Mono- and Binuclear Gold(I) Amido Compounds of Purine Derivatives

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Dedicated to Professor Hubert Schmidbaur on the occasion of his 70th birthday in recognition of his continuing contributions to inorganic and organometallic chemistry

A series of neutral dinuclear and mononuclear gold(I) complexes with phosphine and *N*-bonded 9*H*-purin-9-ate or 9*H*-purin-6-ylamine-9-ate have been synthesised under basic conditions and characterised by gHSQC, ^{1}H,^{13}C gHMQC and ^{1}H detected ^{1}H,^{15}N gHMQC experiments in addition to ESI-MS and IR spectroscopy. Intermolecular aurophilic interactions are present in the structures of polymeric 1,2-bis(diphenylphosphine)ethane(9*H*-purin-9-ate)gold(I) **1**, (3.1641(4) Å) and 1,3-bis(diphenylphosphine)propane(9*H*-purin-9-ate)gold(I) **3**, (3.52 Å). The N-Au-P angle in **1** is exceptionally small (166.3(1)°). Intramolecular aurophilic interaction (3.63 Å) complemented by hydrogen bonding dictates the non-oligomeric structure of 1,3-bis(diphenylphosphine)propane(9*H*-purin-6-ylamin-9-ate)gold(I) (**7**). Dimeric aurophilic interactions appear in the structure of (tributylphosphine)(9*H*-purin-9-ate)gold(I) (**11**) (3.2311(7) Å), while the structure in the other mononuclear compound, (triphenylphosphine)(9*H*-purin-9-ate)gold(I) (**9**) is organised by Au…N-interactions.

Key words: Gold(I) Complexes, Aurophilic Interactions, Amido Ligands, 9H-Purine, DNA Base

Pharmacological application of gold(I) compounds in the treatment of rheumatoid arthritis and their potential activity as anticancer, antiviral and antimicrobial agents provide powerful motivation for the continued interest in the bonding of biologically active molecules to gold(I) [1 – 5].

The prevalence of five-membered nitrogen-containing ring systems and thiolate bonding sites in biologically active molecules, identifies them as ideal candidates for enquiry as far as bonding to gold(I) is concerned. Coordination of gold(I) to 8-mercaptotheophylline [6], xanthine, xanthine derivatives [7], phthalimide and ribovlavin [8] has been explored. Diphosphines and phosphinegold(I) compounds exhibit anticancer activity [3]. An interest in the bonding of gold(I) to thiolate functions has resulted in a thorough investigation of mono- and phosphine(dithiolate)gold(I) compounds [9]. Although several amido complexes of gold(I) have been characterised [4, 10 – 12], the coordination of DNA bases or purines to (phosphine)gold(I) compounds remains of interest.

Factors determining aurophilic interactions yielding dimers, oligomers and polymers, *e.g.* electronic effects of the ligands on gold(I), steric effects and packing forces are actively pursued and have propelled aurophilic interactions into the domain of supramolecular chemistry [9, 13 – 16].

In pursuit of the above fields of interest we investigated and now report the preparation and characterisation of neutral dinuclear and mononuclear gold(I) complexes with phosphine and *N*-bonded 9*H*-purin-9-ate or 9*H*-purin-6-ylamine-9-ate ligands under basic conditions.

Results and Discussion

Syntheses and characterisation

Deprotonated (NaOH) purine dissolved in methanol, reacted with the appropriate gold starting material to yield complexes **1** – **3**, **10** and **11** (Scheme 1). The analogous purin-6-ylamine anion was prepared in DME by deprotonation with NaOH in the presence of small amounts of water. Reaction of this anion with chloro(phosphine)gold(I) complexes gave the amido complexes **5** – **8**, **12** and **13**. Complexes **4** and **9** did not form according to the first protocol, but the synthetic methodology followed for

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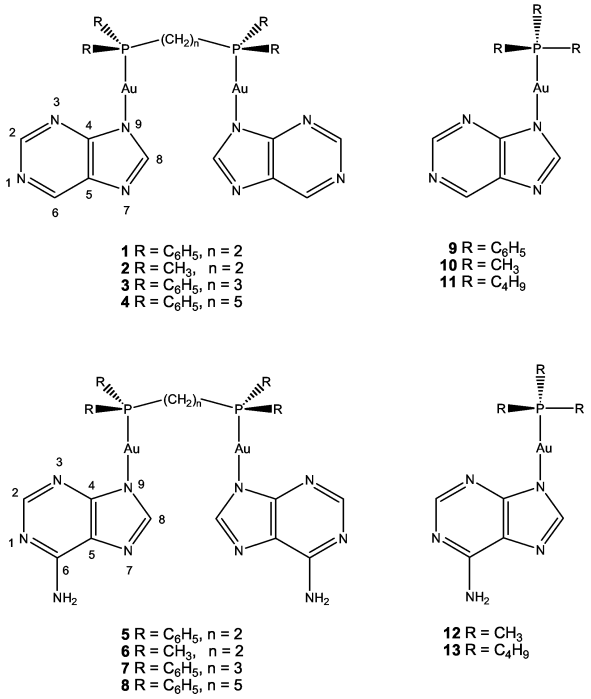

Scheme 1. Gold(I) complexes of 9*H*-purin-9-ate (**1**–**4**, **9**–**11**) and 9*H*-purin-6-ylamine-9-ate (**5**–**8**, **12**–**13**).

the purin-6-ylamine deprotonation was successful. The unreacted gold starting materials were separated by filtration from methanol suspensions of the crude product. After *in vacuo* stripping of methanol, the unreacted purine or purin-6-ylamine and formed NaCl were removed from the product by repeated washing with deoxygenated water. The new complexes are stable in deoxygenated water and decompose slowly in air. Compounds **1** and **8** are selectively soluble in a 1:1 mixture of CH_2Cl_2 and methanol, while **2**, **6**, **10** and **12** dissolve in water and all the other complexes in methanol and organic solvents.

The purin-9-ate compounds **3**, **4** and **11** melt at temperatures lower than 100 °C, while the purin-6-ylamine-9-ate compounds, **5** and **8**, and the purin-9-ate monophosphine compounds, **9** and **10**, melt at temperatures above 150 °C. All other compounds decompose on heating.

The molecular ions are not observed in the ESI mass spectra of these compounds. All complexes that contain diphosphine ligands (**1**–**8**) show m/z-values representing the combined diphosphine, two gold atoms and either a purine or purin-6-ylamine unit. The spectra of the monophosphine compounds (**9**–**13**) contain fragments consisting of the target molecule and an extra gold phosphine unit as well as a fragment representing Au(phosphine)$_2$.

Spectroscopy

The IR spectra of all purin-9-ate-containing compounds (**1**–**4**, **9**–**11**) show no ν(NH) stretching band at 3432 cm^{-1}. This suggests that the ionisable proton on the nitrogen atom of the five membered ring in purine has been substituted by (phosphine)gold(I) or (diphosphine)digold(I) moieties. The ν(C=N) stretching frequency at 1570 cm^{-1} in purine appears at higher wavenumbers in the gold complexes while all other bands show no significant change from their position in purine.

The detection of the $\nu_s(NH_2)$ and $\nu_{as}(NH_2)$ stretching bands excludes coordination of the gold to purin-6-ylamine-9-ate *via* the amino group. The very strong $\nu(NH_2)$ bending mode of all purin-6-ylamine-9-ate-containing complexes (**5**–**8**, **12** and **13**) appears at 1633–1674 cm^{-1}. The absence of bands at *ca.* ν = 3432 cm^{-1} suggests substitution of H(9) by (phosphine)gold(I) or (diphosphine)digold(I) units.

The absence of signals for H(9) ($\delta = -13$) in the ^{1}H NMR spectra of all compounds, again indicates anion formation and coordination to gold. Small changes in chemical shift are observed in the ^{1}H and ^{13}C NMR spectra of the new compounds in comparison to the spectra of purine, purin-6-ylamine and the gold complex starting materials. The largest change ($\delta = 9$, downfield) is observed for C(8) in the purin-6-ylamine-9-ate compounds (**5**–**8**, **12** and **13**). The assignments of the signals observed for **9** and **13** were confirmed by gHSQC and ^{1}H,^{13}C gHMQC experiments. In the gHMQC spectrum of **9**, H(8) shows two correlations to the ^{13}C dimension, one at $\delta = 160.4$ and one at $\delta = 134.7$. As long-range coupling of H(8) with the carbons in the phenyl rings is unlikely, this indicates that one of the quatenary carbon atoms C(4) or C(5) is obscured by the signal of the *meta* carbons on the phenyl rings of PPh_3 at $\delta = 134.7$. H(6) also shows correlations to the same ^{13}C signals while H(2) only correlates with the signal at $\delta = 160.4$. Thus the latter signal at $\delta = 160.4$ can be assigned to C(4) and the one at $\delta = 134.7$ to C(5), the bridge carbon on the imine side of the five-membered ring in the purin-9-ate ligand. A carbon peak at $\delta = 126.6$ tentatively assigned by Rosopulos *et al.* [12], is due either to unreacted purine or to the sodium salt of purine.

The ^{31}P NMR signals are shifted upfield by less than 4.5 ppm upon coordination of the gold compounds to purin-9-ate or purin-6-ylamine-9-ate. The observation that the phosphorus chemical shift in the diphosphine compounds becomes more positive as the number of connecting carbons (n) increases (except when $n = 2$), has been ascribed to small variations in the dihedral or bond angles at the phosphorus atom as the length of the alkyl backbone changes [7, 9].

The NH_2 protons at $\delta = 7.09$ in the ^{1}H NMR of purin-6-ylamine ($CDCl_3$ solution) appear at $\delta = 5.78$ in **13** (measured in CD_2Cl_2) and were not observed for any of the other purin-6-ylamine-9-ate complexes (in CD_3OD).

