing metal complexes capable of forming hydrogen bonds, which is an important topic in bioinorganic chemistry. Several gold(I) complexes with aminophosphanes have been reported to date,[9] but as far as we are aware not many with thiolato ligands.[10] The formation of gold(I) thiolate derivatives with aminophosphane ligands can enhance the properties shown by (phosphane)gold thiolate compounds and the possibility of forming hydrogen bonds, the final objective being the development of biologically active molecules. The susceptibility of several

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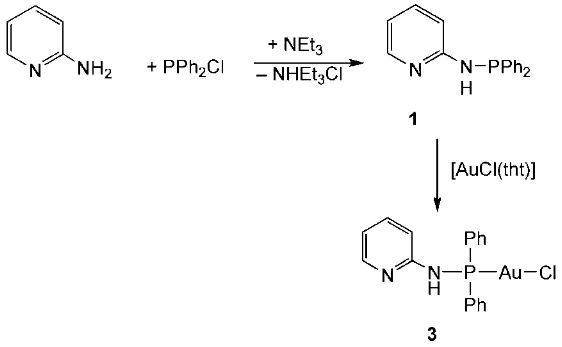
bacteria towards the gold complexes has been evaluated, and some of them exhibit excellent antimicrobial activities against two epidemiologically important Gram-positive bacteria, namely *Enterococcus faecalis* and *Staphylococcus aureus*, and moderate bacteriostatic properties against the Gram-negative *Escherichia coli*.

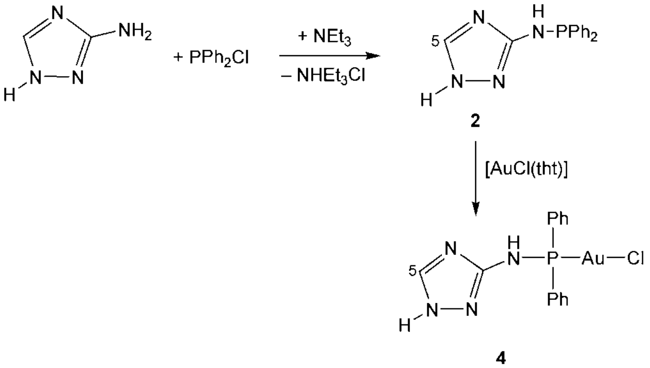
Results and Discussion

Synthesis and Characterization

The ligand 2-(diphenylphosphanylamino)pyridine (dppap, Ph_2PNHpy, **1**) was prepared by the reaction of chlorodiphenylphosphane, 2-aminopyridine and Et_3N in THF as solvent, as described previously by Aucott et al.[8] The synthesis of the gold(I) complex [AuCl(Ph_2PNHpy)] (**3**) by the reaction of [AuCl(tht)] and the phosphane ligand **1** in CH_2Cl_2 was also described in this paper (see Scheme 1). The new ligand 3-(diphenylphosphanylamino)-1,2,4-triazole [$Ph_2PNH(Htrz)$, **2**] was synthesized in a way similar to that for **1** by reaction of chlorodiphenylphosphane, 3-amino-1,2,4-triazole and Et_3N in THF. The ^1H NMR spectrum shows, apart from the multiplets of the phenyl groups, a broad singlet for 5-H of the triazole at δ = 8.15 ppm, a broad signal for HN(Htrz) at δ = 13.04 ppm and another for the H of the HN–P group at δ = 12.55 ppm. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at δ = 36.90 ppm. The reaction of $Ph_2PNH(Htrz)$ (**2**) with [AuCl(tht)] led to the complex [AuCl{$Ph_2PNH(Htrz)$}] (**4**) (see Scheme 2). Complex **4** displays one resonance in its $^{31}P\{^1H\}$ NMR spectrum at δ = 54.01 ppm, which confirms the coordination to the gold(I) centre through the phosphorus atom. In the IR spectrum the ν(Au–Cl) band characteristic of gold(I) coordinated to chloride appears at 316 cm^{-1}. In the ESI$^+$ mass spectrum the fragment $[M - Cl]^+$ is present at *m*/*z* (%) = 465 (100).

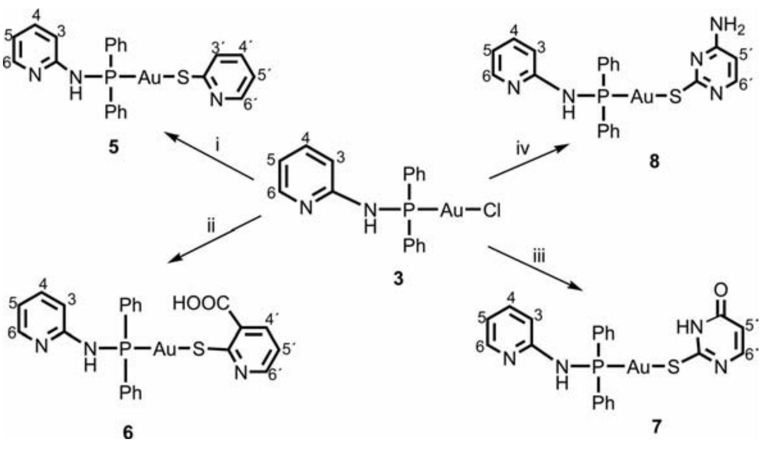


Scheme 1.



Scheme 2.

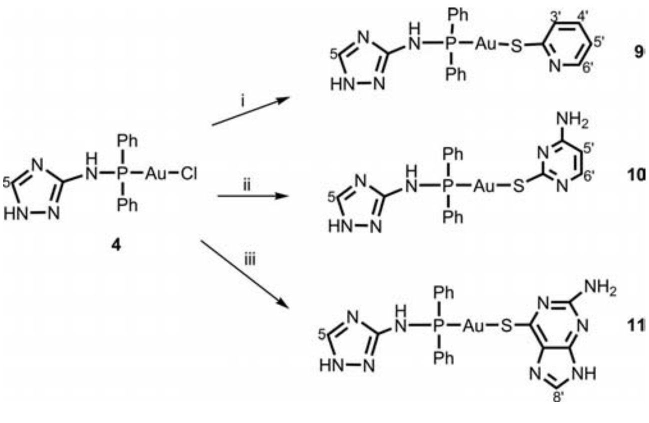
The gold(I) thiolate complexes **5**–**11** were prepared by the reaction of the (phosphane)gold(I) chloride **3** or **4** with 1 equiv. of the appropriate thiolato ligand (see Schemes 3 and 4). Complexes **5**–**8** (Scheme 3) were synthesized by the reaction between the (aminophosphane)gold(I) chloride **3** and the respective thiol HSR [HSR = 2-mercaptopyridine (2-HSpy) (for **5**), 2-mercaptonicotinic acid (2-H_2-mna) (for **6**), 2-thiouracil (2-HTU) (for **7**) or 2-thiocytosine (2-HTC) (for **8**)] in the presence of sodium carbonate or triethylamine. The ^1H and $^{13}C\{^1H\}$ NMR spectra show the expected resonances. A broad singlet was assigned to the



Scheme 3. Reagents: (i) 2-HSPy, K_2CO_3; (ii) 2-H_2-mna, NEt_3; (iii) 2-HTU, NEt_3; (iv) 2-HTC, NEt_3.

