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Gold(I) complexes with heteroaryl phosphine ligands

Christian Sarcher, Saeid Farsadpour, Leila Taghizadeh Ghoochany, Yu Sun, Werner Thiel* and Peter W. Roesky*

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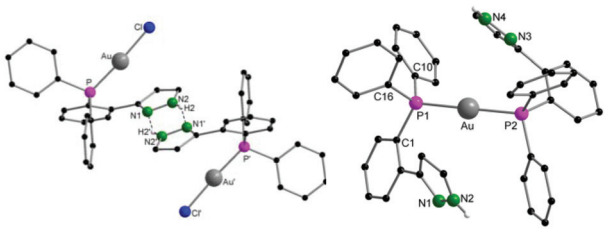

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Dalton Transactions

PAPER

Gold(I) complexes with heteroaryl phosphine ligands†

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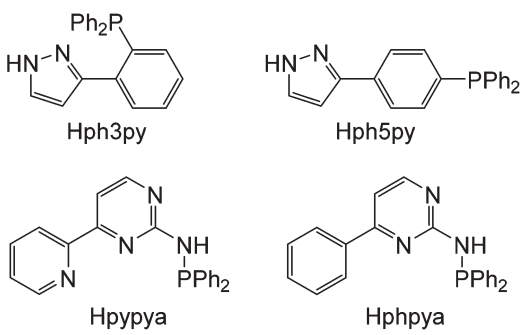
Gold(I) complexes ligated by phosphines with *N*-heterocycles in the periphery were prepared. First the synthesis of the ligands *N*-(diphenylphosphino)-4-(pyridin-2-yl)pyrimidin-2-amine (Hpypya) and *N*-(diphenylphosphino)-4-phenylpyrimidin-2-amine (Hphpya) are reported. These two compounds together with the earlier published related ligands 3-(2-(diphenylphosphino)phenyl)-1*H*-pyrazole (Hph3py) and 5-(4-(diphenylphosphino)phenyl)-1*H*-pyrazole (Hph5py) were reacted with [(tht)AuCl] and $[Au(tht)_2]ClO_4$ to give the heteroleptic complexes [(L)AuCl] and the homoleptic compounds $[(L)_2Au]ClO_4$ (L = Hpypya, Hphpya, Hph3py, and Hph5py). Single crystal X-ray diffraction studies revealed that the heteroleptic complexes form hydrogen bonds between two *N*-heterocycles of neighboring complexes resulting in dimeric structures. The homoleptic complexes show different behavior.

Introduction

The chemistry of gold is currently one of the emerging fields in chemistry.[1–6] This area which covers the synthesis and application of gold and gold compounds in synthesis,[7–13] materials and surface sciences,[14–18] for biological applications,[19,20] in heterogeneous[21–25] and especially in homogeneous catalysis[26–30] was summarized in a number of reviews dealing with various topics of gold chemistry. Molecular gold(I) compounds with a closed shell d^{10} electronic configuration are in most cases two-fold coordinated in a linear manner. However, there are also gold(I) complexes possessing higher coordination numbers, although they are less common. According to Pearson's HSAB concept,[31] the gold(I) ion is usually considered as a soft metal ion preferring coordination by soft ligands such as phosphines, organic sulphur ligands, and N-heterocyclic carbenes (NHC). Although known for quite a long time,[32] gold(I) complexes with P,N ligands having a hard as well as a soft donor function have recently attracted attention.[33–40] These types of compounds were investigated closer in terms of their structural properties,[34,39,40] their catalytic behavior,[36–38] and their luminescence properties.[33,35] In catalysis P,N-ligands can act as hemilabile ligands.

Some of us have been working for some time on phosphine ligands having an *N*-heterocycle bound to the phosphorus center.[41–43] The *N*-heterocycle decreases the electron-density at the phosphorus atom. For square planar coordinate group 10 complexes these compounds may act as chelating ligands coordinating *via* the P and one N atom to the metal atom.[41] In the case of N–H functions being present on the ligand scaffold, the formation of intramolecular hydrogen bonds may also result in dimeric or polymeric structures.

Herein we report on two new phosphines with *N*-heterocycles in the periphery: *N*-(diphenylphosphino)-4-(pyridin-2-yl)-pyrimidin-2-amine (Hpypya) and *N*-(diphenylphosphino)-4-phenylpyrimidin-2-amine (Hphpya) (Scheme 1), which we used to prepare gold(I) complexes. Additionally the earlier published and structurally related ligands 3-(2-(diphenylphosphino)-phenyl)-1*H*-pyrazole (Hph3py)[41] and 5-(4-(diphenylphosphino)-phenyl)-1*H*-pyrazole (Hph5py)[43] (Scheme 1) were utilized for the synthesis of gold(I) complexes, too.



Scheme 1

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†Electronic supplementary information (ESI) available. CCDC 960836–960840. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt52893f

Results and discussion

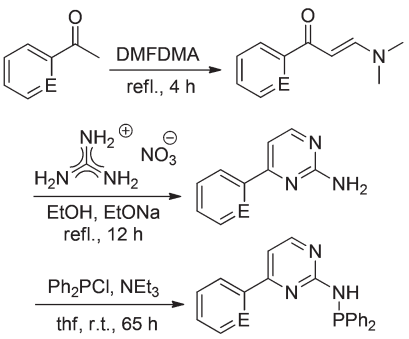
Ligand synthesis

The ligands Hpypya and Hphpya are available in three steps from versatile 2-acetylpyridine and acetophenon, respectively (Scheme 2). Condensation of arylmethylketones with *N*,*N*-dimethylformamidedimethylacetal (DMFDMA) gave the corresponding 1-aryl-3-dimethylaminoprop-2-en-1-ones,[44] which underwent ring closure to 2-amino-4-arylpyrimidines when reacted with guanidinium salts under basic conditions.[45]

Subsequent P–N bond formation with Ph_2PCl in the presence of triethylamine (NEt_3) gave the desired ligands Hpypya and Hphpya. They show $^{31}P\{^1H\}$ NMR resonances at about 24–30 ppm (Table 1) as expected for R_2P-N units. The resonance of the N–H unit appears at about 8.3 ppm in the ^1H NMR spectra of Hpypya and Hphpya, thus being shifted to a lower field compared to the signal of the amino substituent in the precursors. Recrystallization of Hphpya from a mixture of ethanol and *n*-pentane led to single crystals suitable for an X-ray structure analysis. As for pyrazoles, aminopyrimidines contain both a proton donating and a proton accepting site that allows the formation of intermolecular hydrogen bonds leading to the formation of dimers in the solid state (Fig. 1). The N–H···N bond distances are in the typical range of hydrogen bonds between aminopyrimidines.

Metal complex synthesis

Reaction of the four phosphine ligands Hpypya, Hphpya, Hph3py, and Hph5py bearing N-heterocycles in the periphery with [(tht)AuCl] (tht = tetrahydrothiophene) in CH_2Cl_2 gave the corresponding heteroleptic gold(I) complexes[(Hph3py)(AuCl)] (**1**), [(Hph5py)(AuCl)] (**2**), [(Hpypya)(AuCl)] (**2**) and [(Hphpya)-(AuCl)] (**4**) (Scheme 3).



Scheme 2 Synthesis of the ligands Hpypya and Hphpya.