The ^{15}N chemical shifts of the nitrogen atoms of **1** were determined in a ^{1}H detected ^{1}H,^{15}N gHMQC experiment. The most shielded nitrogen at $\delta = -179.2$ is assigned to the nitrogen atom bonded to the gold, N(9). The nitrogen atoms in the six-membered ring are less shielded ($\delta = -122.0$, N(1) and $\delta = -130.6$, N(3)) than those in the five membered ring ($\delta = -159.3$, N(7) and N(9)) of the purin-9-ate ligand. The ^{15}N chemical shifts of the nitrogen atoms of purin-6-ylamine-9-ate in compound **13**, were determined in the same manner. The nitrogen bonded to gold (N(9)) is again highly shielded at $\delta = -174.2$. However, due to the presence of the NH_2 group, the nitrogens in the six-membered ring are more shielded than those found in **1**, appearing at $\delta = -150.3$ (N(1)) and $\delta = -144.5$ (N(3)). N(7) is slightly deshielded from the corresponding nitrogen in **1**, appearing at $\delta = -147.0$. As expected, the NH_2 nitrogen appears significantly upfield from the other nitrogens in the compound at $\delta = -311.9$. Attempts to locate the nitrogen atoms in the other purinate compounds were not as successful and only the two nitrogens in the six-membered rings of **2**, **3** and **10** were detected. Since the ^{1}H,^{15}N gHMQC indirect detection method is ^{1}H detected, and the notion that H(8) ($pK_a \sim 7.3$ [17]) is involved in some migratory process along the aromatic system in the five-membered ring of the anionic ligand is not unreasonable, the failure to detect the other nitrogen atoms is not completely unexpected. Direct detection of ^{15}N atoms requires high sample concentration and extended data collection times. This is not feasible when the solubility of the compounds is low. The effects of migrating protons are also visible in the ^{13}C NMR spectra of some compounds. The signals for the carbons carrying the NH_2 group (C(6)) and the acidic hydrogen (C(8)) in the purin-6-ylamine-9-ate complexes **8**, **12** and **13** are broad. The signals for the bridge carbons (C(4) and C(5)) in the purin-9-ate ligand and the other two carbon atoms in the six-membered ring (C2 and C6) of the purin-9-ate ligand in **9** – **11**, are also slightly broadened.

The ^{13}C NMR spectra of the new compounds display other unusual features. The phenyl rings of the phosphine ligands in **1** and **5** contain magnetically inequivalent carbon atoms resulting in triplets for the *meta* and *ortho* carbons (doublet of doublets with $J_{PC} = J_{PC}$, 6 and 8 Hz). The magnetic inequivalence is not unexpected based on the symmetry of the molecule [18]. The *para* carbons appear as a singlet and the *ipso* as a doublet, $J_{PC} = 60$ Hz. The carbons in the phenyl rings of the rest of the compounds appear as doublets ($J_{PC} = 13$ (*meta*), 2.4 (*para*), 12 (*ortho*) and 62 (*ipso*) Hz). The methyl groups on the phosphine ligands in compounds **2** and **6** also display magnetic inequivalence resulting in signals for an AA'XX' spin system. The same signal pattern is observed for the bridging CH_2 groups in **2** and **6**, suggesting magnetic inequivalence in these carbon atoms as well. The carbon atoms in the bridge of the 1,2-bis(diphenylphosphine)ethane ligands in **1** and **5** also experience magnetic inequivalence resulting in complicated multiplets.

In compounds that contain longer bridges (**3**, **4**, **7** and **8**) and in the P(n-Bu)$_3$ compounds (**11** and **13**), no magnetic inequivalence and no coupling (only a slightly broadened signal) is detected for the second carbon from the phosphine atom. The C-C-P angles of **3**, **7** and **11** are all larger than the preferred 109° for effective geminal coupling (*vide infra*) and the β carbon experiences only a small coupling resulting in a slightly broader signal. With the bridge consisting of three carbon atoms (**3** and **7**), the signal for the carbon bonded to the phosphine appears as a doublet of doublets ($J_{PC} = 38$ and 10 Hz) as a result of coupling to two P atoms. A doublet ($J_{PC} = 39$ Hz) for the carbon next to the P atom and a triplet ($J_{PC} = 14.6$ Hz) for the middle carbon atom are observed for the bridge of the 1,5-bis(diphenylphosphine)pentane ligands of **4** and **8**. Similar values are found for the carbons in the butyl groups of **11** and **13** while the terminal carbon experiences no coupling.

Molecular structure

The molecular structures of **1**, **3**, **7**, **9** and **11** with the atom numbering schemes are depicted in Figs 1 – 5.

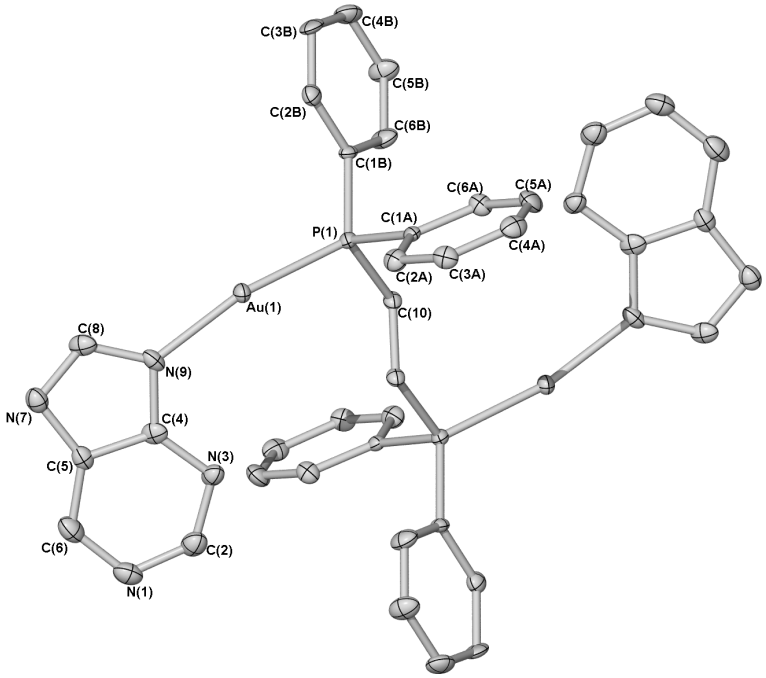

Fig. 1. Molecular structure of **1** showing the numbering scheme. Only crystallographically unique atoms are labelled.

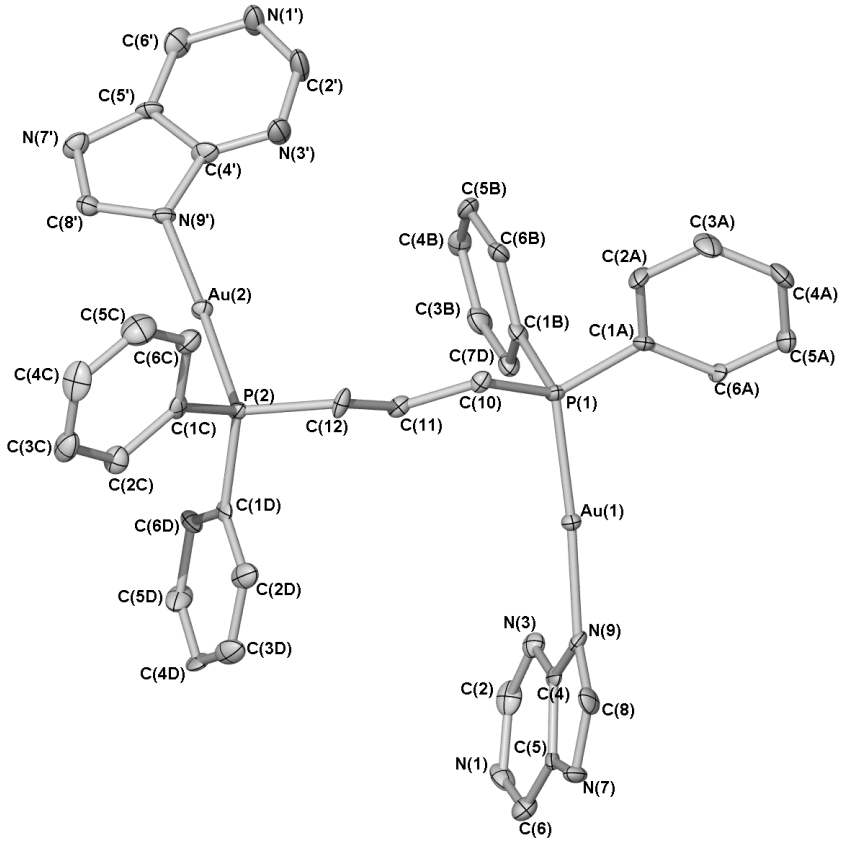

Fig. 2. Molecular structure of **3**.