–NH–P– proton, and four separated signals were attributed to the pyridine protons of the aminophosphane ligand. Furthermore, the ^{1}H NMR spectrum of complex **5** shows four different resonances that were assigned to the 2-thiopyridine protons. Complex **6** presents three broad signals attributed to the 2-mercaptonicotinic acid aromatic protons, and in complex **7** one of the doublets corresponding to the 2-thiouracil group is overlapped by phenyl protons. The IR spectrum of solid complex **6** presents an intense carbonyl stretching band at 1677 cm^{-1}, almost unchanged from that of the free ligand (1675 cm^{-1} for 2-H_2-mna), which suggests that the carboxylic group remains protonated and does not coordinate to the metal atom. The IR spectrum of solid compound **7** presents a stretching carbonyl band at 1631 cm^{-1} (1680 cm^{-1} in the free ligand), which indicates that the thiouracil is coordinated to the gold centre through the sulfur atom in the form of thiolate, and consequently there is a –C=O bond at the 4-position.[11,12] In the ^{1}H NMR spectrum of complex **8** a broad singlet at δ = 12.30 ppm was assigned to the NH_2 group and one doublet and one broad signal to the aromatic protons of the 2-thiocytosine group. The ^{31}P{^{1}H} NMR spectra of these compounds show single resonances significantly downfield relative to their precursor (^{31}P{^{1}H} NMR: δ = 53.47 ppm in complex **3**). In addition, the 2D ^{1}H COSY and HSQC spectra were recorded to confirm the proton assignments. Complete spectroscopic data for complexes **5**–**8** are presented in the Exp. Sect. In the ESI^{+} mass spectra of **5**–**8** the protonated molecular peaks $[M + H]^{+}$ appear at m/z (%) = 586 (99), 630 (10), 603 (89) and 602 (98), respectively.

The reactions of complex **4** with the thiols 2-mercaptopyridine (2-HSpy), 2-thiocytosine (2-HTC) or 6-thioguanine (6-HTG) and triethylamine led to the complexes **9**–**11**, respectively (see Scheme 4). The ^{31}P{^{1}H} NMR spectra show single resonances with the expected downfield shifts compared with their precursor (complex **4**). The ^{1}H NMR spectra show signals for the protons of the aminophosphane ligand and the thiolate group in the appropriate ratio. In the spectrum of complex **9** four signals were assigned to the protons of the 2-mercaptopyridine. In the spectrum of complex **10** were identified one doublet and a broad signal due to the aromatic protons and a broad singlet at δ = 6.49 ppm for the amino group of the 2-thiocytosine. Complex **11** presents the resonance of the amino group at δ = 5.97 ppm and two broad singlets corresponding to the NH group and the aromatic proton of the 6-thioguanine. Assignments of the signals were made on the basis of 2D ^{1}H COSY and HSQC spectra. Complete spectroscopic data for ligand **2** and complexes **4** and **9**–**11** are presented in the Exp. Sect. In the ESI^{+} mass spectra of **9**–**11** the protonated molecular peaks $[M + H]^{+}$ appear at m/z (%) = 576 (100), 592 (100) and 632 (100), respectively.



Scheme 4. Reagents: (i) 2-HSpy, NEt_3; (ii) 2-TC, NEt_3; (iii) 6-HTG, NEt_3.

Crystallography

We confirmed the molecular structures of complexes **4**, **5**, **8** and **9** (Figures 1, 2, 3 and 4, respectively) by an X-ray crystallographic study. Selected bond lengths and angles are shown in Table 1. Complexes **4**, **5** and **8** crystallize in the monoclinic system and complex **9** in the triclinic system. None of the four compounds shows aurophilic interactions

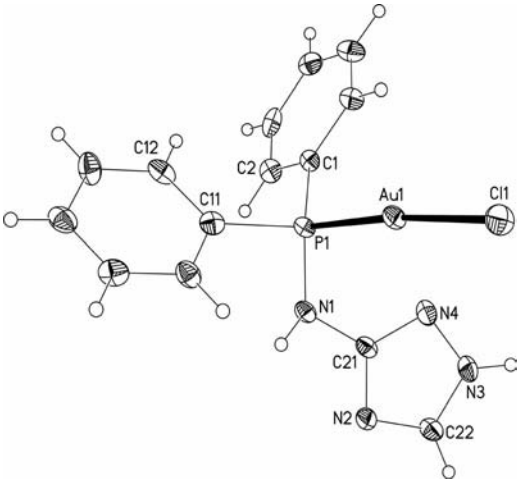


Figure 1. Structure of complex **4** (50% probability ellipsoids).

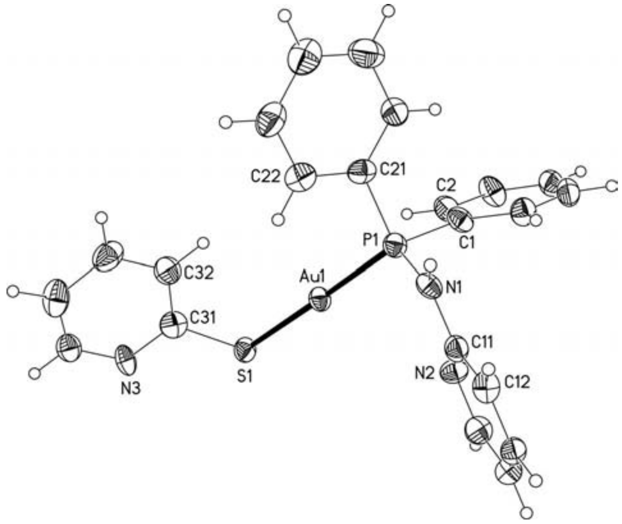


Figure 2. Structure of complex **5** (50% probability ellipsoids).

between the gold(I) centres in the crystals. The Au atoms lie in the almost linear geometry expected for gold(I) derivatives defined by the P atom of the corresponding aminophosphane and the chloride (**4**) or the S atom of the thiolato ligand (**5**, **8**, and **9**). The P–Au–Cl bond angle in **4** is 174.49(8)°, and the P–Au–S bond angles range from 177.26(4)° in **9** to 177.76(2)° in **8**.