Table 1 $^{31}P\{^1H\}$ NMR data of **1–4** in comparison to the non-coordinated ligand

Ligand	Non-coordinated ligand $\delta(^{31}P\{^1H\})$ [ppm]	[(L)AuCl] $\delta(^{31}P\{^1H\})$ [ppm]
Hph3py	−10.5	28.4
Hph5py	−5.7	32.7
Hpypya	29.7	55.6
Hphpya	24.7	57.2

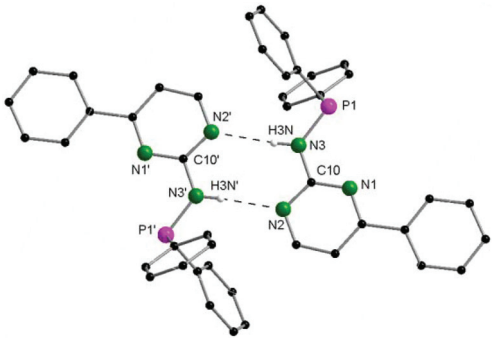
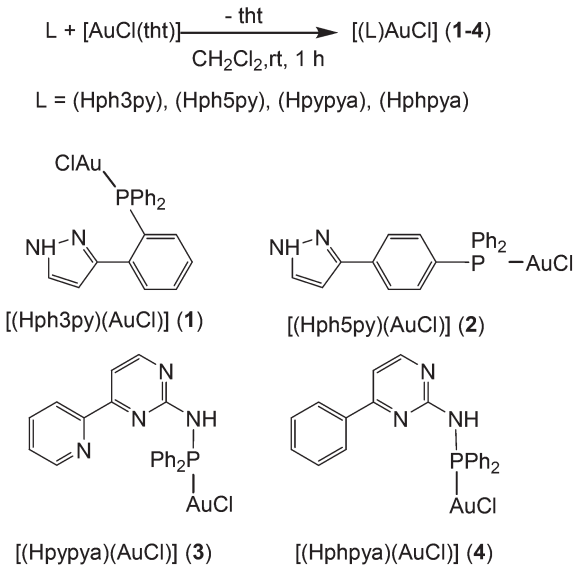


Fig. 1 Dimeric solid-state structure of Hphpya, which is formed by two hydrogen bonds, omitting all carbon bound hydrogen atoms. Selected bond lengths [Å] and angles [°]: P1–N3 1.7148(12), N3–H3N 0.863(14), H3N···N2 2.18, N3···N2 3.038(4), N3–H3N···N2 175.4(15).

Compounds **1–4** were characterized by standard analytic/spectroscopic techniques and the solid state structures of **1**, **3**, and **4** could be established by single crystal X-ray diffraction. In the ^1H NMR spectra the expected sets of signals are observed mostly down-field shifted and often broadened in comparison to the non-coordinated ligand. In contrast the $^{31}P\{^1H\}$ NMR spectra of **1–4** show a very characteristic down-field shift of about 25–40 ppm in comparison to the non-coordinated ligands (Table 1).

In FAB-MS the molecular peaks for **1**, **3**, and **4** were observed at m/z = 560 (**1**), 589 (**3**), and 588 amu (**4**), respectively. For all compounds the cationic species $[M - Cl]^+$ was detected at m/z = 525 (**1**), 525 (**2**), 554 (**3**) and 552 amu (**4**).

Single crystals of **1**, **3**, and **4** were obtained by slow diffusion of *n*-pentane in saturated CH_2Cl_2 solutions of the



Scheme 3 Synthesis of the gold(I) chloride complexes **1–4**.

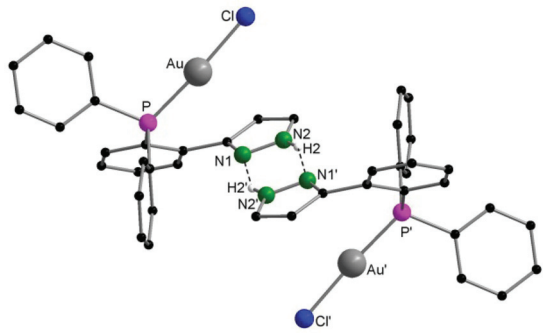


Fig. 2 Dimeric solid-state structure of **1**, which is formed by two hydrogen bonds, omitting all carbon bound hydrogen atoms. Selected bond lengths [Å] and angles [°]: Au–Cl 2.2768(13), Au–P 2.2347(11), P–C1 1.830(5), P–C10 1.820(4), P–C16 1.820(4), N1–N2 1.360(5); P–Au–Cl 174.34(5), Au–P–C1 112.47(15), Au–P–C10 118.70(15), Au–P–C16 110.25(15), C1–P–C10 106.3(2); N2–H2 0.77(6), N1′–H2 2.19(5), N2–N1′ 2.887(5); N1–H1–N2′ 152(5).

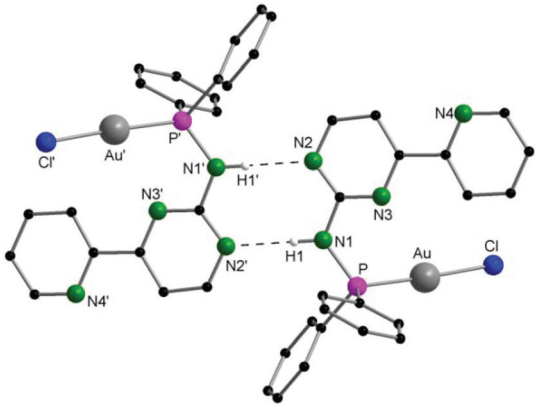


Fig. 3 Dimeric solid-state structure of **3**, which is formed by two hydrogen bonds, omitting all carbon bound hydrogen atoms and the cocrystallized solvent CH_2Cl_2. Selected bond lengths [Å] and angles [°]: Au–Cl 2.2748(11), Au–P 2.2225(10), P–N1 1.689(2), P–C1 1.808(3), P–C7 1.820(3); P–Au–Cl 177.35(3), Au–P–N1 114.05(9), Au–P–C1 114.64(10), Au–P–C7 113.13(9), N1–P–C1 106.47(12), N1–P–C7 100.56(12), C1–P–C7 106.77(13);N1–H1 0.89(4), N2′–H1 2.04(4), N1–N2′ 2.923(3); N1–H1–N2′ 178(3).