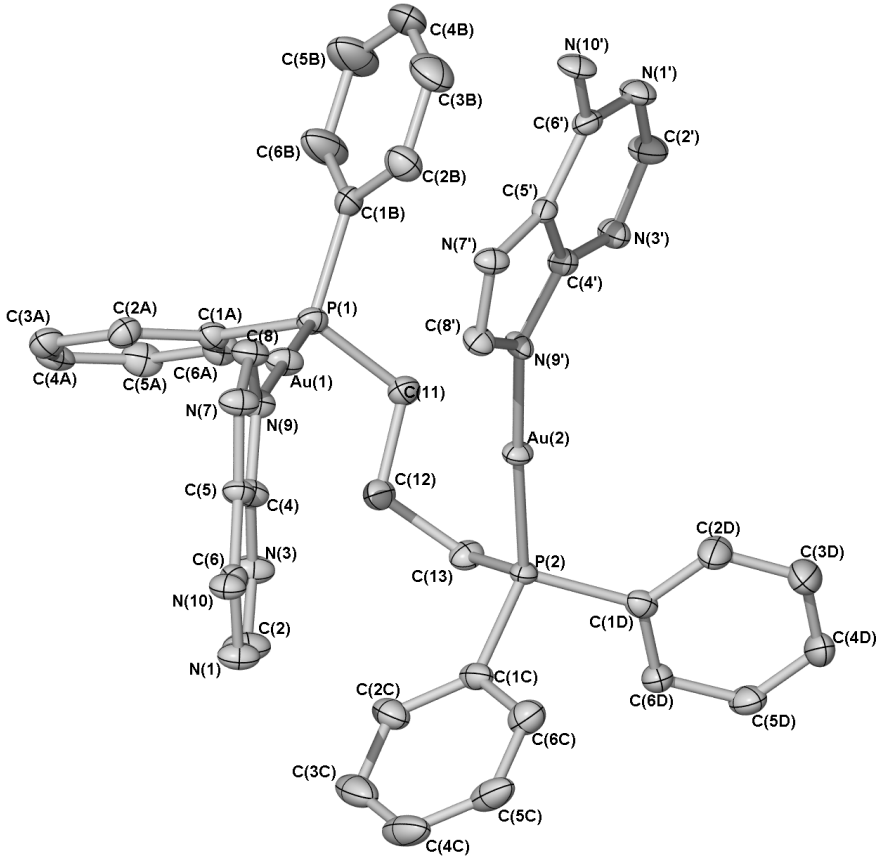

Fig. 3. Molecular structure of **7**.

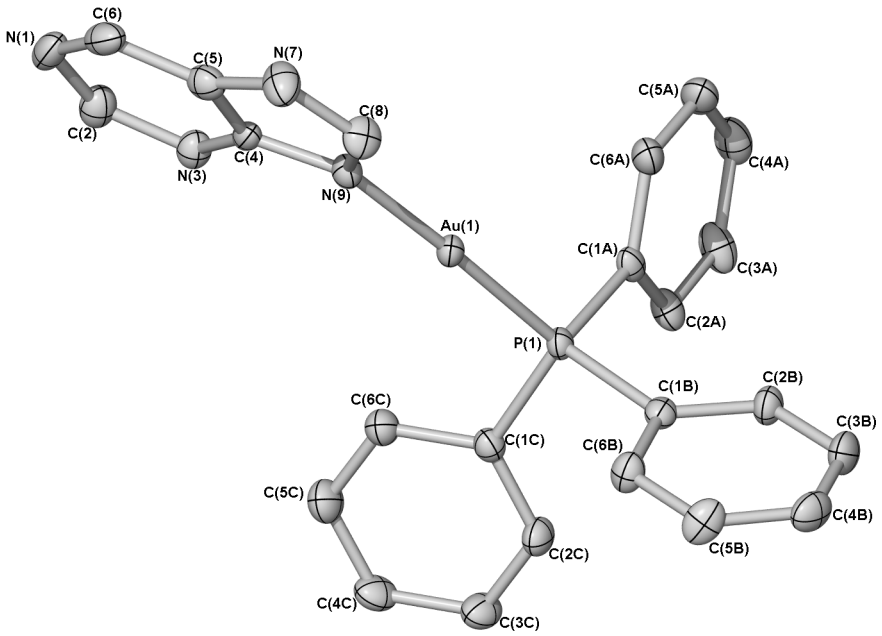

Fig. 4. Molecular structure of **9**.

Table 1. Selected bond lengths [Å] and angles [°] of **1**, **3**, **7**, **9** and **11**.

	1	**3**	**7**	**9**	**11**
Au(1)–N(9)	2.052(4)	2.050(7)	2.040(4)	2.042(3)	2.050(9)
Au(1)–P(1)	2.244(1)	2.242(2)	2.235(1)	2.236(1)	2.225(3)
Au(2)–N(9')		2.053(7)	2.036(3)		
Au(2)–P(2)		2.243(2)	2.236(1)		
N(9)–Au(1)–P(1)	166.3(1)	175.6(2)	177.8(1)	177.78(8)	172.7(3)
N(9')–Au(2)–P(2)		176.7(2)	177.0(1)		

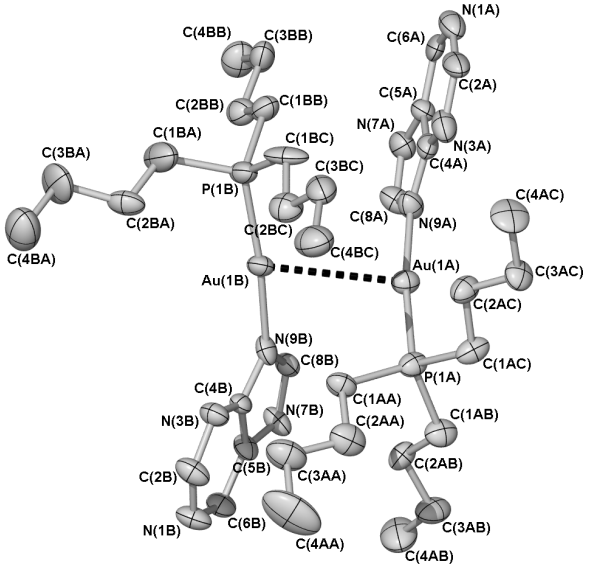

Fig. 5. The dimeric molecular structure of **11** showing the numbering scheme. Au(I)…Au(I) interaction is shown as dashed lines.

Selected bond lengths and angles are summarised in Table 1.

All the gold atoms are bonded to phosphorus and amido-nitrogen atoms with bridged phosphines affording dinuclear compounds.

Complex **1** exhibits crystallographic inversion symmetry (midpoint of the two-carbon chain). Molecules of **3** possess no crystallographically imposed symmetry, however, an approximate two-fold axis passes through C(11) and lies perpendicular to the plane of Fig. 2. The gold atoms in **1** and **3** are bound to the diphosphine ligand on opposite (*trans*) sides of the plane defined by the carbon atoms and phosphorus atoms of the chain, with torsion angles Au-P-P-Au of 180(0) and −129.33(9)° respectively.

Each gold atom is two-coordinate and essentially linear. Larger deviations from 180° for the N-Au-P angles are detected in compounds which experience aurophilic interactions. In compound **1**, with an unusually small N-Au-P angle of 166.3(1)°, Au…Au interactions of 3.1641(4) Å result in the oligomerisation of the open-chain digold molecules into an extended polymer (Fig. 6). An edge-to-face π-π-interaction between C(3B)-H(3B) and the phenyl ring, A, (C(3B)…centroid C(1-6A) 3.58 Å) on an adjacent molecule, results in the *ca*. 14° digression from 180°. This interaction also seems to limit the distance of the Au…Au separation. Similar polymers have been reported for Au_2(*p*-thiocresol)$_2$(1,4-bis(diphenylphosphine)butane) and Au_2(*p*-thiocresol)$_2$(1,5-bis(diphenylphosphine)pentane) [9].

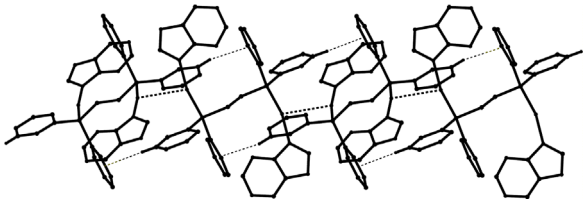

Fig. 6. The polymeric structure of **1** with Au(I)…Au(I) and π-π-interactions shown as dashed lines.

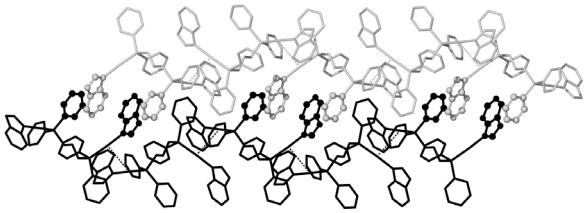

Fig. 7. The polymeric structure of **3** with Au(I)…Au(I) interactions shown as dashed lines.

An analogous polymeric open-chain structure consisting of strands of molecules with aurophilic interactions (3.52 Å) parallel to [0, 1, 0] is observed in the lattice of **3** (Fig. 7). Additional stabilisation is achieved by means of π-stacking interactions between purin-9-ate rings (centroid N(1)-C(6)…centroid N(1)-C(6) 3.59 Å) and the phenyl rings, D, (centroid N(1)-C(6)…centroid C(1-6D) 3.76 Å) of an adjacent chain. All purin-9-ate and purin-6-ylamine-9-ate ligands are essentially planar.

The 1,3-bis(diphenylphosphine)propane bridge in **7** is not planar as in **3** and the two gold atoms on each side of the diphosphine ligand are located across each other with an Au…Au separation of 3.63 Å, the same distance as the sum of the Van der Waals radii for gold [14]. The torsion angle Au-P-P-Au is −51.31(3)°. Very small departures from linear coordination are evident in the N-Au-P angles of 177.9(1) and 177.0(1)°. The neutral molecules are held to-

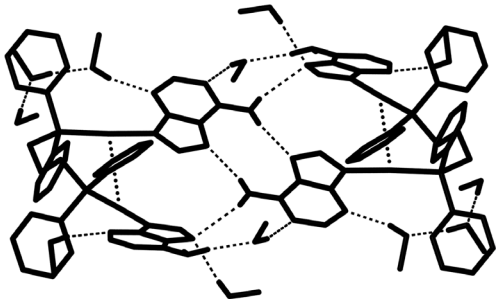

Fig. 8. Two molecules of **7** related by a center of inversion and six methanol molecules. Hydrogen bonds are shown as dashed lines.

gether in pairs by two sets of hydrogen bonds involving the NH_2 groups [N(1)...N(10)-H(10A) 2.96 and H(10B)-N(10)...O(6) 2.95 Å] and the imine nitrogen atoms N(7) and N(7)', N(7)...N(10)'-H(10B)' 3.08 Å, N(7)'...N(10)'-H(10A)' 2.98 Å, and are related by a center of inversion. Complimentary N(3)...O(4)-H 2.84 and N(1)'...O(6)-H 2.83 Å hydrogen bonds with six enclathrated methanol molecules support this arrangement (Fig. 8).