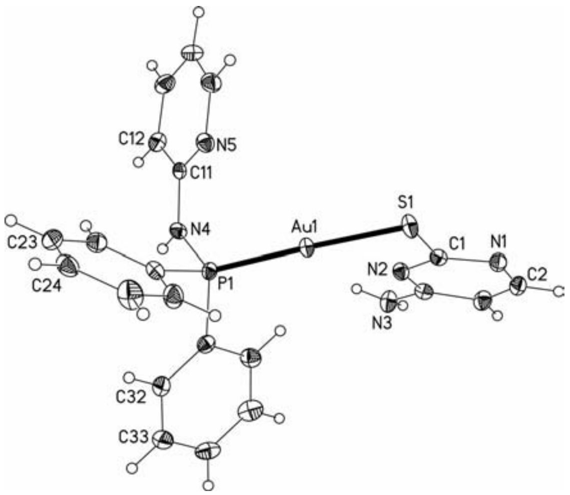


Figure 3. Structure of complex **8** (50 % probability ellipsoids).

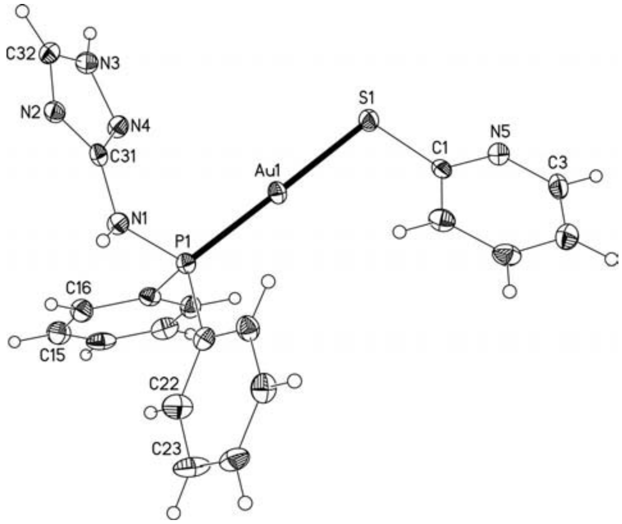


Figure 4. Structure of complex **9** (50 % probability ellipsoids).

The Au–P [2.223(2) Å] and Au–Cl [2.293(2) Å] bond lengths in complex **4** are similar to those found in the closely related complex **3** [2.2187(11) and 2.2813(12) Å, respectively].[8] In the lattice of **4** the molecules are organized into dimers as a result of hydrogen bonding between the NH–P proton and one nitrogen atom of the triazole group of neighbouring molecules in a head-to-tail arrangement (Figure 5) that is reminiscent of the arrangement observed in the solid structure of ligand **1** (Ph_2PNHpy).[8]

The Au–P and Au–S distances in complexes **5** [2.251(2) and 2.308(2) Å], **8** [2.2464(8) and 2.3130(8) Å] and **9** [2.2500(11) and 2.3035(11) Å] are normal and compare well with most of the distances found in related complexes with the same S–Au–P core.[11–22] The longer Au–P distances in the thiolate derivatives compared with those in complexes **3** [2.2187(11) Å] and **4** [2.223(2) Å] are in agreement with the higher *trans* influence of the thiolato ligand compared with the chlorido ligand.

Table 1. Selected bond lengths [Å] and angles [°] for complexes **4**, **5**, **8**, and **9**.

Complex **4**			
Au(1)–P(1)	2.223(2)	P(1)–N(1)	1.679(7)
Au(1)–Cl(1)	2.293(2)	N(1)–C(21)	1.391(1)
P(1)–Au(1)–Cl(1)	174.49(8)	C(21)–N(1)–P(1)	122.4(6)
Complex **5**			
Au(1)–P(1)	2.251(2)	P(1)–N(1)	1.680(7)
Au(1)–S(1)	2.308(2)	S(1)–C(31)	1.776(9)
P(1)–Au(1)–S(1)	177.62(8)	C(31)–S(1)–Au(1)	103.4(3)
Complex **8**			
Au(1)–P(1)	2.2464(8)	S(1)–C(1)	1.761(3)
Au(1)–S(1)	2.3130(8)	P(1)–N(4)	1.670(2)
P(1)–Au(1)–S(1)	177.76(2)	C(1)–S(1)–Au(1)	101.27(9)
Complex **9**			
Au(1)–P(1)	2.2500(11)	S(1)–C(1)	1.764(5)
Au(1)–S(1)	2.3035(11)	P(1)–N(1)	1.677(4)
P(1)–Au(1)–S(1)	177.26(4)	C(1)–S(1)–Au(1)	102.93(14)

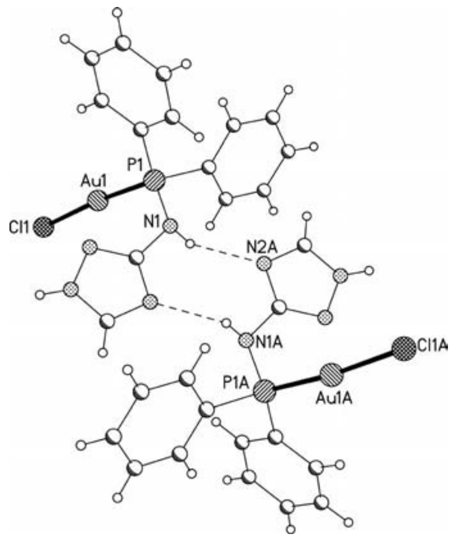


Figure 5. Molecules of complex **4** organized into dimers through hydrogen bonds.