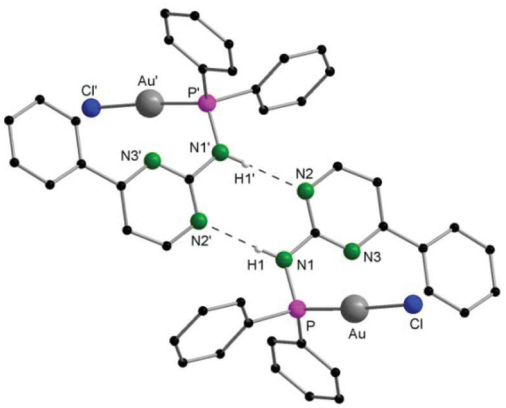


Fig. 4 Dimeric solid-state structure of **4**, which is formed by two hydrogen bonds, omitting all carbon bound hydrogen atoms. Selected bond lengths [Å] and angles [°]: Au–Cl 2.2845(10), Au–P 2.2271(9), P–N1 1.702(3), P–C1 1.816(3), P–C7 1.813(3); P–Au–Cl 176.72(3), Au–P–N1 112.81(10), Au–P–C1 113.25(10), Au–P–C7 114.81(10), N1–P–C1 99.91(13), N1–P–C7 107.15(14), C1–P–C7 107.69(14); N1–H1 0.88(5), N2′–H1 2.09(4), N1–N2′ 2.957(3); N1–H1–N2′ 176(4).

complexes. Compound **1** crystallizes in the monoclinic space group $P2_1/a$ with four molecules of **1** in the unit cell (Fig. 2). All hydrogen atoms could be localized in the difference Fourier map. As expected, the gold atom is almost linearly coordinated with a P–Au–Cl angle of 174.34(5)°. The Au–Cl (2.2768(13) Å) and Au–P bond distances (2.2347(11) Å) are in the range of $[AuCl(PPh_3)]$ (Au–Cl 2.279(3) Å, Au–P 2.235(3) Å, P–Au–Cl 179.68(8)°)[46] and $[AuCl\{P(p\text{-}C_6H_4OMe)_3\}]$ (Au–Cl 2.2885(9) Å, Au–P 2.2333(8) Å, P–Au–Cl 175.94(3)°).[47] The nitrogen atoms of the pyrazole ring are oriented towards the Au atom. As a result of the geometrical restrictions of the ligand there is no interaction of the Au and the N atoms. The closest distance (Au–N1) is 3.127(5) Å. Due to this geometrical setup no aurophilic contacts are observed in the solid state. On the other hand a dimerization is observed by formation of hydrogen bonds. The hydrogen bonds are exhibited between the N2–H2 group of one pyrazole ring with the N1 atom of the pyrazole ring of a neighboring molecule (Fig. 2). As a result a six-membered N1–N2–H2–N1′–N2′–H2′ ring is formed including a crystallographic inversion center in the middle of this ring. The N–H–N bond distances are in the typical range of hydrogen bonds. The N1′–N1 distance is 2.887(5) Å and the N1–H2–N2′ angle 152(2)°. The exhibition of intermolecular hydrogen bonds between pyrazoles including a proton donor and a proton acceptor site in one molecule often results in the generation of hydrogen bonded trimers and tetramers.[48–51] The formation of the dimer found in the solid state structure of compound **1** is quite a rare example.

Both **3** and **4** crystallize in the triclinic space group $P\bar{1}$ with one molecule each in the asymmetric unit. In the solid state structure of compound **3** one additional molecule of CH_2Cl_2 is present in the asymmetric unit (Fig. 3 and 4). All hydrogen atoms could be localized in the difference Fourier maps. Although **3** and **4** are not isomorphs, their molecular structures are very similar in the solid-state differing only in the nitrogen atom of the pyridyl group of **3** which is absent in the phenyl group of **4**. As already observed for **1**, the gold(I) centers are almost linearly coordinated showing P–Au–Cl angles of 177.35(3)° (**3**) and 176.72(3)° (**4**). The Au–Cl (2.2748(11) Å (**3**) and 2.2845(10) Å (**4**)) and Au–P distances (2.2225(10) Å (**3**) and 2.2271(9) Å (**4**)) are found in the expected range.[46,47]

Due to the geometry of the ligands Hph3py and Hph5py, hydrogen bonds are formed between two molecules resulting in dimeric structures. The hydrogen bonds are formed by the exocyclic N1–H1 aminofunction and the endocyclic pyrimidine nitrogen atom N2, resulting in the eight-membered ring structures H1–N1–C–N2–H1′–N1′–C′–N2′ (Fig. 3 and 4) with an inversion center in the middle of these rings. The distances

between nitrogen atoms N1 and N2′ of the symmetry equivalent molecules are 2.923(3) Å (**3**) and 2.957(3) Å (**4**). As expected, the hydrogen bonds are almost linear showing angles of N1–H1–N2 178(3)° and 176(4)°.

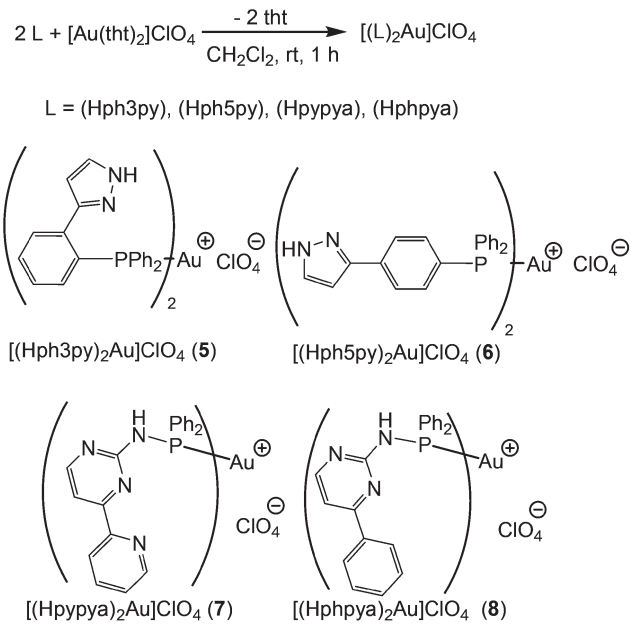
To obtain homoleptic complexes, the four phosphine ligands Hph3py, Hph5py, Hpypya, and Hphpya with N-heterocycles in the periphery were reacted with $[Au(tht)_2]ClO_4$ in CH_2Cl_2 at room temperature to obtain $[(Hph3py)_2Au]ClO_4$ (**5**), $[(Hph5py)_2Au]ClO_4$ (**6**) $[(Hpypya)_2Au]ClO_4$ (**7**), and $[(Hphpya)_2Au]ClO_4$ (**8**) (Scheme 4).

As already mentioned for compounds **1–4**, the ^1H NMR spectra of **5–8** do not show very characteristic but broad signals. Most of the signals are slightly shifted to lower field in comparison to the non-coordinated ligands. As a result of the coordination to the gold(I) cation the $^{31}P\{^1H\}$ NMR signals of **5–8** are shifted more than 10 ppm towards lower field compared to the heteroleptic compounds **1–4** ($\delta(^{31}P\{^1H\})$ = 41.2 (**5**), 42.4 (**6**), 66.9 (**7**), and 66.6 (**8**) ppm), reflecting the reduced electron density at the phosphorous sites caused by the cationic nature of the compounds. Traces of the ligand are seen in the spectra of **5** which may result from some instability of the complex in solution.