The monophosphine complexes **9** and **11** only differ as far as the substituents on phosphorus are concerned. The structure of **9** is analogous to that of triphenylphosphine(9*H*-purin-6-ylamine-9-ate)- gold(I) [12].

No aurophilic interactions are present in the structure of **9** but interaction between N(1) of the purin-9-ate ligand and Au atoms in a neighbouring molecule [N(1)...Au 3.47 and C(4)...C(4) 3.32 Å] and an edge-to-face π-π-interaction of 3.64 Å between C(8)-H(8) and the phenyl ring, A, [centroid C(1-6A)] govern lattice organization (Fig. 9). The asymmetric unit contains the gold complex and solvent modelled as two highly disordered methanol molecules. The N-Au-P angle is normal at 177.78(8)°. Aurophilic interactions are rare in monophosphine gold complexes but have previously been reported for [Au(1,2,4-triazolate)(PPh_3)], Au...Au 3.1971(6) Å [11]. A slightly larger separation is observed in the structure of **11** (3.2311(7) Å) as well as a smaller N-Au-P angle of 172.7(3)° (Fig. 5). The unit cell of **11** contains two molecules in the asymmetric unit. One of them has a slightly disordered butyl chain.

Au-P and Au-N bond distances and the N-Au-P angle correspond to reported values for amido(gold) phosphine complexes in Table 2. The C-C-P angles of **3**, **7** and **11**, C(11)-C(10)-P(1) 113.4(6), C(11)-C(12)-P(2) 111.9(6) in **3**, C(12)-C(11)-P(1) 112.1(3), C(12)-C(13)-P(2) 113.6(3) in **7** and C(2AA)-C(1AA)-P(1AA) 114.7(8), C(2AB)-C(1AB)-P(1AB) 116.1(8) and C(2AC)-C(1AC)-P(1AC) 113.4(8)° in **11**, all larger than 109°, support the observation of the very small geminal C-P coupling resulting in broadening of the signal for the β carbon in their ^{13}C NMR spectra.

Table 2. Comparison of bond lengths and angles in amido(gold)phosphine complexes.

Complex	Au-P [Å]	Au-N [Å]	N-Au-P [°]	Ref.
[Au(1,2,4-triazolate)PPh_3]$_2$	2.243(2)	2.026(7)	177.1(2)	[11]
	2.238(2)	2.037(7)	172.7(3)	
Au(imidazolate)PPh_3	2.234(2)	2.027(4)	178.4(3)	[4]
Au(pyrazolate)PPh_3	2.232(2)	2.024(7)	178.0(2)	[4]
Au(tetrazolate)PPh_3	2.239(2)	2.043(5)	178.4(1)	[10]
Au(purin-6-ylaminate)PPh_3	2.240(1)	2.038(4)	177.6(1)	[12]

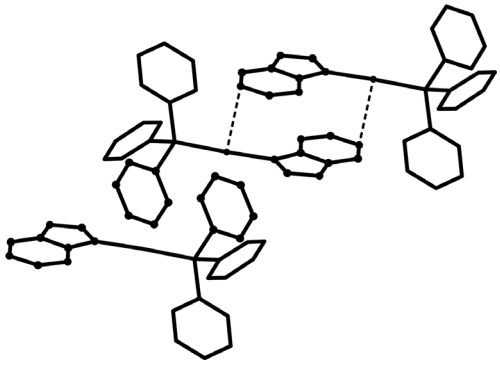

Fig. 9. Molecules of **9** showing interactions between N(1) of the purin-9-ate ligand and the Au atom of a neighbour.

The crystal structures of **1** and **3** show polymeric intermolecular aurophilic interactions. An increase in the number of carbon atoms (n) [(diphenylphosphine)methane to 1,2-bis(diphenylphosphine)ethane to 1,3-bis(diphenylphosphine)propane] in the diphosphine backbone results in a change from intramolecular to intermolecular aurophilic interactions (dimer for $n = 2$ or polymer formation for $n \geq 2$) in the structure [9]. The strength of aurophilic interactions is influenced by the electronic effects of the substituents on gold(I). These weak forces, still in excess of standard Van der Waals (dispersion) interactions and comparable to hydrogen bonding interactions, can overrule substantial repulsive forces, but steric effects and packing forces play a decisive role in their formation [13, 14]. This is clearly demonstrated in the crystal structures of **3** and **7**. Both contain the 1,3-bis(diphenylphosphine)propane but one forms oligomeric aurophilic intramolecular interactions effecting oligomers whereas the other exhibits intramolecular aurophilic interaction.

Conclusions

Deprotonation of 9*H*-purine and 9*H*-purin-6-ylamine with NaOH and subsequent complexation to gold(I)phosphine is solvent dependent. The signals in the ^{1}H NMR and ^{13}C NMR spectra of **9** and **13** were unequivocally assigned with gHSQC and ^{1}H,^{13}C gHMQC experiments. ^{1}H detected ^{1}H,^{15}N gHMQC experiments yielded the chemical shifts of the nitrogen atoms in **1** and **13**. Magnetic inequivalence of the bridge carbon atoms and methyl groups of the 1,2-bis(diphenylphosphine)ethane and 1,2-bis(dimethylphosphine)ethane ligands in **1**, **2**, **5** and **6** complicates the signals in the ^{13}C NMR spectra with an AA'XX' spin system in which $J_{XX'} = 0$. No coupling is detected for the carbon atom β to the phosphorus atom in the bridges of 1,3-bis(diphenylphosphine)propane and 1,5-bis(diphenylphosphine)pentane and PBu_3 in compounds **3**, **4**, **7**, **8**, **11** and **13**. Doublets as a result of C-P-coupling are observed for the other carbon signals. Aurophilic interactions, hydrogen bonding and π-π-interactions direct lattice organisation in the crystal structures of **1**, **3**, **7**, **9** and **11**. Intermolecular aurophilic interactions are present in **1** and **3** affording 'polymers' in the solid state but intramolecular aurophilic interactions and hydrogen bonding prevail in **7**. Compounds **2**, **6**, **10** and **12** are soluble in water and will be screened to determine their biological activity.

Experimental Section

General

Reactions were carried out under argon using standard Schlenk and vacuum-line techniques. Tetrahydrofuran and diethyl ether were distilled under N_2 from sodium diphenylketyl, *n*-pentane from sodium and CH_2Cl_2 and methanol from CaH_2. Melting points were determined on a Stuart Scientific Melting Point Apparatus SMP3 and are uncorrected. Mass spectra were recorded on a VG Quattro (ESI, 70 eV) or AMD 604 (EI, 70 eV) instrument, the infrared spectra on a Perkin-Elmer 1600 Series FTIR and NMR spectra on a Varian VXR 300 or INOVA 600 spectrometer (δ reported relative to the solvent resonance or external reference 85% H_3PO_4 or CH_3NO_2). Elemental analyses were carried out by Anorganisches Chemisches Institut der TU München in Garching, Department of Chemistry, University of Cape Town or Microanalytisches Labor Pascher, Remagen-Bandorf, Germany. Gold(I) starting materials ((μ-1,2-bis(diphenylphosphine)ethane)bis(chlorogold), (μ-1,2-bis(dimethylphosphine)ethane)bis(chlorogold), (μ-1,3-bis(diphenylphosphine)propane)bis(chlorogold), (μ-1,5-bis(diphenylphosphine)pentane)bis(chlorogold), (triphenylphosphine)gold chloride, (trimethylphosphine)-gold chloride, (tributylphosphine)gold chloride) were prepared by substitution of tht in ClAutht [19, 20] with the appropriate phosphine. Comparison of the characterisation data [21 – 24] in the literature confirmed their purity. All the other starting materials are commercially available and were used without further purification.

*(μ-1,2-Bis(diphenylphosphine)ethane)bis(9H-purin-9-ate)-gold(I) (**1**)*

A suspension of purine (0.24 g, 2.0 mmol) and (μ-1,2-bis(diphenylphosphine)ethane)bis(chlorogold) (0.86 g, 1.0 mmol) in methanol (20 ml) was treated with NaOH (0.08 g, 2.0 mmol) dissolved in methanol (10 ml) and stirred for 2 h at room temperature. The mixture was filtered and reduced to dryness *in vacuo*. After the addition of H_2O (30 ml) to the residue, filtration, washing with H_2O (2×15 ml) and diethyl ether (3×20 ml), the residue was evaporated to dryness *in vacuo* to yield colourless, microcrystalline material (0.76 g, 74%).