Complexes **5**, **8** and **9** possess intermolecular hydrogen bonds that lead to supramolecular arrays. In **5** the interaction between neighbouring molecules through the NHP proton and the thiopyridine nitrogen atom as proton acceptor organizes the molecules into chains (Figure 6). In **8** a similar interaction through the NHP proton and one thiocytosine nitrogen atom as proton acceptor leads to chains that are organized into a 3D structure through hydrogen bonds between amino protons and DMSO oxygen atoms (solvent of crystallization) as protons acceptors (Figure 7). In **9** pairs of molecules are formed by interaction of the NHP proton and the triazole N atom in a head-to-tail fashion, similarly to observations with complex **4**. These pairs are further joined by hydrogen bonding through the NH group of the triazole ring and the pyridine nitrogen atom (Figure 8). Hydrogen-bond data for complexes **4**, **5**, **8** and **9** are presented in Table 2.

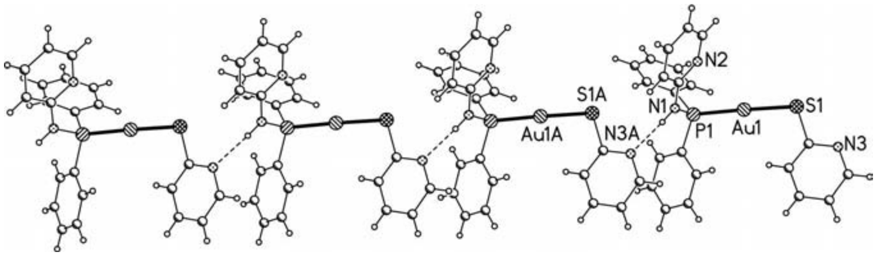


Figure 6. Hydrogen-bonding interactions between molecules of complex **5** (arrangement in chains).

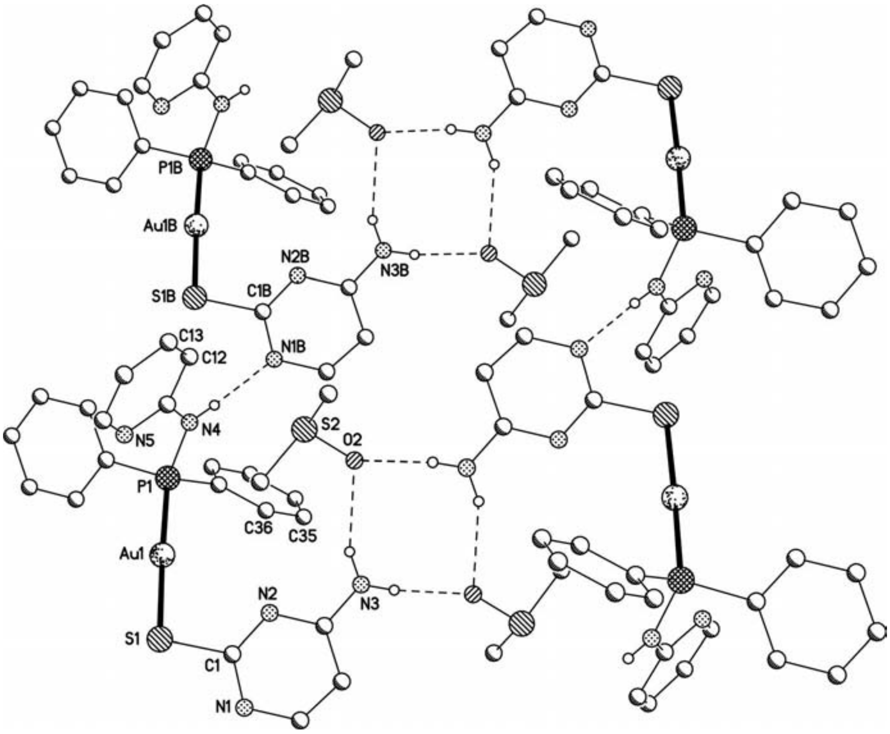


Figure 7. 3D structure of molecules of complex **8** formed by hydrogen-bonding interactions (DMSO solvent molecules are involved in the arrangement).

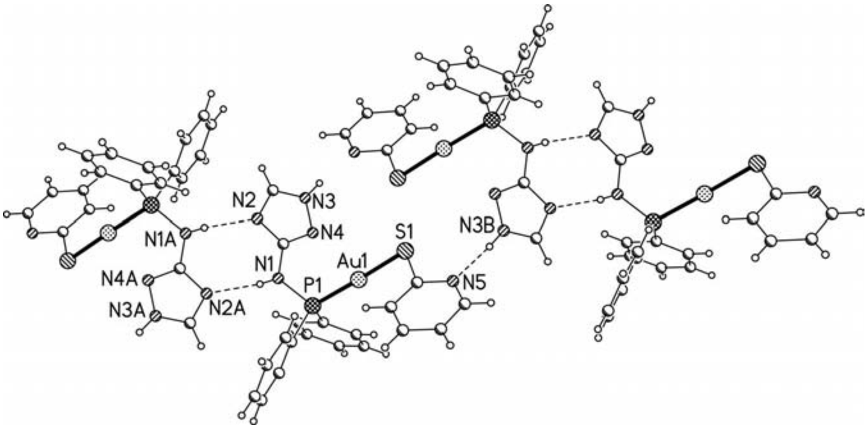


Figure 8. Hydrogen bonding between pairs of molecules of complex **9**.

Table 2. Hydrogen-bond data for complexes **4**, **5**, **8**, and **9**.

D–H···A	*d*(D–H) [Å]	*d*(H···A) [Å]	*d*(D···A) [Å]	<(DHA) [°]
Complex **4**[a]				
N(3)–H(3A)···O(1)#1	0.86	1.91	2.745(9)	161.8
N(1)–H(1A)···N(2)#2	0.90	2.21	2.821(10)	124.2
Complex **5**[b]				
N(1)–H(1)···N(3)#1	0.88	2.09	2.973(10)	177.1
Complex **8**[c]				
N(3)–H(11)···O(2)	0.84(3)	2.26(3)	3.035(3)	154(3)
N(3)–H(1)···O(2)#1	0.83(3)	2.11(3)	2.919(3)	164(3)
N(4)–H(0)···N(1)#2	0.83(3)	2.06(3)	2.881(3)	176(3)
Complex **9**[d]				
N(1)–H(1)···N(2)#1	0.77(5)	2.09(5)	2.854(5)	172(5)
N(3)–H(3A)···N(5)#2	0.88	1.91	2.783(5)	170.6

[a] #1: $x + 1, y, z$; #2: $-x + 1, -y + 2, -z + 1$. [b] #1: $x, y - 1, z$. [c] #1: $-x, -y + 1, -z + 1$; #2: $x, y - 1, z$. [d] #1: $-x + 1, -y + 2, -z$; #2: $-x + 1, -y + 1, -z + 1$.