Since **5–8** are composed of a $[(L)_2Au]^+$ cation and a ClO_4^- anion electrospray ionization mass spectrometry (ESI MS) is a suitable tool to characterize these ions. For **5–8** signals of the $[(L)_2Au]^+$ cations were detected in the positive MS mode. Besides the molecular peak, some higher charged species could be observed in the gas phase, *e.g.* for compound **5** the mass of the cation ($[(Hph3py)_2Au]^+$) at *m*/*z* = 853.16 amu and further peaks at *m*/*z* = 426.58 amu ($[(Hph3py)_2Au]^{2+}$) and *m*/*z* = 284.51 amu ($[(Hph3py)_2Au]^{3+}$) were detected. The situation was similar for compound **7** (($[(Hpypya)_2Au]^+$): *m*/*z* = 909.17), where peaks additional to the molecular peak *e.g.* at *m*/*z* = 454.59 amu ($[(Hpypya)_2Au]^{2+}$) and 303.08 amu ($[(Hpypya)_2Au]^{3+}$) were found. The compositions of these compounds were assigned based on simulations. A collision experiment with argon resulted in the loss of one ligand (553.08 amu ($[(Hpypya)Au]^+$)). Also for **8** higher charged species such as $[(Hphpya)_2Au]^{2+}$ (*m*/*z* = 453.60 amu) and $[(Hphpya)_2Au]^{3+}$ (*m*/*z* = 302.41 amu) were observed.

Single crystals of **5** and **7** suitable for an X-ray diffraction analysis were obtained by slow evaporation of a concentrated chloroform solution (**5**) or slow diffusion of *n*-pentane into a concentrated CH_2Cl_2 solution (**7**). **5** crystallizes in the triclinic space group $P\bar{1}$ with one molecule of **5** and three molecules of $CHCl_3$ in the asymmetric unit (Fig. 5). The quality of the collected X-ray data was poorer than for **1**, **3**, and **4** which did not allow the localization of the hydrogen atoms. In **5** the ClO_4^- anion is severely disordered. The ClO_4^- anion could be localized on two positions each being half occupied. Within the $[(Hph3py)_2Au]^+$ cation both Au–P distances are almost similar (Au–P1 2.3023(14) Å and Au–P2 2.3049(14) Å). Although there is no steric hindrance, the observed Au–P bond length is about 0.07 Å longer than in **1** (Au–P 2.2347(11) Å). However, the observed bond lengths in **5** are in agreement with the data of similar compounds in the literature, *e.g.* $[(Ph_3P)_2Au][C(CN)_3]$ (Au–P 2.315(2) Å, P–Au–P 180°)[52] and $[(Mes_3P)_2Au](BF_4)$ (Au–P 2.3525(10) Å, P–Au–P 179.72(7)°, Mes = 2,4,6-Mesityl).[53] As expected the gold atom is almost linearly coordinated with an angle of 177.36(5)°. In the crystal lattice N1 and N2 are located within the range of hydrogen bonds to N1′ and N2′ of a neighboring molecule.

Single crystals of compound **7** could be obtained. Although the quality of the X-ray data collected from **7** was poor, the connectivity of **7** and its composition were deduced but bonding parameters will not be further discussed (Fig. 6). As seen from Fig. 6, the gold(I) atom is again linearly coordinated by two phosphorus atoms of the Hpypya ligand.



Scheme 4 Synthesis of the homoleptic gold(I) complexes **5–8**.

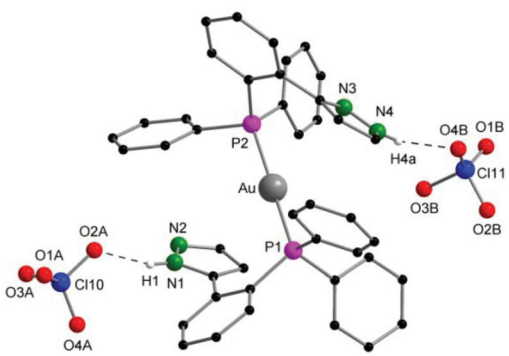


Fig. 5 Solid-state structure of the cation of **5**, omitting carbon bound hydrogen atoms. The ClO_4^- anion could be localized on two positions each being half occupied. Selected bond lengths [Å] and angles [°]: Au–P1 2.3023(14), Au–P2 2.3049(14), P1–C1 1.817(6), P1–C10 1.818(6), P1–C16 1.810(6); P1–Au–P2 177.36(5), Au–P1–C1 116.0(2), Au–P1–C10 111.0(2), Au–P1–C16 113.0(2), C1–P1–C10 104.3(3), C1–P1–C16 106.5(3), C10–P1–C16 105.0(3).

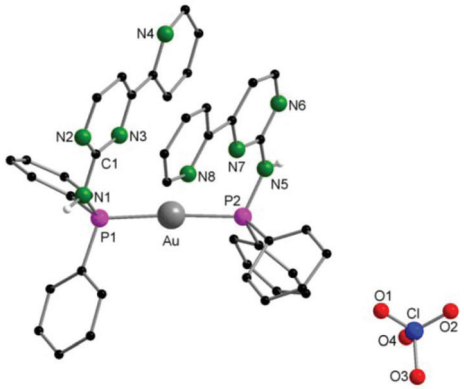


Fig. 6 Solid-state structure of **7**, omitting all hydrogen atoms.

Conclusions

Two new and two established phosphines bearing *N*-heterocyclic substituents were introduced in gold(I) chemistry to study their intra- and intermolecular coordination behavior. The heteroleptic complexes [(L)AuCl] and the homoleptic compounds $[(L)_2Au]ClO_4$ (L = Hpypya, Hphpya, Hph3py, and Hph5py) were obtained by reaction of L with [(tht)AuCl] and $[Au(tht)_2]ClO_4$ in CH_2Cl_2. Due to the multifunctional nature of the ligands, intermolecular hydrogen bonds between two *N*-heterocycles of neighboring complexes were found. For [(L)AuCl] dimeric units were always thus observed.

Experimental section

General considerations

Although all products are not very air sensitive, all manipulations were performed with the rigorous exclusion of oxygen and moisture in a flame-dried Schlenk-type glassware or in an argon-filled MBraun glove box. THF was distilled under nitrogen from potassium benzophenone ketyl prior to use. Hydrocarbon solvents (toluene and *n*-pentane) were dried using an MBraun solvent purification system (SPS-800). All solvents for vacuum line manipulations were stored *in vacuo* over $LiAlH_4$ in resealable flasks. Deuterated solvents were obtained from Aldrich (99 atom% D). NMR spectra were recorded on a Bruker Avance II 300 MHz or Avance 400 MHz spectrometer. Chemical shifts are referenced to internal solvent resonances and are reported relative to tetramethylsilane. IR spectra were obtained on a Bruker Tensor 37 spectrometer. Raman spectra were carried out with a BrukerMultiRAM spectrometer. Mass spectra were recorded at 70 eV on a Thermo Scientific DFS machine and on an Ionspec FTIR spectrometer. FAB-MS were recorded on a Finnigan MAT 90 spectrometer. Elemental analyses were carried out with an ElementarVario EL or Micro Cube analyzer. [(tht)AuCl][54,55] (tht = tetrahydrothiophene) was prepared according to modified standard procedures. $[Au(tht)_2]ClO_4$ [56] (Hph3py),[41] (Hph5py),[43] 4-(pyridin-2-yl)-pyrimidin-2-amine[45] and 3-dimethylamino-4-phenylprop-2-en-1-on[44] were prepared according to literature procedures.

Warning: Perchlorates with organic cations can be explosive.