M. p. 210 °C (dec.). – $C_{36}H_{30}Au_2N_8P_2$ (1030.57): calcd. C 41.96, H 2.93, N 10.87; found C 41.69, H 2.88, N 10.75. – IR (KBr): ν = 3054 (aromatic C-H), 2926 (aliphatic C-H), 2854 (aliphatic C-H), 1585 (C=N), 1549, 1458, 1389, 1173, 1108, 789, 735 cm^{-1}. – ^{1}H NMR (300 MHz, CD_2Cl_2/MeOH-d_4): δ = 8.91 (s, 2H, H6), 8.72 (s, 2H, H2), 8.01 (s, 2H, H8), 7.85 (m, 8H, C_6H_5-*meta*), 7.59 (m, 4H, C_6H_5-*para*), 7.53 (m, 8H, C_6H_5-*ortho*), 3.09 (d, 4H, ^2J = 7.2 Hz, P-(C*H*$_2$)$_2$-P). – ^{13}C NMR (75 MHz, CD_2Cl_2/MeOH-d_4): δ = 160.1 (s, C4), 155.1 (s, C2), 151.1 (s, C8), 145.7 (s, C6), 134.5 (s, C5), 134.2 (t, ^3J = 6.7 Hz, C_6H_5-*meta*), 133.3 (s, C_6H_5-*para*), 130.3 (t, ^2J = 6.1 Hz, C_6H_5-*ortho*), 128.7 (d, ^1J = 61.5 Hz, C_6H_5-*ipso*), 24.1 (m, P-(*C*H$_2$)$_2$-P). – ^{31}P NMR (121 MHz, CD_2Cl_2/MeOH-d_4): δ = 29.3. – ^{1}H detected ^{1}H,^{15}N gHMQC (61 MHz, CD_2Cl_2/MeOH-d_4): δ = −122.0 (s, N1), −130.6 (s, N3), −159.3 (s, N7), −179.2 (s, N9). ESI-MS (MeOH/CH_2Cl_2, 50%): m/z = [M$^+$-$C_5H_3N_4$] calcd. for $C_{31}H_{27}Au_2N_4P_2$ 911, found 911.

*(μ-1,2-Bis(dimethylphosphine)ethane)bis(9H-purin-9-ate)-gold(I) (**2**)*

Compound **2** was prepared in a similar manner to **1** from purine (0.24 g, 2.0 mmol), (μ-1,2-bis(dimethylphosphine)ethane)bis(chlorogold) (0.64 g, 1.0 mmol) and NaOH (0.08 g, 2.0 mmol) in methanol (45 ml) and the mixture was stirred for 1.5 h at room temperature. The mixture was filtered over Na_2SO_4 and reduced to dryness *in vacuo*. After treatment with diethyl ether (2×15 ml) the residue was evaporated to dryness *in vacuo* to yield colourless, microcrystalline material (0.84 g), contaminated with NaCl.

M. p. 179 °C (dec.). – $C_{16}H_{22}Au_2N_8P_2.1.3NaCl$ (858.26): calcd. C 22.39, H 2.58, N 13.06; found C 22.20, H 2.83, N 13.32. – IR (KBr): ν = 2978 (aliphatic C-H), 2901 (aliphatic C-H), 1591 (C=N), 1556, 1464, 1393, 1291, 1193, 1100, 911, 800, 648 cm^{-1}. – ^1H NMR (300 MHz, MeOH-d_4): δ = 8.79 (s, 2H, H6), 8.64 (s, 2H, H2), 7.92 (s, 2H, H8), 2.49 (d, 4H, ^2J = 8.9 Hz, P-(CH_2)$_2$-P), 1.87 (d, 12H, ^2J = 11.1 Hz, CH_3). – ^{13}C NMR (75 MHz, MeOH-d_4): δ = 161.1 (s, C4), 156.7 (s, C2), 151.3 (s, C8), 145.8 (s, C6), 135.4 (s, C5), 24.8 (m, P-(*C*H$_2$)$_2$-P), 13.4 (m, CH_3). – ^{31}P NMR (121 MHz, MeOH-d_4): δ = −0.2. – ^1H detected ^1H,^{15}N gHMQC (61 MHz, MeOH-d_4): δ = −123.4 (s, N1), −131.6 (s, N3). – ESI-MS (MeOH): m/z = [MH^+-$C_5H_3N_4$] calcd. for $C_{11}H_{20}Au_2N_4P_2$ 664, found 664.

*(μ-1,3-Bis(diphenylphosphine)propane)bis(9H-purin-9-ate)gold(I) (**3**)*

Complex **3** was prepared as above from purine (0.24 g, 2.0 mmol), (μ-1,3-bis(diphenylphosphine)propane) bis(chlorogold) (0.88 g, 1.0 mmol) and NaOH (0.08 g, 2.0 mmol) in methanol (35 ml). The mixture was stirred for 1 h at room temperature, filtered over celite and reduced to dryness *in vacuo*. The crude product was treated with H_2O (25 ml), filtered and washed with H_2O (3 × 15 ml) and diethyl ether (3 × 15 ml). The product was evaporated to dryness, to yield slightly pinkish, microcrystalline material (0.59 g, 57%).

M. p. 90 – 97 °C. – $C_{37}H_{32}Au_2N_8P_2$ (1044.60): calcd. C 42.54, H 3.09, N 10.73; found C 42.23, H 3.01, N 10.95. – IR (KBr): ν = 3050 (aromatic C-H), 2919 (aliphatic C-H), 2855 (aliphatic C-H), 1590 (C=N), 1551, 1464, 1436, 1393, 1193, 1104, 744, 692 cm^{-1}. – ^1H NMR (300 MHz, CD_2Cl_2): δ = 8.99 (s, 2H, H6), 8.64 (s, 2H, H2), 8.01 (s, 2H, H8), 7.69 (m, 8H, C_6H_5-*meta*), 7.48 (m, 4H, C_6H_5-*para*), 7.38 (m, 8H, C_6H_5-*ortho*), 3.11 (m, 4H, P-CH_2CH$_2$CH_2-P), 2.06 (m, 2H, P-CH$_2$CH_2CH$_2$-P). – ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 160.4 (s, C4), 154.5 (s, C2), 151.6 (s, C8), 146.5 (s, C6), 135.0 (s, C5), 133.8 (d, ^3J = 12.8 Hz, C_6H_5-*meta*), 132.9 (d, ^4J = 2.4 Hz, C_6H_5-*para*), 130.9 (d, ^2J = 11.6 Hz, C_6H_5-*ortho*), 128.7 (d, ^1J = 60.9 Hz, C_6H_5-*ipso*), 27.5 (dd, ^1J = 38.6 Hz, ^3J = 9.8 Hz, P-*C*H$_2$CH$_2$*C*H$_2$-P), 19.7 (bs, P-CH$_2$*C*H$_2$CH$_2$-P). – ^{31}P NMR (121 MHz, CD_2Cl_2): δ = 23.3. – ^1H detected ^1H,^{15}N gHMQC (61 MHz, CD_2Cl_2): δ = −109.4 (s, N1), −123.0 (s, N3). – ESI-MS (MeOH/CH_2Cl_2, 50%): m/z = [MH^+-$C_5H_3N_4$] calcd. for $C_{32}H_{30}Au_2N_4P_2$ 926, found 926.

*(μ-1,5-Bis(diphenylphosphine)pentane)bis(9H-purin-9-ate)gold(I) (**4**)*

A suspension of purine (0.12 g, 1.0 mmol) and (μ-1,5-bis(diphenylphosphine)pentane)bis(chlorogold) (0.45 g, 0.5 mmol) in DME (20 ml) was treated with NaOH (40 mg, 1.0 mmol) dissolved in H_2O (1 ml) and stirred for 2 h at 50 °C. The mixture was reduced to dryness *in vacuo*. After the addition of THF (15 ml) the solution was layered with *n*-pentane. The resulting precipitate was dissolved in acetone (15 ml) and filtered over Na_2SO_4. The clear solution was layered with diethyl ether and the resulting precipitate was filtered off, washed with diethyl ether (15 ml) and dried *in vacuo* to give a beige, microcrystalline material (0.13 g, 24%).

M. p. 96 °C (dec.). – $C_{39}H_{36}Au_2N_8P_2$ (1072.66): calcd. C 43.67, H 3.38, N 10.45; found C 43.29, H 2.99, N 10.46. – IR (KBr): ν = 3051 (aromatic C-H), 2924 (aliphatic C-H), 2856 (aliphatic C-H), 1590 (C=N), 1557, 1464, 1436, 1393, 1192, 1104, 908, 743, 692 cm^{-1}. – ^1H NMR (300 MHz, MeOH-d_4): δ = 8.90 (s, 2H, H6), 8.66 (s, 2H, H2), 8.39 (s, 2H, H8), 7.68 (m, 8H, C_6H_5-*meta*), 7.44 (m, 12H, C_6H_5-*para*, -*ortho*), 2.66 (m, 4H, P-CH_2(CH$_2$)$_3$CH_2-P), 1.82 (m, 6H, P-CH$_2$(CH_2)$_3$CH$_2$-P). – ^{13}C NMR (75 MHz, MeOH-d_4): δ = 160.8 (s, C4), 156.6 (s, C2), 151.9 (s, C8), 146.4 (s, C6), 135.2 (s, C5), 134.5 (d, ^3J = 12.8 Hz, C_6H_5-*meta*), 133.5 (d, ^4J = 2.4 Hz, C_6H_5-*para*), 130.7 (d, ^2J = 11.6 Hz, C_6H_5-*ortho*), 130.6 (d, ^1J = 60.9 Hz, C_6H_5-*ipso*), 31.0 (t, ^3J = 15.2 Hz, P-(CH$_2$)$_2$*C*H$_2$(CH$_2$)$_2$-P), 26.4 (d, ^1J = 39.0 Hz, P-*C*H$_2$(CH$_2$)$_3$*C*H$_2$-P), 25.0 (s, P-CH$_2$*C*H$_2$CH$_2$*C*H$_2$CH$_2$-P). – ^{31}P NMR (121 MHz, MeOH-d_4): δ = 29.3. – ESI-MS (MeOH): m/z = [MH^+-$C_5H_3N_4$] calcd. for $C_{34}H_{34}Au_2N_4P_2$ 954, found 954.