Antimicrobial Activity

The susceptibility of *E. faecalis* ATCC25923, *S. aureus* ATCC29213 and *E. coli* TG1 to gold(I) complexes was evaluated by the Kirby–Bauer disk-diffusion test using the broad-spectrum antibiotic kanamicin as control. The solvent used to dissolve the complexes (DMSO) and the ligands **1** and **2** did not inhibit bacterial growth, which indicates that the metal was responsible for the observed activities.

Complexes **3** and **7**–**11** presented semiquantitative antimicrobial activities similar to controls in the disk-diffusion tests (not shown), whereas complexes **4**–**6** exhibited no activity against any of the microorganisms tested. Minimum inhibitory concentrations (MICs) and minimal bactericidal concentrations (MBCs) were determined for complexes displaying significant activity (Table 3). The results show that complexes **7**–**9** and **11** present excellent activity against *E. faecalis*, whereas the highest sensitivity of *S. aureus* was against complexes **7** and **8**.

Table 3. Antimicrobial activities evaluated as minimum inhibitory concentrations [μM] and minimum bactericidal concentrations [μM].

	E. faecalis		*S. aureus*		*E. coli*	
	MIC	MBC	MIC	MBC	MIC	MBC
3	10	30	>50	>50	–	
7	5	50	5	>50	>100	>100
8	5	20	5	>50	30	100
9	5	>50	40	50	50	>100
10	15	>50	30	>50	50	>100
11	5	30	30	>50	–	
Kanamicin	100	>100	>100		50	50

Enterococci and *Streptococcus sp.* are capable of infecting humans, companion animals and livestock.[23,24] *Enterococci* are normal gastrointestinal flora of dairy cows and cattle, but are also opportunistic pathogens that can cause intramammary infection (IMI), also known as mastitis, often aggravated by the presence of *S. aureus*.[25] Because many of these microorganisms are resistant to one or more antibiotics, there is increasing interest in the development of alternative forms of bacterial control. Because antibiotic concentrations used in clinical practice usually range between 5 and 50 μM, our results suggest that some of the compounds reported in this work might have potential applications in the impairment of the proliferation of *E. faecalis* and *S. aureus*. In contrast, the efficiency of gold(I) complexes against the Gram-negative *E. coli* TG1 strain was lower, although complexes **8**–**10** still displayed moderate bacteriostatic properties. This is in good agreement with previous studies indicating that gold(I) complexes are, in general, less active against Gram-negative than against Gram-positive bacteria.[3b,4d] The lower susceptibility could be attributed to the structural differences in the cell walls of those types of microorganisms.[3b,4d] Further studies to identify new bacterial targets as well as the mechanisms displayed by the gold(I) complexes should be performed in order to outline their potential chemotherapeutic properties.

Conclusions

A series of new gold(I) thiolate derivatives with aminophosphanes as auxiliary ligands have been synthesized and characterized. The aminophosphane ligand allows the formation of hydrogen bonding, which is of great importance in bioinorganic chemistry and can help to produce more active compounds. The crystal structures of some of the complexes reveal the formation of supramolecular arrays through hydrogen bonding, and 2D and 3D motifs have been found. Some of them exhibit good/satisfactory antibacterial activity, being more efficient against Gram-positive microorganisms. Complexes **7**–**9** and **11** present excellent activity against *E. faecalis*, whereas the highest sensitivity of *S. aureus* was against complexes **7** and **8**. The excellent activity shown by some of the complexes leads to the possibility of further biological studies.

Experimental Section

Instrumentation: IR spectra were recorded in the range 4000–200 cm^{-1} with a Perkin–Elmer Spectrum 100 spectrophotometer on solid samples by using an ATR accessory. C, H and N analyses were carried out with a Perkin–Elmer 2400 Series 2 microanalyser. Mass spectra were recorded with a VG Austopec by using the ESI technique. NMR spectra were recorded in [D$_6$]DMSO solution, most of them with a Bruker ARX 400 spectrometer; some of the ^{13}C{^{1}H} NMR spectra were recorded with a Bruker ARX 300 spectrometer. Chemical shifts are cited relative to SiMe$_4$ (^{1}H, ^{13}C, external) and 85% H_3PO_4 (^{31}P, external). Unfortunately, in the ^{13}C{^{1}H} NMR spectra of several complexes we did not observe all of the signals expected, probably as a consequence of the poor solubility of the complexes.

Starting Materials: The phosphane ligand Ph$_2$PNHpy (**1**)[8] and the starting materials [AuCl(tht)][26] and [AuCl(Ph$_2$PNHpy)][8] (**3**) were prepared by applying published procedures. All other chemicals used were commercially available and used without further purification.

Antibacterial Assays: The antibacterial activities of the gold(I) complexes were tested against the Gram-positive strains *E. faecalis* ATCC25923 and *S. aureus* ATCC29213 and the Gram-negative *E. coli* TG1. Cells were grown in Luria–Bertani liquid broth or agar medium at 37 °C. Semiquantitative bioassays were performed by using the Kirby–Bauer disk-diffusion test. Whatman paper disks loaded with 4×10^{-8} mol of each complex dissolved in DMSO were placed on LB plates containing 200 µL of 8×10^8 CFU/mL of *E. faecalis*, 4×10^8 CFU/mL of *S. aureus* or 4×10^8 CFU/mL of *E. coli* cells. Disks loaded with the same concentration of kanamycin were used as controls. Then the plates were incubated at 37 ± 2 °C overnight, and the inhibition diameters were measured. For quantitative determination of the susceptibility to gold(I) complexes, minimum inhibitory concentrations (MICs) were calculated by using the broth dilution method. Stock solutions of each complex in DMSO were prepared at a concentration of 8 mM. Luria–Bertani liquid broth (2 mL) was supplemented with serial dilutions of the gold(I) complexes and inoculated with the appropriate bacterial strain (100 µL) at the CFU/mL indicated above. The tubes were incubated at 37 °C for 24 h. The MIC is defined as the lowest concentration of antimicrobial agent that inhibits visible growth. Minimal bactericidal concentrations (MBCs) were evaluated by streaking in LB plates cells (200 µL) from cultures that in the presence of gold(I) complexes did not show apparent growth. The presence of bacterial colonies was monitored after incubation at 37 °C overnight. All the disk-diffusion tests and MIC and MBC bioassays were repeated three times.