4-Phenylpyrimidin-2-amine. 2.62 g (114.02 mmol) of sodium were dissolved in 150 ml of dry ethanol. After adding 8.72 g (71.60 mmol) of guanidinium nitrate and 10.00 g (57.00 mmol) of 3-dimethylamino-4-phenylprop-2-en-1-on, the mixture was refluxed for 12 h. The solvent was removed and the residue was redissolved in 50 ml of CH_2CH_2. After concentrating the solution to 30 ml, 5 ml of diethyl ether were added and the mixture was kept in a refrigerator for several hours leading to precipitation of the product, which was filtered and dried in a vacuum. Yield: 7.16 g (73%). $C_{10}H_9N_3$ (171.20): calcd C, 70.16; H, 5.30; N, 24.54; found C, 69.95; H, 5.35; N, 24.33. ^{1}H NMR ([D$_6$]DMSO, 400.13 MHz, 20 °C): δ (ppm) = 8.31 (d, $^3J_{HH}$ = 5.1 Hz, 1H, Pyrim), 8.07 (m, 2H, Ph), 7.45–7.55 (m, 3H, Ph), 7.12 (d, $^3J_{HH}$ = 5.1 Hz, 1H, Pyrim), 6.68 (br, 2H, NH_2). ^{13}C{^{1}H} NMR ([D$_6$]DMSO, 100.61 MHz, 20 °C): δ (ppm) = 163.8 (Pyrim), 163.6 (Pyrim), 159.0 (Pyrim), 137.0 (Ph), 130.5 (Ph), 128.7 (Ph), 126.7 (Pyrim), 105.8 (Ph).

***N*-(Diphenylphosphino)-4-(pyridin-2-yl)pyrimidin-2-amine (Hpypya).** 2.00 g (11.68 mmol) of 4-(pyridin-2-yl)pyrimidin-2-amine were added under an atmosphere of nitrogen to 20 ml of dry THF. The resulting solution was cooled to 0 °C and 1.70 ml (12.26 mmol) of freshly dried NEt_3 were added. After adding 2.20 ml (11.68 mmol) of chlorodiphenylphosphine dropwise with a syringe within a period of 15 minutes, the reaction mixture was stirred at room temperature for 65 h and then was filtered to remove $(HNEt_3)Cl$. After removing the solvent, the product was recrystallized from ethanol–pentane. Yield: 3.75 g (90%). $C_{21}H_{17}N_4P\cdot(EtOH)_{0.3}$ (356.36): calcd C, 70.08; H, 5.12; N, 15.13; found C, 69.65; H, 4.98; N, 15.48. ^{1}H NMR ([D$_6$]DMSO, 400.13 MHz, 20 °C): δ (ppm) = 8.70 (d, $^3J_{HH}$ = 4.2 Hz, 1H, Pyrid), 8.56 (d, $^3J_{HH}$ = 5.1 Hz, 1H, Pyrim), 8.29–8.34 (m, 2H, Pyrid + NH), 7.98 (td, J_{HH} = 7.8, 1.5 Hz, 1H, Pyrid), 7.68 (d, $^3J_{HH}$ = 5.0 Hz, 1H, Pyrim), 7.33–7.43 (m, 6H, Ph), 7.49–7.56 (m, 5H, Pyrid + Ph). ^{13}C{^{1}H} NMR ([D$_6$]DMSO, 101 MHz, 20 °C): δ (ppm) = 163.3 (d, $^2J_{CP}$ = 17.2 Hz, Pyrim), 162.8 (Pyrim), 159.6 (d, $^4J_{CP}$ = 2.2 Hz, Pyrim), 153.5 (Pyrid), 149.5 (Pyrid), 139.7 (d, $^1J_{CP}$ = 14.9 Hz, Ph), 137.4 (Pyrid), 131.2 (d, $^2J_{CP}$ = 22.1 Hz, Ph), 128.9 (Ph), 128.3 (d, $^3J_{CP}$ = 6.6 Hz, Ph), 125.6 (Ph), 121.0 (Pyrid), 108.0 (Pyrim). ^{31}P{^{1}H} NMR ([D$_6$]DMSO, 161.98 MHz, 20 °C): δ (ppm) = 24.95.

***N*-(Diphenylphosphino)-4-phenylpyrimidin-2-amine (Hphpya).** The synthesis of Hphpya was carried out as described for Hpypya using 4-phenylpyrimidin-2-amine instead of 4-(pyridin-2-yl)pyrimidin-2-amine. Yield: 2.68 g (64%, colorless solid). $C_{22}H_{18}N_3P$ (355.37): calcd C, 74.35; H, 5.11; N, 11.82; found C, 74.23; H, 5.29; N, 11.80. ^{1}H NMR ([D$_6$]DMSO, 400.13 MHz, 20 °C): δ (ppm) = 8.46 (d, $^3J_{HH}$ = 5.2 Hz, 1H, Pyrim), 8.24 (d, $^2J_{HP}$ = 8.4 Hz, 1H, NH), 8.10 (m, 2H, Ph), 7.47–7.58 (m, 7H, Ph), 7.32–7.42 (m, 7H, Ph + Pyrim). ^{13}C{^{1}H} NMR ([D$_6$]DMSO, 101 MHz, 20 °C): δ (ppm) = 163.5 (Pyrim), 163.2 (d, $^2J_{CP}$ = 17.4 Hz, Pyrim), 159.2 (Pyrim), 139.9 (d, $^1J_{CP}$ = 15.0 Hz, Ph), 136.4 (Ph), 131.2 (d, $^2J_{CP}$ = 22.1 Hz, Ph), 130.8 (Ph), 128.9 (s, Ph), 128.8 (Ph), 128.3 (d, $^3J_{CP}$ = 6.6 Hz,

Ph), 126.9 (Ph), 107.9 (Pyrim). $^{31}P\{^1H\}$ NMR ([D$_6$]DMSO, 161.98 MHz, 20 °C): δ (ppm) = 24.64.

[(Hph3py)(AuCl)] (1). 321 mg (1.00 mmol) of chloro(tetrahydrothiophene)gold(I) and 328 mg (1.00 mmol) of 3-(2-(diphenylphosphino)phenyl)-1*H*-pyrazole were dissolved in 25 ml of CH_2Cl_2 under stirring. The colorless mixture was stirred for 1 hour at ambient temperature. The solution was then evaporated. The remaining residue was washed with diethylether (3 × 10 ml) and subsequently dried *in vacuo*. The product was obtained as a colorless powder. Yield: 510 mg (90%). Anal. Calcd $C_{21}H_{17}AuClN_2P{\cdot}0.5C_4H_8S$ – C 45.67, H 3.50, N 4.63, S 2.65, found C 45.46, H 3.51, N 4.59, S 2.84. ^1H NMR (300.13 MHz, $CDCl_3$): δ (ppm) = 7.77–7.39 (m, 15H, Ph, pyrazole-5-*H*), 7.06 (dd, $^3J_{HH}$ = 11.8, 7.8 Hz, 1H, pyrazole-4-*H*), 6.32 (s, br, 1H, N*H*). $^{13}C\{^1H\}$ NMR (75.48 MHz, $CDCl_3$): δ (ppm) = 134.5 (pyrazole-1-*C*), 134.3 (pyrazole-3-*C*), 132.1 (Ph), 132.0 (Ph), 131.8 (Ph), 130.2 (Ph), 129.3 (Ph), 129.2 (Ph), 128.8 (Ph), 128.7 (Ph), 128.3 (Ph), 127.5 (Ph), 107.8 (pyrazole-2-*C*). $^{31}P\{^1H\}$ NMR (121.48 MHz, $CDCl_3$): δ (ppm) = 28.4. IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3234 (m), 3126 (w), 1585 (w), 1540 (w), 1477 (m), 1432 (s), 1357 (w), 1299 (w), 1261 (w), 1188 (m), 1098 (s), 1043 (m), 999 (w), 953 (m), 873 (w), 786 (s), 759 (vs), 707 (m), 690 (vs), 603 (m), 549 (vs), 532 (m), 509 (vs). Raman (solid state): $\tilde{\nu}$ (cm^{-1}) = 3140 (w), 3055 (s), 2948 (w), 2910 (w), 2858 (w), 1588 (s), 1525 (w), 1497 (w), 1441 (w), 1351 (w), 1298 (w), 1185 (w), 1161 (w), 1101 (w), 1040 (m), 1029 (m), 1000 (s), 698 (w), 656 (w), 618 (w), 358 (w), 330 (w) 243 (w). FAB-MS: *m*/*z* (%) = 560 ($[M]^+$, 4), 525 ($[M - Cl]^+$, 32), 327 ($[M - AuCl]^+$, 44).