*(μ-1,2-Bis(diphenylphosphine)ethane)bis(9H-purin-6-ylamine-9-ate)gold(I) (**5**)*

Compound **5** was prepared in the same manner as **4** from NaOH (65 mg, 1.6 mmol), purin-6-ylamine (0.22 g, 1.6 mmol) and (μ-1,2-bis(diphenylphosphine)ethane) bis(chlorogold) (0.70 g, 0.8 mmol) in DME (30 ml). The mixture was stirred for 2 h at 45 °C and reduced to dryness *in vacuo*. After the addition of methanol (30 ml) to the residue, the mixture was stirred at 50 °C, followed by hot filtration over Na_2SO_4 and solvent removal. The crude product was washed with H_2O (2 × 15 ml) and diethyl ether (2 × 20 ml) and dried *in vacuo*, to yield colourless, microcrystalline material (0.45 g, 53%).

M. p. 179 °C (dec.). – $C_{36}H_{32}Au_2N_{10}P_2$ (1060.60): calcd. C 40.77, H 3.04, N 13.21; found C 40.57, H 3.00, N 12.97. – IR (KBr): ν = 3319, 3166 (N-H), 1633 (N-H), 1595 (C=N), 1553, 1462, 1436, 1393, 1193, 1104, 692 cm^{-1}. – ^1H NMR (300 MHz, MeOH-d_4): δ = 8.07 (s, 2H, H2), 7.86 (m, 8H, C_6H_5-*meta*), 7.71 (s, 2H, H8), 7.52 (m, 12H, C_6H_5-*para*, -*ortho*), 3.09 (d, 4H, ^2J = 9.4 Hz, P-(CH_2)$_2$-P). – ^{13}C NMR (75 MHz, MeOH-d_4): δ = 157.9 (s, C4), 156.8 (s, C6), 152.0 (s, C2), 150.0 (s, C8), 135.0 (t, ^3J = 6.7 Hz, C_6H_5-*meta*), 133.9 (s, C_6H_5-*para*), 130.9 (t, ^2J = 5.5 Hz, C_6H_5-*ortho*), 130.1 (d, ^1J = 60.9 Hz, C_6H_5-*ipso*), 120.6 (s, C5),

23.5 (m, P-(CH_2)$_2$-P). – ^{31}P NMR (121 MHz, MeOH-d_4): $\delta = 28.2$. – ESI-MS (MeOH): m/z = [M^+-$C_5H_4N_5$] calcd. for $C_{31}H_{28}Au_2N_4P_2$ 926, found 926.

*(μ-1,2-Bis(dimethylphosphine)ethane)bis(9H-purin-6-ylamine-9-ate)gold(I) (**6**)*

Complex **6** was obtained in a similar fashion to **4** from NaOH (65 mg, 1.6 mmol), purin-6-ylamine (0.22 g, 1.6 mmol) and (μ-1,2-bis(dimethylphosphine)ethane) bis(chlorogold) (0.50 g, 0.81 mmol) in DME (20 ml). The mixture was stirred for 1.5 h at 45 °C and reduced to dryness *in vacuo*. After treatment with methanol (30 ml) at 45 °C, hot filtration over Na_2SO_4 and solvent removal the residue was treated with *n*-pentane (15 ml) and dried *in vacuo*, to yield colourless, microcrystalline material (0.61 g, 92%), contaminated with NaCl.

M. p. 165 °C (dec.). – $C_{16}H_{24}Au_2N_{10}P_2$.1.8NaCl.1.1C$H_3$OH (952.76): calcd. C 21.56, H 3.00, N 14.70; found C 21.40, H 3.08, N 14.91. – IR (KBr): $\nu = 3280$ (N-H), 2955 (aliphatic C-H), 2880 (aliphatic C-H), 1632 (N-H), 1553, 1460, 1388, 1191, 1135, 952, 801, 654 cm^{-1}. – ^{1}H NMR (300 MHz, MeOH-d_4): $\delta = 8.08$ (s, 2H, H2), 7.69 (s, 2H, H8), 2.41 (d, 4H, $^2J = 9.1$ Hz, P-(CH_2)$_2$-P), 1.90 (d, 12H, $^2J = 11.1$ Hz, CH_3). – ^{13}C NMR (75 MHz, MeOH-d_4): $\delta = 157.4$ (s, C4), 156.8 (s, C6), 152.0 (s, C2), 149.5 (s, C8), 120.4 (s, C5), 24.4 (m, P-(CH_2)$_2$-P), 13.4 (m, CH_3). – ^{31}P NMR (121 MHz, MeOH-d_4): $\delta = 0.2$. – ESI-MS (MeOH): m/z = [MH^+-$C_5H_4N_5$] calcd. for $C_{11}H_{21}Au_2N_5P_2$ 679, found 679.

*(μ-1,3-Bis(diphenylphosphine)propane)bis(9H-purin-6-ylamine-9-ate)gold(I) (**7**)*

Compound **7** was prepared by the same method as complex **4** from NaOH (0.07 g, 1.8 mmol), purin-6-ylamine (0.23 g, 0.85 mmol) and (μ-1,3-bis(diphenylphosphine)propane)bis(chlorogold) (0.75 g, 0.85 mmol) in DME (30 ml) and stirred for 1 h at 45 °C, followed by filtration. The filtrate was reduced to dryness *in vacuo*. After addition of methanol (30 ml) to the residue, the mixture was stirred for 15 min at 45 °C, followed by hot filtration over Na_2SO_4 and solvent removal. The crude product was washed with H_2O (2×15 ml) and diethyl ether (2×20 ml) and evaporated to dryness *in vacuo*, to yield colourless, microcrystalline material (0.48 g, 53%).

M. p. 224 °C (dec.). – $C_{37}H_{34}Au_2N_{10}P_2$.0.1$CH_3OH$ (1077.83): calcd. C 41.34, H 3.22, N 13.00; found C 41.55, H 2.98, N 13.24. – IR (KBr): $\nu = 3325$, 3190 (N-H), 1633 (N-H), 1595 (C=N), 1554, 1462, 1436, 1393, 1196, 1104, 692 cm^{-1}. – ^{1}H NMR (300 MHz, MeOH-d_4): $\delta =$ 7.99 (s, 2H, H2), 7.74 (m, 10H, H8, C_6H_5-*meta*), 7.49 (m, 4H, C_6H_5-*para*), 7.42 (m, 8H, C_6H_5-*ortho*), 3.18 (m, 4H, P-CH_2CH$_2$CH_2-P), 2.06 (m, 2H, P-CH$_2$CH_2CH$_2$-P). – ^{13}C NMR (75 MHz, MeOH-d_4): $\delta = 158.8$ (s, C4), 156.7 (s, C6), 151.7 (s, C2), 150.8 (s, C8), 134.8 (d, $^3J = 12.8$ Hz, C_6H_5-*meta*), 133.5 (d, $^4J = 1.3$ Hz, C_6H_5-*para*), 130.7 (d, $^2J = 11.6$ Hz, C_6H_5-*ortho*), 129.8 (s, C_6H_5-*ipso*), 120.8 (s, C5), 27.6 (dd, $^1J = 38.0$ Hz, $^3J = 9.1$ Hz, P-CH_2CH$_2$CH_2-P), 20.7 (bs, P-CH$_2$CH_2CH$_2$-P). – ^{31}P NMR (121 MHz, MeOH-d_4): $\delta = 25.0$. – ESI-MS (MeOH): m/z = [M^+-$C_5H_4N_5$-H] calcd. for $C_{32}H_{29}Au_2N_5P_2$ 940, found 940.

*(μ-1,5-Bis(diphenylphosphine)pentane)bis(9H-purin-6-ylamine-9-ate)gold(I) (**8**)*

The same method as described above was used to prepare **8** from NaOH (64 mg, 1.6 mmol), purin-6-ylamine (0.22 g, 1.6 mmol) and (μ-1,5-bis(diphenylphosphine)pentane)bis(chlorogold) (0.72 g, 0.8 mmol) in DME (30 ml). The mixture was stirred for 1 h at 50 °C, filtered and the remaining precipitate was washed with DME (10 ml), CH_2Cl_2 (2×30 ml), H_2O (2×40 ml) and MeOH (30 ml) to remove unreacted material as well as side products. After the addition of diethyl ether (3×30 ml) to the residue, the filtrate was dried *in vacuo* to give a colourless, microcrystalline product (0.37 g, 42%).

M. p. 170 – 175 °C. – $C_{39}H_{38}Au_2N_{10}P_2$ (1102.68): calcd. C 42.48, H 3.47, N 12.70; found C 42.18, H 3.63, N 12.31. – IR (KBr): $\nu = 3456$, 3307, 3152 (N-H), 1640 (C=O), 1590 (N-H), 1551 (C=N), 1463, 1436, 1391, 1198, 1107, 977, 748, 693 cm^{-1}. – ^{1}H NMR (300 MHz, CD_2Cl_2/MeOH-d_4): $\delta = 8.07$ (s, 2H, H2), 7.84 (s, 2H, H8), 7.69 (m, 8H, C_6H_5-*meta*), 7.47 (m, 12H, C_6H_5-*para*, -*ortho*), 2.54 (m, 4H, P-CH_2(CH$_2$)$_3$CH_2-P), 1.73 (m, 6H, P-CH$_2$(CH_2)$_3$CH$_2$-P). – ^{13}C NMR (75 MHz, CD_2Cl_2/MeOH-d_4): $\delta = 160.0$ (s, C4), 156.1 (s, C6), 151.6 (s, C2), 149.3 (bs, C8), 134.0 (d, $^3J = 12.2$ Hz, C_6H_5-*meta*), 132.8 (s, C_6H_5-*para*), 130.1 (d, $^2J = 11.0$ Hz, C_6H_5-*ortho*), 129.8 (d, $^1J = 60.3$ Hz, C_6H_5-*ipso*), 119.9 (s, C5), 31.5 (t, $^3J = 14.6$ Hz P-CH$_2$CH$_2$CH$_2$CH_2CH$_2$-P), 27.1 (d, $^1J =$ 37.8 Hz, P-CH_2(CH$_2$)$_3$CH_2-P), 25.1 (P-(CH$_2$)$_2$CH_2(CH$_2$)$_2$-P). – ^{31}P NMR (121 MHz, CD_2Cl_2/MeOH-d_4): $\delta = 28.4$. – ESI-MS (MeOH/CH_2Cl_2, 50%): m/z = [M^+-$C_5H_4N_5$-H] calcd. for $C_{34}H_{33}Au_2N_5P_2$ 968, found 968.