Synthesis of Ph$_2$PNH(Htrz) (2): Et$_3$N (2.3 g, 3.16 mL, 23 mmol) was added to a solution of 3-amino-1,2,4-triazole (1.68 g, 20 mmol) in THF (60 mL) under argon, and then the mixture was cooled to 0 °C. Neat chlorodiphenylphosphane (4.41 g, 3.6 mL, 20 mmol) was added dropwise to this mixture. The mixture was allowed to warm to room temperature and stirred for 24 h, after which time it was filtered to remove the triethylamine hydrochloride precipitate. The precipitate was washed with THF (2×20 mL). The washings and the filtrate were combined and concentrated to dryness under reduced pressure to leave a white solid. The solid was removed from the flask, washed with diethyl ether (2×10 mL) and dried in vacuo. Yield: 4.88 g, 91%. ^{1}H NMR: δ = 13.04 (br. s, 1 H, NH, Htrz), 12.55 (br. s, 1 H, NH-P), 8.15 (br. s, 1 H, 5-H), 7.50 (m, 4 H, Ph), 7.40 (m, 6 H, Ph) ppm. ^{31}P{^{1}H} NMR: δ = 36.90 (s, 1 P, PPh$_2$) ppm. $C_{14}N_4H_{13}P$ (268.25): calcd. C 62.68, H 4.88, N 20.89; found C 62.47, H 4.61, N 20.79.

Synthesis of [AuCl{Ph$_2$PNH(Htrz)}] (4): Ph$_2$PNH(Htrz) (**2**; 0.134 g, 0.5 mmol) was added to a dichloromethane solution (20 mL) of [AuCl(tht)] (0.160 g, 0.5 mmol). The reaction mixture was stirred for 1 h, concentrated to around 5 mL, and addition of hexane (15 mL) led to complex **4** as a white solid. Yield: 0.209 g, 83.50%. ^{1}H NMR: δ = 13.44 (br. s, 1 H, NH triazole), 9.07 (br. s, 1 H, NH-P), 8.26 (br. s, 1 H, 5-H), 7.70 (m, 4 H, Ph-H), 7.60 (m, 6 H, Ph-H) ppm. ^{31}P{^{1}H} NMR: δ = 54.01 (s, 1 P, PPh$_2$) ppm. ^{13}C{^{1}H} NMR: δ = 132.74 (d, $^2J_{\text{P-C}}$ = 15.60 Hz, C$_{ortho}$, PPh$_2$), 132.54 (s, C$_{para}$, PPh$_2$), 129.54 (d, $^3J_{\text{P-C}}$ = 12.30 Hz, C$_{meta}$, PPh$_2$) ppm. MS (ESI$^+$): *m/z* (%) = 465 (100) [M – Cl]$^+$, 929 (62) [(M – Cl)$_2$ – H]$^+$. $C_{14}H_{13}AuClN_4P$ (500.67): calcd. C 33.58, H 2.62, N 11.19; found C 33.56, H 2.55, N 10.93.

Synthesis of [Au(Spy)(Ph$_2$PNHpy)] (5): [AuCl(Ph$_2$PNHpy)] (**3**; 0.102 g, 0.20 mmol) and 2-mercaptopyridine (2-HSpy; 0.022 g, 0.20 mmol) were added to a suspension of K_2CO_3 (0.014 g, 0.1 mmol) in dichloromethane (20 mL), and the mixture was stirred for 3 h. The suspension was filtered to remove the KCl formed. Concentration of the solution to approximately 5 mL and addition of hexane gave complex **5** as a white solid. Yield: 0.060 g, 51.2%. ^{1}H NMR: δ = 8.81 (br. s, 1 H, NH), 8.19 (m, 1 H, 6′-H), 8.06 (m, 1 H, 6-H), 7.79 (m, 4 H, Ph-H), 7.59 (m, 7 H, Ph-H, 4-H), 7.39 (m, 2 H, 4′-H, 5′-H), 7.04 (d, $^3J_{\text{H-H}}$ = 8.0 Hz, 1 H, 3-H), 6.87 (m, 2 H, 5-H, 3′-H) ppm. ^{31}P{^{1}H} NMR: δ = 59.76 (s, 1 P, PPh$_2$) ppm. ^{13}C{^{1}H} NMR (300 MHz): δ = 167.49 (s, C-2′), 155.77 (s, C-2), 148.97 (s, C-6′), 147.70 (s, C-6), 138.40 (s, C-4), 135.74 (s, C-4′), 133.72 (s, C$_{ipso}$, PPh$_2$), 132.80 (d, $^2J_{\text{P-C}}$ = 16.08 Hz, C$_{ortho}$, PPh$_2$), 132.27 (s, C$_{para}$, PPh$_2$), 129.59 (d, $^3J_{\text{P-C}}$ = 11.83 Hz, C$_{meta}$, PPh$_2$), 126.64 (s, C-5′), 118.35 (s, C-3′), 116.63 (s, C-5), 112.46 (s, C-3) ppm. MS (ESI$^+$): *m/z* (%) = 586 (99) [M + H]$^+$. $C_{22}H_{19}AuN_3PS$ (585.41): calcd. C 45.14, H 3.27, N 7.18, S 5.48; found C 45.34, H 3.13, N 7.33, S 5.12.

Synthesis of [Au(Hmna)(Ph$_2$PNHpy)] (6): 2-Mercaptonicotinic acid (2-H$_2$-mna; 0.031 g, 0.20 mmol) and NEt$_3$ (0.025 g, 0.034 mL, 0.25 mmol) were added to a dichloromethane solution (20 mL) of [AuCl(Ph$_2$PNHpy)] (**3**; 0.102 g, 0.20 mmol). The reaction was stirred at room temperature for 18 h. After that, the mixture was washed with a saturated aqueous NaHCO$_3$ solution (50 mL) to remove the triethylamine hydrochloride, and the organic phase was dried with Na$_2$SO$_4$. Concentration of the solution to approximately 5 mL and addition of hexane gave complex **6** as a white solid. Yield: 0.089 g, 70.7%. ^{1}H NMR: δ = 14.45 (br. s, 1 H, COOH), 9.03 (br. s, 1 H, NH), 8.21 (m, 1 H, 6′-H), 7.93 (m, 1 H, 6-H), 7.75 (m, 4 H, Ph-H), 7.58 (m, 1 H, 4-H), 7.55 (m, 6 H, Ph-H), 7.38 (m, 1 H, 4′-H), 7.07 (m, 2 H, 3-H, 5′-H), 6.84 (m, 1 H, 5-H) ppm. ^{31}P{^{1}H} NMR: δ = 59.16 (s, 1 P, PPh$_2$) ppm. ^{13}C{^{1}H} NMR: δ = 155.21 (s, C-2), 148.02 (s, C-6), 138.06 (s, C-4), 132.23 (d, $^2J_{\text{P-C}}$ = 12.70 Hz, C$_{ortho}$, PPh$_2$), 131.83 (s, C$_{para}$, PPh$_2$), 129.45 (m, C$_{ipso}$, PPh$_2$), 129.09 (m, C$_{meta}$, PPh$_2$), 116.20 (s, C-5), 112.12 (s, C-3) ppm. MS (ESI$^+$): *m/z* (%) = 630 (10) [M + H]$^+$. $C_{23}H_{19}AuN_3O_2PS$ (629.42): calcd. C 43.89, H 3.04, N 6.68, S 5.09; found C 43.53, H 3.11, N 6.87, S 4.75.