[(Hph5py)(AuCl)] (2). 160 mg (0.50 mmol) of chloro(tetrahydrothiophene)gold(I) and 164 mg (0.50 mmol) of 5-(4-(diphenylphosphino)phenyl)-1*H*-pyrazole were dissolved in 10 ml of CH_2Cl_2 under stirring. The colorless mixture was stirred for 1 hour at ambient temperature. The solution was then evaporated. The remaining residue was washed with diethylether (3 × 5 ml) and subsequently dried *in vacuo*. The product was obtained as a colorless powder. Yield: 255 mg (91%). Anal. Calcd $C_{21}H_{17}AuClN_2P$ – C 44.98, H 3.06, N 5.00, found C 44.92, H 3.06, N 4.81. ^1H NMR (300.13 MHz, $CDCl_3$): δ (ppm) = 7.95 (d, $^3J_{HH}$ = 8.2 Hz, 2H, Ph_2P-*o*-Ph), 7.73 (s, br, 1H, pyrazole-3-*H*), 7.63–7.49 (m, 13H, Ph, N*H*), 6.75 (s, br, 1H, pyrazole-4-*H*). $^{13}C\{^1H\}$ NMR (75.48 MHz, $CDCl_3$): δ (ppm) = 135.3 (pyrazole-1-*C*), 134.7 (pyrazole-3-*C*), 134.3 (Ph), 134.1 (Ph), 132.1 (Ph), 129.4 (Ph), 129.3 (Ph), 129.0 (Ph), 128.8 (Ph), 128.2 (Ph), 128.0 (Ph), 126.5 (Ph), 103.7 (pyrazole-2-*C*). $^{31}P\{^1H\}$ NMR (121.48 MHz, $CDCl_3$): δ (ppm) = 32.7. IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3268 (m), 3043 (w), 1604 (m), 1559 (w), 1533 (w), 1506 (w), 1482 (w), 1462 (w), 1434 (m), 1403 (m), 1330 (w), 1303 (w), 1291 (w), 1262 (w), 1178 (m), 1100 (s), 1043 (m), 1026 (w), 997 (w), 950 (s), 929 (w), 848 (m), 828 (m), 773 (vs), 748 (w), 736 (vs), 714 (m), 690 (vs), 634 (w), 605 (s), 557 (vs), 531 (s), 521 (vs). Raman (solid state): $\tilde{\nu}$ (cm^{-1}) = 3059 (m), 2926 (m), 1604 (vs), 1586 (m), 1526 (m), 1449 (m), 1346 (w), 1305 (w), 1190 (w), 1098 (m), 1074 (w), 1027 (m), 999 (s), 943 (m), 715 (w), 333 (w), 252 (vs), 181 (m). FAB-MS: *m*/*z* (%) = 525 ($[M - Cl]^+$, 40), 328 ($[M - AuCl]^+$, 7).

[(Hpypya)(AuCl)] (3). 160 mg (0.50 mmol) of chloro(tetrahydrothiophene)gold(I) and 178 mg (0.50 mmol) of *N*-(diphenylphosphino)-4-(pyridin-2-yl)pyrimidin-2-amine were dissolved in 10 ml of CH_2Cl_2 under stirring. The colorless mixture was stirred for 1 hour at ambient temperature. The solution was then evaporated. The remaining residue was washed with diethylether (3 × 5 ml) and subsequently dried *in vacuo*. The product was obtained as a colorless powder. Yield: 271 mg (92%). Anal. Calcd $C_{21}H_{17}AuClN_4P$ – C 42.84, H 2.91, N 9.52, found C 42.41, H 2.92, N 9.10. ^1H NMR (300.13 MHz, $CDCl_3$): δ (ppm) = 8.70 (s, br, 1H, N*H*), 8.38 (d, $^3J_{HH}$ = 7.8 Hz, 1H, pyridine-3-*H*), 8.00–7.83 (m, 8H, Ph, pyridine-6-*H*), 7.66–7.49 (m, 6H, Ph, pyrimidine-6-*H*), 7.48–7.40 (m, 1H, pyrimidine-5-*H*). $^{13}C\{^1H\}$ NMR (75.48 MHz, $CDCl_3$): δ (ppm) = 158.4 (Ar), 152.4 (Ar), 148.9 (Ar), 138.1 (Ar), 132.8 (Ar), 132.7 (Ar), 132.6 (Ar), 131.1 (Ar), 130.1 (Ar), 129.5 (Ar), 129.3 (Ar), 126.1 (Ar), 123.0 (Ar). $^{31}P\{^1H\}$ NMR (121.48 MHz, $CDCl_3$): δ (ppm) = 55.6. IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3056 (w), 2963 (w), 2847 (w), 1577 (m), 1549 (s), 1483 (w), 1463 (s), 1436 (w), 1417 (s), 1314 (w), 1260 (s), 1202 (w), 1103 (vs), 1019 (s), 957 (s), 873 (m), 849 (m), 799 (s), 782 (vs), 758 (s), 746 (m), 737 (m), 691 (vs), 648 (s), 616 (m), 537 (vs), 510 (vs). Raman (solid state): $\tilde{\nu}$ (cm^{-1}) = 3056 (m), 1588 (s), 1491 (w), 1416 (w), 1312 (m), 1104 (w), 1045 (w), 1028 (w), 997 (s), 742 (w), 617 (w), 334 (m), 281 (w), 266 (w), 229 (m), 205 (w). FAB-MS: *m*/*z* (%) = 589 ($[M]^+$, 12), 553 ($[M - Cl]^+$, 26), 355 ($[M - AuCl]^+$, 3).

[(Hphpya)(AuCl)] (4). 160 mg (0.50 mmol) of chloro(tetrahydrothiophene)gold(I) and 178 mg (0.50 mmol) of *N*-(diphenylphosphino)-4-phenylpyrimidin-2-amine were dissolved in 10 ml of CH_2Cl_2 under stirring. The colorless mixture was stirred for 1 hour at ambient temperature. The solution was then evaporated. The remaining residue was washed with diethylether (3 × 5 ml) and subsequently dried *in vacuo*. The product was obtained as a colorless powder. Yield: 267 mg (91%). Anal. Calcd $C_{22}H_{18}AuClN_3P{\cdot}0.25CH_2Cl_2$ – C 43.88, H 3.06, N 6.90, found C 43.81, H 3.26, N 6.47.