*Triphenylphosphine(9H-purin-9-ate)gold(I) (**9**)*

Complex **9** was prepared in the same fashion as detailed above from NaOH (0.04 g, 1.0 mmol), purine (0.12 g, 1.0 mmol) and (triphenylphosphine)gold chloride (0.50 g, 1.0 mmol) in DME (20 ml). The mixture was stirred for 1 h at 45 °C and reduced to dryness *in vacuo*. After treatment with H_2O (20 ml) for 10 min at 45 °C and hot filtration, the filtrate was washed with H_2O (2×10 ml) and diethyl ether (2×15 ml) and dried *in vacuo*. The residue was treated with methanol (20 ml), filtered and, after solvent removal, the colourless product (0.43 g, 80%) was dried *in vacuo*.

M. p. 235 – 237 °C. – $C_{23}H_{18}AuN_4$P.1.0CH_3OH (610.41): calcd. C 47.23, H 3.63, N 9.18; found C 46.85, H 3.25,

N 9.31. – IR (KBr): ν = 3376, 3282 (N-H), 3072 (aromatic C-H), 1590 (C=N), 1551, 1464, 1434, 1393, 1181, 1098, 747 cm^{-1}. – ^1H NMR (600 MHz, CD_2Cl_2): $\delta = 9.02$ (s, 1H, H6), 8.82 (s, 1H, H2), 8.14 (s, 1H, H8), 7.65 (m, 6H, C_6H_5-*meta*), 7.60 (m, 3H, C_6H_5-*para*), 7.55 (m, 6H, C_6H_5-*ortho*). – ^{13}C NMR (151 MHz, CD_2Cl_2): $\delta = 160.4$ (s, C4), 154.1 (s, C2), 151.5 (s, C8), 146.0 (s, C6), 134.6 (d, $^3J = 13.4$ Hz, C_6H_5-*meta*, C5), 132.6 (d, $^4J = 2.4$ Hz, C_6H_5-*para*), 129.8 (d, $^2J = 12.2$ Hz, C_6H_5-*ortho*), 128.8 (d, $^1J = 62.9$ Hz, C_6H_5-*ipso*). – ^{31}P NMR (121 MHz, CD_2Cl_2): $\delta = 32.4$. – ESI-MS (CH_2Cl_2): m/z = [M^+-H] calcd. for $C_{23}H_{17}AuN_4P$ 538, found 538; [$((C_6H_5)_3P)_2$Au-H] calcd. for $C_{36}H_{29}AuP_2$ 721, found 721; [M^++AuP(C_6H_5)$_3$-H] calcd. for $C_{41}H_{32}Au_2N_4P_2$ 1037, found 1037.

*Trimethylphosphine(9H-purin-9-ate)gold(I) (**10**)*

Compound **10** was prepared in the same manner as **1** from NaOH (0.04 g, 1.0 mmol), purine (0.12 g, 1.0 mmol) and (trimethylphosphine)gold chloride (0.31 g, 1.0 mmol) in methanol (20 ml). The mixture was stirred for 1 h at room temperature and reduced to dryness *in vacuo*. After treatment with CH_2Cl_2 (30 ml), filtration over Na_2SO_4 and solvent removal the colourless product (0.33 g, 84%) was dried *in vacuo*.

M. p. 155 – 160 °C. – $C_8H_{12}AuN_4P$ (392.15): calcd. C 24.50, H 3.08, N 14.29; found C 24.65, H 3.20, N 13.92. – IR (KBr): ν = 2986 (aliphatic C-H), 2955 (aliphatic C-H), 2875 (aliphatic C-H), 1589 (C=N), 1551, 1461, 1391, 1172, 1103, 969, 650 cm^{-1}. – ^1H NMR (600 MHz, MeOH-d_4): $\delta = 8.98$ (s, 1H, H6), 8.76 (s, 1H, H2), 8.26 (s, 1H, H8), 1.69 (d, 9H, $^2J = 11.2$ Hz, CH_3). – ^{13}C NMR (151 MHz, MeOH-d_4): $\delta = 160.8$ (s, C4), 156.1 (s, C2), 151.4 (s, C8), 146.0 (m, C6), 135.2 (s, C5), 15.2 (d, ^1J = 42.1 Hz, CH_3). – ^{31}P NMR (243 MHz, MeOH-d_4): δ = −9.0. – ^1H detected ^1H,^{15}N gHMQC (61 MHz, MeOH-d_4): δ = −122.4 (s, N1), −132.6 (s, N3). – MS (EI, 70 eV): m/z (%) = 392 (3) [M^+], 273 (6) [M-$C_5H_5N_4$], 120 (100) [$C_5H_5N_4$], 76 (42) [$P(CH_3)_3$], 61 (58) [$P(CH_3)_2$]. – ESI-MS (MeOH/CH_2Cl_2, 50%): m/z = [$((CH_3)_3P)_2$Au] calcd. for $C_6H_{18}AuP_2$ 349, found 349; [M^+] calcd. for $C_8H_{12}AuN_4P$ 392, found 392; [M^++AuP(CH_3)$_3$] calcd. for $C_{11}H_{22}Au_2N_4P_2$ 666, found 666.

*Tributylphosphine(9H-purin-9-ate)gold(I) (**11**)*

Complex **11** was prepared in a similar fashion to **1** from NaOH (0.06 g, 1.5 mmol), purine (0.18 g, 1.5 mmol) and (tributylphosphine)gold chloride (0.64 g, 1.5 mmol) in methanol (11 ml). The mixture was stirred for 2 h at room temperature and reduced to dryness *in vacuo*. After the addition of CH_2Cl_2 (30 ml) to the residue, filtration over Na_2SO_4 and solvent removal, the colourless product (0.16 g, 21%) was dried *in vacuo*.

M. p. 79 – 80 °C. – $C_{17}H_{30}AuN_4P$ (518.40): calcd. C 39.39, H 5.83, N 10.81; found C 39.42, H 5.56, N 10.67. – IR (KBr): ν = 3076, 3034 (N-H), 2956 (aliphatic C-H), 2926 (aliphatic C-H), 2869 (aliphatic C-H), 1584 (C=N), 1552, 1464, 1387, 1194, 1177, 1096, 902, 787, 652, 482 cm^{-1}. – ^1H NMR (300 MHz, CD_2Cl_2): $\delta = 9.00$ (s, 1H, H6), 8.80 (s, 1H, H2), 8.06 (s, 2H, H8), 1.91 (m, 6H, P-C*H*$_2$CH$_2$CH$_2$CH$_3$), 1.64 (m, 6H, P-CH$_2$C*H*$_2$CH$_2$CH$_3$), 1.52 (m, 6H, P-CH$_2$CH$_2$C*H*$_2$CH$_3$), 0.95 (t, 9H, $^3J = 7.17$ Hz, P-CH$_2$CH$_2$CH$_2$C*H*$_3$). – ^{13}C NMR (75 MHz, CD_2Cl_2): $\delta = 160.7$ (s, C4), 154.4 (s, C2), 151.7 (s, C8), 146.0 (s, C6), 134.9 (s, C5), 27.6 (s, P-CH$_2$*C*H$_2$CH$_2$CH$_3$), 25.2 (d, $^1J = 37.2$ Hz, P-*C*H$_2$CH$_2$CH$_2$CH$_3$), 24.3 (d, $^3J = 14.6$ Hz, P-CH$_2$CH$_2$*C*H$_2$CH$_3$), 13.6 (s, P-CH$_2$CH$_2$CH$_2$*C*H$_3$). – ^{31}P NMR (121 MHz, CD_2Cl_2): $\delta = 20.0$. – ESI-MS (MeOH): m/z = [MH^+] calcd. for $C_{17}H_{31}AuN_4P$ 519, found 519, [$((C_4H_9)_3P)_2$Au-H] calcd. for $C_{24}H_{53}AuP_2$ 601, found 601; [M^++AuP(C_4H_9)$_3$-H] calcd. for $C_{29}H_{56}Au_2N_4P_2$ 917, found 917.

*Trimethylphosphine(9H-purin-6-ylamine-9-ate)gold(I) (**12**)*

Compound **12** was prepared in the same manner as **4** from NaOH (42 mg, 1.1 mmol), purin-6-ylamine (0.10 g, 1.0 mmol) and (trimethylposphine)gold chloride (0.32 g, 1.0 mmol) in THF (20 ml). The mixture was stirred for 2 h at 50 °C and reduced to dryness *in vacuo*. After the addition of methanol (20 ml) to the residue and filtration over Na_2SO_4, the solvent was reduced to dryness *in vacuo*. The product was treated with CH_2Cl_2 (60 ml) for 30 min at 30 °C followed by filtration over Na_2SO_4. Solvent was removed and the residue was dried *in vacuo* to give a colourless product (0.42 g, 99%).