Synthesis of [Au(SR)(Ph$_2$PNHpy)] [R = TU (7), TC (8)]: NEt$_3$ (0.025 g, 0.034 mL 0.25 mmol) was added to a solution of [AuCl(Ph$_2$PNHpy)] (**3**; 0.102 g, 0.20 mmol) and 2-thiouracil (2-HTU; 0.026 g, 0.20 mmol) or 2-thiocytosine (2-HTC; 0.025 g, 0.20 mmol) in dichloromethane (20 mL), and the mixture was stirred for 18 h. Complexes **7** and **8** precipitated as white solids and were filtered off.

Complex 7: Yield: 0.106 g, 87.9%. ^{1}H NMR: δ = 8.84 (br. s, 1 H, NH-P), 8.06 (m, 1 H, 6-H), 7.70 (m, 12 H, Ph-H, 4-H, 6′-H), 7.03 (d, $^3J_{\text{H-H}}$ = 10.8 Hz, 1 H, 3-H), 6.86 (m, 1 H, 5-H), 5.88 (d, $^3J_{\text{H-H}}$

Table 4. Details of data collection and structure refinement for complexes **4**, **5**, **8** and **9**.

	4·$(C_2H_5)_2O$	**5**	**8**·$(CH_3)_2SO$	**9**
Empirical formula	$C_{18}H_{23}AuClN_4OP$	$C_{22}H_{19}AuN_3PS$	$C_{23}H_{25}AuN_5OPS_2$	$C_{19}H_{17}AuN_5PS$
Crystal habit	colourless plate	colourless plate	colourless plate	colourless plate
Crystal size [mm]	0.32 × 0.10 × 0.04	0.12 × 0.08 × 0.08	0.21 × 0.10 × 0.08	0.12 × 0.08 × 0.04
Crystal system	monoclinic	monoclinic	monoclinic	triclinic
Space group	$P2_1/c$	$P2_1/n$	$C2/c$	$P\bar{1}$
a [Å]	10.3917(16)	14.6562(2)	35.493(7)	9.4778(12)
b [Å]	14.868(2)	9.1092(12)	9.0951(18)	9.5204(12)
c [Å]	12.0632(17)	15.613(2)	15.231(3)	12.1498(15)
α [°]	90	90	90	73.194(2)
β [°]	93.236(3)	90.334(3)	91.46(3)	72.239(2)
γ [°]	90	90	90	84.879(2)
U [Å^3]	2039.9(5)	2084.4(5)	4977.5(17)	999.4(2)
Z	4	4	8	2
$D_{\text{calcd.}}$ [Mg m^{-3}]	1.872	1.865	1.814	1.912
M	574.79	585.40	679.54	575.37
F(000)	1112	1128	2656	552
T [°C]	–173	–173	–173	–173
$2\theta_{\max}$ [°]	54	54	52	54
μ(Mo-K_α) [mm^{-1}]	7.436	7.247	6.169	7.558
Transmission	0.4439–0.1995	0.5948–0.4767	0.6381–0.3574	0.7520–0.5641
No. of refl. measured	12554	12909	37189	8963
No. of unique refl.	4437	4521	4876	4309
R_{int}	0.0741	0.0773	0.0296	0.0375
R [$F > 4\sigma(F)$]	0.0510	0.0534	0.0172	0.0301
$wR2$ ($F2$, all refl.)	0.1211	0.01077	0.0400	0.0718
No. of refl. used	4437	4521	4876	4309
No. of parameters	237	253	312	247
No. of restraints	0	0	0	0
S	1.031	1.017	1.055	1.045
Max./min. $\Delta\rho$ [e Å^{-3}]	2.699/–2.991	2.166/–1.189	1.190/–0.552	1.545/–1.574

= 8.8 Hz, 1 H, 5′-H) ppm. ^{31}P{^{1}H} NMR: δ = 57.49 (s, 1 P, PPh_2) ppm. ^{13}C{^{1}H} NMR: δ = 155.56 (s, C-2), 147.72 (s, C-6), 138.43 (s, C-4), 132.94 (d, $^1J_{\text{P-C}}$ = 83.3 Hz, C_{ipso},PPh_2), 132.86 (d, $^2J_{\text{P-C}}$ = 21.2 Hz, C_{ortho}, Ph), 132.37 (s, C_{para}, Ph), 129.61 (d, $^3J_{\text{P-C}}$ = 15.40 Hz, C_{meta}, Ph), 116.63 (s, C-5), 112.41 (s, C-3) ppm. MS (ESI$^+$): m/z (%) = 603 (89) [M + H]$^+$. $C_{21}H_{18}AuN_4OPS$ (602.40): calcd. C 41.87, H 3.01, N 9.30, S 5.32; found C 41.79, H 3.29, N 9.45, S 5.47.