^1H NMR (300.13 MHz, DMSO): δ (ppm) = 8.07 (d, $^3J_{HH}$ = 7.5 Hz, 2H, Ph), 7.95 (d, $^3J_{HH}$ = 6.7 Hz, 2H, Ph), 7.91 (d, $^3J_{HH}$ = 6.3, 2H, Ph), 7.64–7.47 (m, 11H, Ph, pyrimidine-5-*H*, pyrimidine-6-*H*). $^{31}P\{^1H\}$ NMR (121.48 MHz, $CDCl_3$): δ (ppm) = 57.2. IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3066 (w), 2963 (w), 2853 (w), 1580 (m), 1550 (s), 1499 (w), 1470 (s), 1436 (m), 1414 (s), 1317 (w), 1261 (s), 1209 (w), 1185 (w), 1103 (vs), 1026 (s), 950 (s), 870 (m), 797 (s), 755 (s), 692 (s), 684 (s), 628 (m), 536 (vs), 511 (vs). Raman (solid state): $\tilde{\nu}$ (cm^{-1}) = 3057 (m), 1588 (s), 1505 (w), 1480 (w), 1338 (w), 1296 (w), 1167 (w), 1099 (w), 1040 (m), 1027 (w), 1000 (s), 934 (m), 701 (w), 653 (w), 618 (w), 366 (w), 327 (w), 288 (w), 246 (w), 225 (w). FAB-MS: *m*/*z* (%) = 588 ($[M]^+$, 2), 552 ($[M - Cl]^+$, 4).

$[(Hph3py)_2Au]ClO_4$ (5). 236 mg (0.50 mmol) of bis(tetrahydrothiophene)gold(I) perchlorate and 328 mg (1.00 mmol) of 3-(2-(diphenylphosphino)phenyl)-1*H*-pyrazole were dissolved in 25 ml of CH_2Cl_2 under stirring. The colorless mixture was stirred for 1 hour at ambient temperature. The solution was then evaporated. The remaining residue was washed with diethylether (3 × 10 ml) and subsequently dried *in vacuo*. The product was obtained as a colorless powder. Yield: 381 mg (80%). Anal. Calcd $C_{42}H_{34}AuClN_4O_4P{\cdot}2CH_2Cl_2$ – C 47.06,

H 3.41, N 4.99, found C 47.44, H 4.11, N 4.54. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ (ppm) = 7.79 (d, $^3J_{HH}$ = 7.3 Hz, 2H, pyrazole-5-*H*), 7.64 (d, $^3J_{HH}$ = 6.7 Hz, 2H, Ph_2P-Phenyl-6-*H*), 7.61–7.46 (m, 14H, Ph), 7.46–7.34 (m, 12H, Ph), 6.97 (d, $^3J_{HH}$ = 7.8 Hz, 2H, pyrazole-4-*H*), 6.23 (s, br, 2H, N*H*). ^{31}P{^{1}H} NMR (121.48 MHz, $CDCl_3$): δ (ppm) = 41.2. IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3268 (m), 3136 (w), 3051 (w), 2963 (w), 1586 (w), 1561 (w), 1480 (m), 1435 (s), 1295 (m), 1259 (m), 1183 (m), 1080 (vs), 1039 (m), 998 (m), 947 (m), 880 (m), 795 (s), 766 (m), 751 (s), 729 (s), 691 (vs), 622 (s), 600 (w), 528 (vs), 503 (vs). Raman (solid state): $\tilde{\nu}$ (cm^{-1}) = 3066 (m), 2907 (w), 1589 (vs), 1490 (m), 1436 (m), 1419 (w), 1314 (s), 1106 (m), 1046 (w), 1027 (m), 997 (vs), 931 (m), 739 (w), 707 (w), 617 (w), 337 (w), 266 (w), 230 (w). ESI-MS (CH_2Cl_2): *m*/*z* = 853.16 ([(Hph3py)$_2$Au]$^+$), 284.51 ([(Hph3py)$_2$Au]$^{3+}$).

[(Hph5py)$_2$Au]ClO$_4$ (6). 236 mg (0.50 mmol) of bis(tetrahydrothiophene)gold(I) perchlorate and 328 mg (1.00 mmol) of 5-(4-(diphenylphosphino)phenyl)-1*H*-pyrazole were dissolved in 25 ml of CH_2Cl_2 under stirring. The colorless mixture was stirred for 1 hour at ambient temperature. The solution was then evaporated. The remaining residue was washed with diethylether (3 × 10 ml) and subsequently dried *in vacuo*. The product was obtained as a colorless powder. Yield: 375 mg (79%). Anal. Calcd $C_{42}H_{34}AuClN_4O_4P{\cdot}0.7C_4H_8S$ – C 53.02, H 3.93, N 5.52, S 2.21, found C 52.38, H 3.95, N 5.29, S 2.11. ^{1}H NMR (300.13 MHz, DMSO): δ (ppm) = 8.07 (d, $^3J_{HH}$ = 8.1 Hz, 2H, Ph_2P-*o*-Ph), 7.82 (s, br, 1H, pyrazole-3-*H*), 7.77–7.54 (m, 13H, Ph, N*H*), 6.86 (d, $^3J_{HH}$ = 2.2 Hz, 1H, pyrazole-4-*H*). ^{31}P{^{1}H} NMR (121.48 MHz, DMSO): δ (ppm) = 42.4. IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3308 (w), 2962 (w), 1602 (w), 1505 (w), 1482 (w), 1436 (m), 1404 (w), 1336 (w), 1308 (w), 1261 (m), 1187 (w), 1097 (vs), 943 (w), 925 (w), 837 (w), 799 (m), 770 (w), 738 (s), 691 (s), 622 (m), 541 (s), 515 (s). – ESI-MS (CH_2Cl_2): *m*/*z* = 853.20 ([(Hph5py)$_2$Au]$^+$).

[(Hpypya)$_2$Au]ClO$_4$ (7). 118 mg (0.25 mmol) of bis(tetrahydrothiophene)gold(I) perchlorate and 178 mg (0.50 mmol) of *N*-(diphenylphosphino)-4-(pyridin-2-yl)pyrimidin-2-amine were dissolved in 10 ml of CH_2Cl_2 under stirring. The colorless mixture was stirred for 1 hour at ambient temperature. The solution was then evaporated. The remaining residue was washed with diethylether (3 × 5 ml) and subsequently dried *in vacuo*. The product was obtained as a colorless powder. Yield: 212 mg (84%). Anal. Calcd $C_{42}H_{34}AuClN_8O_4P_2{\cdot}0.5CH_2Cl_2$ – C 48.54, H 3.35, N 10.66, found C 48.50, H 3.59, N 10.24.