M. p. 163 °C (dec.). – $C_8H_{13}AuN_5P$ (407.17): calcd. C 23.60, H 3.22, N 17.20; found C 23.82, H 3.19, N 17.52. – IR (KBr): ν = 3258, 3092 (N-H), 2898 (aliphatic C-H), 2704, 1674 (C=O), 1698 (N-H), 1543 (C=N), 1459, 1391, 1319, 1195, 1032, 962, 801, 747, 680 cm^{-1}. – ^1H NMR (300 MHz, MeOH-d_4): $\delta = 8.11$ (s, 1H, H2), 7.85 (s, 1H, H8), 1.69 (d, 9H, $^2J = 11.8$ Hz, CH_3). – ^{13}C NMR (75 MHz, MeOH-d_4): $\delta = 158.3$ (s, C4), 157.1 (s, C6), 152.0 (s, C2), 150.3 (s, C8), 120.6 (s, C5), 14.9 (d, $^1J = 41.4$ Hz, CH_3). – ^{31}P NMR (121 MHz, MeOH-d_4): $\delta = -8.7$. – ESI-MS (MeOH/CH_2Cl_2, 50%): m/z = [$((CH_3)_3P)_2$Au] calcd. for $C_6H_{18}AuP_2$ 349, found 349; [MH^+] calcd. for $C_8H_{14}AuN_5P$ 408, found 408; [M^++$(CH_3)_3$PAu] calcd. for $C_{11}H_{22}Au_2N_5P_2$ 680, found 680.

*Tributylphosphine(9H-purin-6-ylamine-9-ate)gold(I) (**13**)*

The same method as described above was used to prepare **13** from NaOH (29 mg, 0.7 mmol), purin-6-ylamine (0.10 g, 0.7 mmol) and (tributylphosphine)gold chloride (0.32 g, 0.7 mmol) in DME (20 ml). The mixture was stirred for 1 h at 45 °C and reduced to dryness *in vacuo*. After the addition of H_2O (50 ml) to the residue, filtration, and washing with H_2O

(20 ml) and diethyl ether (3 × 11 ml), the colourless product (0.25 g, 60%) was dried *in vacuo*.

M. p. 102 °C (dec.). – $C_{17}H_{31}AuN_5P$ (533.41): calcd. C 38.28, H 5.86, N 13.13; found C 37.97, H 5.56, N 13.23. – IR (KBr): ν = 3305, 3126 (N-H), 2953, 2926, 2868, 2706 (aliphatic C-H), 1670 (C=O), 1596 (N-H), 1548 (C=N), 1461, 1393, 1316, 1194, 1039, 905, 802, 724, 656 cm^{-1}. – ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 8.19 (s, 1H, H2), 7.73 (s, 1H, H8), 5.70 (s, 2H, NH_2), 1.86 (m, 6H, P-CH_2CH$_2$CH$_2$CH$_3$), 1.61 (m, 6H, P-CH$_2$CH_2CH$_2$CH$_3$), 1.51 (m, 6H, P-CH$_2$CH$_2$CH_2CH$_3$), 0.94 (t, 9H, ^3J = 7.1 Hz, P-CH$_2$CH$_2$CH$_2$CH_3). – ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 158.9 (s, C4), 155.7 (s, C6), 151.6 (s, C2), 149.1 (s, C8), 120.7 (s, C5), 27.5 (s, P-CH$_2$CH_2CH$_2$CH$_3$), 25.2 (d, ^1J = 36.7 Hz, P-CH_2CH$_2$CH$_2$CH$_3$), 24.3 (d, ^3J = 10.7 Hz, P-CH$_2$CH$_2$CH_2CH$_3$), 13.6 (s, P-CH$_2$CH$_2$CH$_2$CH_3). – ^{31}P NMR (121 MHz, CD_2Cl_2): δ = 20.1. – ^{1}H detected ^{1}H,^{15}N gHMQC (61 MHz, CD_2Cl_2/MeOH-d_4): δ = −144.5 (s, N3), −147.0 (s, N7), −150.3 (s, N1), −174.2 (s, N9), −311.9 (s, N10). – ESI-MS (MeOH/CH_2Cl_2, 50%): m/z = [M$^+$] calcd. for $C_{17}H_{31}AuN_5P$ 533, found 533; [((C$_4$H$_9$)$_3$P)$_2$Au] calcd. for $C_{24}H_{54}AuP_2$ 602, found 602.

X-ray crystal structure determinations

Single crystals of **1** and **9** suitable for X-ray analysis, were obtained by slow crystallisation from methanol/diethyl ether at −30 °C; those of **3** and **11** from dichloromethane and **7** from methanol. A Bruker SMART Apex diffractometer [25–27] with graphite monochromated Mo-K$_\alpha$ radiation (λ = 0.71073 Å) was used to collect intensity data. Intensities were measured using the ω-scan mode and corrected for Lorentz and polarisation effects. All structures were solved by direct methods and refined by full matrix least squares on F^2 using the SHELXL-97 program package [28] and X-seed [29, 30]. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in calculated positions. Figures were generated with X-seed [30], (displacement ellipsoids are at the 50% probability level). Hydrogen atoms and solvent molecules were omitted for clarity.

Crystal data for **1***:* $C_{36}H_{30}Au_2N_8P_2$, M = 1030.55, colourless cube, 0.10 × 0.12 × 0.08 mm^3, monoclinic, space group $C2/c$ (No. 15), a = 15.4448(10), b = 19.9492(13), c = 11.1836(7) Å, β = 106.9670(10)°, V = 3295.8(4) Å^3, Z = 4, D_c = 2.077 g/cm^3, F_{000} = 1960, T = 273(2) K, $2\theta_{max}$ = 56.5°, 10294 reflections collected, 3801 unique (R_{int} = 0.0352). Final *GooF* = 0.991, $R1$ = 0.0327, $wR2$ = 0.0695, R indices based on 3236 reflections with $I > 2\sigma(I)$ (refinement on F^2), 217 parameters, 0 restraints, μ = 9.031 mm^{-1}.

Crystal data for **3***:* $C_{37}H_{32}Au_2N_8P_2$, M = 1044.58, colourless cube, 0.20 × 0.15 × 0.10 mm^3, monoclinic, space group $P2_1/n$ (No. 14), a = 11.473(6), b = 18.097(9), c = 17.462(9) Å, β = 103.979(9)°, V = 3518(3) Å^3, Z = 4, D_c = 1.972 g/cm^3, F_{000} = 1992, T = 273(2) K, $2\theta_{max}$ = 56.7°, 21292 reflections collected, 8066 unique (R_{int} = 0.0578). Final *GooF* = 0.951, $R1$ = 0.0564, $wR2$ = 0.1373, R indices based on 6584 reflections with $I > 2\sigma(I)$ (refinement on F^2), 443 parameters, 0 restraints, μ = 8.461 mm^{-1}.

Crystal data for **7***:* $C_{43}H_{58}Au_2N_{10}O_6P_2$, M = 1266.87, colourless cube, 0.3 × 0.2 × 0.1 mm^3, triclinic, space group $P\bar{1}$ (No. 2), a = 13.7375(14), b = 13.8501(14), c = 14.1405(15) Å, α = 105.856(2), β = 103.057(2), γ = 97.354(2)°, V = 2469.0(4) Å^3, Z = 2, D_c = 1.704 g/cm^3, F_{000} = 1244, T = 273(2) K, $2\theta_{max}$ = 56.6°, 28316 reflections collected, 11294 unique (R_{int} = 0.0224). Final *GooF* = 1.045, $R1$ = 0.0328, $wR2$ = 0.0822, R indices based on 10297 reflections with $I > 2\sigma(I)$ (refinement on F^2), 597 parameters, 0 restraints, μ = 6.055 mm^{-1}.

Crystal data for **9***:* $C_{25}H_{26}AuN_4O_2P$, M = 642.43, colourless cube, 0.2 × 0.18 × 0.1 mm^3, triclinic, space group $P\bar{1}$ (No. 2), a = 9.0338(9), b = 11.8382(11), c = 13.0714(13) Å, α = 97.746(2), β = 107.9950(10), γ = 111.1330(10)°, V = 1191.4(2) Å^3, Z = 2, D_c = 1.791 g/cm^3, F_{000} = 628, T = 100(2) K, $2\theta_{max}$ = 56.5°, 13688 reflections collected, 5470 unique (R_{int} = 0.0226). Final *GooF* = 0.739, $R1$ = 0.0271, $wR2$ = 0.0817, R indices based on 5208 reflections with $I > 2\sigma(I)$ (refinement on F^2), 305 parameters, 2 restraints, μ = 6.271 mm^{-1}.

Crystal data for **11***:* $C_{17}H_{30}AuN_4P$, M = 518.39, colourless cube, 0.20 × 0.20 × 0.15 mm^3, triclinic, space group $P\bar{1}$ (No. 2), a = 15.3118(18), b = 15.5609(18), c = 18.467(2) Å, α = 106.099(2), β = 105.031(2), γ = 98.973(2)°, V = 3957.9(8) Å^3, Z = 8, D_c = 1.740 g/cm^3, F_{000} = 2032, T = 100(2) K, $2\theta_{max}$ = 56.8°, 45658 reflections collected, 18205 unique (R_{int} = 0.0644). Final *GooF* = 1.019, $R1$ = 0.0674, $wR2$ = 0.1498, R indices based on 11786 reflections with $I > 2\sigma(I)$ (refinement on F^2), 826 parameters, 17 restraints, μ = 7.520 mm^{-1}.

Crystallographic data for the structures have been deposited with the Cambridge Crystallographic Data Centre, CCDC 250917 - 250921. 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+(1223)336-033; e-mail for inquiry: fileserv@ccdc.cam.ac.uk).

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