Complex 8: Yield: 0.097 g, 81.4%. ^{1}H NMR: δ = 12.30 (br. s, 2 H, NH_2), 8.83 (br. s, 1 H, NH), 8.06 (m, 1 H, 6-H), 7.78 (m, 4 H, Ph-H), 7.59 (m, 8 H, Ph-H, 4-H, 6′-H), 7.03 (d, $^3J_{\text{H-H}}$ = 8.40 Hz, 1 H, 3-H), 6.86 (m, 1 H, 5-H), 5.86 (d, $^3J_{\text{H-H}}$ = 7.20 Hz, 1 H, 5′-H) ppm. ^{31}P{^{1}H} NMR: δ = 57.91 (s, 1 P, PPh_2) ppm. ^{13}C{^{1}H} NMR: δ = 162.53 (s, C-2′), 155.32 (s, C-2), 147.22 (s, C-6), 137.77 (s, C-4), 133.15 (d, $^1J_{\text{P-C}}$ = 60.30 Hz, C_{ipso}, Ph), 132.41 (d, $^2J_{\text{P-C}}$ = 16.30 Hz, C_{ortho}, Ph), 131.60 (s, C_{para}, Ph), 128.98 (d, $^3J_{\text{P-C}}$ = 11.80 Hz, C_{meta}, Ph), 115.96 (s, C-5), 111.89 (s, C-3) ppm. MS (ESI$^+$): m/z (%) = 602 (98) [M + H]$^+$. $C_{21}H_{19}AuN_5PS$ (601.41): calcd. C 41.94, H 3.18, N 11.64, S 5.33; found C 41.96, H 3.02, N 11.55, S 5.35.

Synthesis of [Au(SR){Ph_2PNH(Htrz)}] [R = py (9), TC (10), TG (11)]: Et_3N (0.025 g, 0.034 mL, 0.25 mmol) was added to a dichloromethane solution (20 mL) of [AuCl{Ph_2PNH(Htrz)}] (**4**; 0.102 g, 0.20 mmol) and 2-mercaptopyridine (2-HSpy; 0.022 g, 0.20 mmol) or 2-thiocytosine (2-TC; 0.025 g, 0.20 mmol) or 6-thioguanine (6-HTG; 0.033 g, 0.20 mmol), and the mixture was stirred for 18 h. Complexes **9**, **10** or **11** precipitated as white solids and were filtered off.

Complex 9: Yield: 0.087 g, 76%. ^{1}H NMR: δ = 13.39 (br. s, 1 H, NH, Htrz), 9.04 (br. s, 1 H, NH-P), 8.20 (m, 2 H, 5-H, 6′-H), 7.80 (m, 4 H, Ph-H), 7.59 (m, 6 H, Ph-H), 7.42 (m, 2 H, 4′-H, 5′-H), 6.89 (m, 1 H, 3′-H) ppm. ^{31}P{^{1}H} NMR: δ = 63.03 (s, 1 P, PPh_2) ppm. ^{13}C{^{1}H} NMR (300 MHz): δ = 148.95 (s, C-6′), 135.85 (s, C-4′), 132.80 (d, $^2J_{\text{P-C}}$ = 15.98 Hz, C_{ortho}, Ph), 132.26 (s, C_{para}, Ph), 129.47 (d, $^3J_{\text{P-C}}$ = 11.91 Hz, C_{meta}, Ph), 126.71 (s, C-5′), 118.35 (s, C-3′) ppm. MS (ESI$^+$): m/z (%) = 576 (100) [M + H]$^+$. $C_{19}H_{17}AuN_5PS$ (575.38): calcd. C 39.66, H 2.98, N 12.17, S 5.57; found C 39.29, H 2.96, N 12.31, S 5.19.

Complex 10: Yield: 0.095 g, 80.3%. ^{1}H NMR: δ = 13.30 (br. s, 1 H, NH, Htrz), 8.94 (br. s, 1 H, NH-P), 8.12 (s, 1 H, 5-H), 7.85 (m, 4 H, Ph), 7.74 (m, 1 H, 6′-H), 7.56 (m, 6 H, Ph), 6.49 (br. s, 2 H, NH_2), 6.02 (d, $^3J_{\text{H-H}}$ = 5.73 Hz, 1 H, 5′-H) ppm. ^{31}P{^{1}H} NMR: δ = 63.05 (s, 1 P, PPh_2) ppm. ^{13}C{^{1}H} NMR (300 MHz): δ = 163.09 (s, C-2′), 133.69 (d, $^1J_{\text{P-C}}$ = 62.73 Hz, C_{ipso}, Ph), 132.92 (d, $^2J_{\text{P-C}}$ = 16.13 Hz, C_{ortho}, Ph), 132.11 (s, C_{para}, Ph), 129.35 (d, $^3J_{\text{P-C}}$ = 11.99 Hz, C_{meta}, Ph), 99.89 (m, C-5′) ppm. MS (ESI$^+$): m/z (%) = 592 (100) [M + H]$^+$. $C_{18}H_{17}AuN_7PS$ (591.38): calcd. C 36.56, H 2.90, N 16.58, S 5.42; found C 36.60, H 3.18, N 16.36, S 5.88.

Complex 11: Yield: 0.106 g, 83.9%. ^{1}H NMR: δ = 13.30, 12.34 (br. s, 2 H, NH, TG, Htrz), 8.85 (br. s, 1 H, NH-P), 8.17 (br. s, 1 H, 5-H), 7.93 (m, 4 H, Ph), 7.76 (br. s, 1 H, 8′-H), 7.57 (m, 6 H, Ph), 5.97 (br. s, 2 H, NH_2) ppm. ^{31}P{^{1}H} NMR: δ = 62.44 (s, 1 P, PPh_2) ppm. ^{13}C{^{1}H} NMR (300 MHz): δ = 133.66 (d, $^1J_{\text{P-C}}$ = 54.59 Hz, C_{ipso}, PPh_2), 133.06 (d, ^2J = 19.83 Hz, C_{ortho}, Ph), 132.06 (s, C_{para}, Ph), 129.29 (d, J = 11.91 Hz, C_{meta}, Ph) ppm. MS (ESI$^+$): m/z (%) = 632 (100) [M + H]$^+$. $C_{19}H_{17}AuN_9PS$ (631.40): calcd. C 36.14, H 2.71, N 19.97, S 5.08; found C 35.94, H 2.63, N 20.16, S 5.34.

Crystal Structure Determinations: Data were recorded with a Bruker Smart 1000 CCD (**4**, **5**, **9**) or Oxford Diffraction Xcalibur (**8**) diffractometer. The crystals were mounted in inert oil on glass fibres and transferred to the cold gas stream of the diffractometer. Data were collected by using monochromated Mo-K_α radiation (λ = 0.71073 Å) in ω-scans. Absorption corrections based on multiple scans were applied by using the SADABS program.[27] The structures were solved by direct methods and refined on F^2 by using the SHELXL-97 program.[28] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included by using a riding model. Further crystal data are given in Table 4. CCDC-783693 (**4**), -783694 (**5**), -783695 (**8**) and -783696 (**9**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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