^{1}H NMR (400.30 MHz, DMSO-d_6): δ (ppm) = 8.68 (s, br, 2H, pyridine-6-*H*), 8.59 (s, br 2H, pyridine-3-*H*), 8.14 (s, br, 2H, pyrimidine-6-*H*), 7.89–7.75 (m, 10H, Ph), 7.72–7.54 (m, 16H, Ph, N*H*), 7.48 (s, br, 2H, Ph). ^{31}P{^{1}H} NMR (162.04 MHz, DMSO-d_6): δ (ppm) = 66.9. IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2964 (w), 1717 (w), 1670 (w), 1577 (s), 1553 (s), 1465 (s), 1436 (m), 1419 (m), 1316 (w), 1261 (m), 1200 (w), 1104 (s), 1084 (vs), 998 (w), 960 (m), 879 (w), 850 (w), 784 (s), 743 (m), 691 (vs), 649 (m), 621 (s), 512 (vs). Raman (solid state): $\tilde{\nu}$ (cm^{-1}) = 3066 (s), 2907 (w), 1589 (vs), 1490 (m), 1436 (m), 1419 (w), 1314 (s), 1242 (w), 1202 (w), 1106 (m), 1046 (w), 1027 (m), 997 (vs), 931 (m), 739 (w), 707 (w), 617 (w), 338 (w), 266 (w), 231 (m). ESI-MS (CH_2Cl_2): *m*/*z* = 909.17 ([(Hpypya)$_2$Au]$^+$), 553.08 ([(Hpypya)Au]$^+$), 454.59 ([(Hpypya)$_2$Au]$^{2+}$), 303.08 ([(Hpypya)$_2$Au]$^{3+}$).

[(Hphpya)$_2$Au]ClO$_4$ (8). 118 mg (0.25 mmol) of bis(tetrahydrothiophene)gold(I) perchlorate and 178 mg (0.50 mmol) of *N*-(diphenylphosphino)-4-phenylpyrimidin-2-amine were dissolved in 10 ml of CH_2Cl_2 under stirring. The colorless mixture was stirred for 1 hour at ambient temperature. The solution was then evaporated. The remaining residue was washed with diethylether (3 × 5 ml) and subsequently dried *in vacuo*. The product was obtained as a colorless powder. Yield: 199 mg (79%). Anal. Calcd $C_{44}H_{36}AuClN_6O_4P_2{\cdot}CH_2Cl_2$ – C 49.49, H 3.51, N 7.70, found C 49.04, H 3.92, N 7.01.

^{1}H NMR (400.30 MHz, DMSO-d_6): δ (ppm) = 8.56 (d, $^3J_{HH}$ = 5.1 Hz, 2H, pyrimidine-6-*H*), 8.03 (d, $^3J_{HH}$ = 7.6 Hz, 4H, pyrimidine-*m*-Ph), 7.78–7.55 (m, 30H, Ph). ^{31}P{^{1}H} NMR (162.04 MHz, DMSO-d_6): δ (ppm) = 66.6. IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2962 (m), 1581 (m), 1553 (m), 1501 (w), 1472 (m), 1437 (w), 1412 (m), 1311 (w), 1259 (s), 1084 (vs), 1016 (vs), 951 (m), 876 (w), 795 (vs), 749 (m), 689 (s), 623 (m), 510 (vs). Raman (solid state): $\tilde{\nu}$ (cm^{-1}) = 3056 (s), 1600 (vs), 1585 (s), 1501 (m), 1411 (w), 1313 (m), 1287 (m), 1162 (w), 1106 (m), 1029 (m), 1002 (vs), 932 (m), 732 (w), 705 (w), 616 (w), 337 (w), 300 (w), 262 (w), 225 (w). ESI-MS (CH_2Cl_2): *m*/*z* = 907.20 ([(Hphpya)$_2$Au]$^+$), 302.41 ([(Hphpya)$_2$Au]$^{3+}$).

X-ray crystallographic studies of Hpypya, 1, 3, 4, and 5

Suitable crystals were covered in mineral oil (Aldrich) and mounted onto a glass fiber. Data were collected on a diffractometer equipped with a STOE imaging plate detector system IPDS2 or a Xcalibur, Sapphire3 using MoKα radiation with graphite monochromatization (λ = 0.71073 Å). Structure solution was performed by direct methods; full-matrix-least squares refinement against F^2 using SHELXS-97, SHELXL-97 and SHELXL-2013 software.[57]

Crystal data for Hphpya: $C_{22}H_{18}N_3P$, M = 355.36, monoclinic, a = 11.7563(2) Å, b = 7.7007(1) Å, c = 20.4757(3) Å, α = 90.00°, β = 100.178(2)°, γ = 90.00°, V = 1824.53(5) Å^3, T = 150(2) K, space group $P2_1/n$, Z = 4, μ(CuKα) = 1.400 mm^{-1}, 10 978 reflections measured, 2920 independent reflections (R_{int} = 0.0590). The final R_1 values were 0.0372 ($I > 2\sigma(I)$). The final w$R(F^2)$ values were 0.1038 (all data). The goodness of fit on F^2 was 1.095.

Crystal data for **1**: $C_{21}H_{17}AuClN_2P$, M = 560.75, monoclinic, a = 11.5763(5) Å, b = 12.1434(5) Å, c = 14.4334(6) Å, β = 107.456(3)°, V = 1935.55(14) Å^3, T = 200(2) K, space group $P2_1/a$, Z = 4, μ(MoKα) = 7.828 mm^{-1}, 10 018 reflections measured, 3506 independent reflections (R_{int} = 0.0488). The final R_1 values were 0.0259 ($I > 2\sigma(I)$). The final w$R(F^2)$ values were 0.0592 (all data). The goodness of fit on F^2 was 1.012.

Crystal data for **3**: $C_{21}H_{17}AuClN_4P{\cdot}CH_2Cl_2$, M = 673.70, triclinic, a = 10.0659(4) Å, b = 11.2041(4) Å, c = 11.2375(4) Å, α = 87.414(3)°, β = 71.501(3)°, γ = 82.113(3)°, V = 1190.51(8) Å^3, T = 200(2) K, space group $P\bar{1}$, Z = 2, μ(MoKα) = 6.600 mm^{-1}, 11 647 reflections measured, 4397 independent reflections (R_{int} = 0.0376). The final R_1 values were 0.0197 ($I > 2\sigma(I)$). The final

w$R(F^2)$ values were 0.0490 (all data). The goodness of fit on F^2 was 1.069.

Crystal data for **4**: $C_{22}H_{18}AuClN_3P$, M = 587.78, triclinic, a = 8.8010(4) Å, b = 11.0375(4) Å, c = 11.7633(5) Å, α = 74.503(3)°, β = 71.796(3)°, γ = 77.520(3)°, V = 1035.01(8) Å^3, T = 200(2) K, space group $P\bar{1}$, Z = 2, μ(MoKα) = 7.326 mm^{-1}, 12 718 reflections measured, 5472 independent reflections (R_{int} = 0.0365). The final R_1 values were 0.0236 ($I > 2\sigma(I)$). The final w$R(F^2)$ values were 0.0613 ($I > 2\sigma(I)$). The goodness of fit on F^2 was 1.076.

Crystal data for **5**: $C_{42}H_{34}AuN_4P_2{\cdot}ClO_4{\cdot}3CHCl_3$, M = 1311.19, triclinic, a = 10.9679(3) Å, b = 13.2655(3) Å, c = 18.0039(5) Å, α = 91.400(2)°, β = 99.377(2)°, γ = 103.517(2)°, V = 2507.54(12) Å^3, T = 200(2) K, space group $P\bar{1}$, Z = 2, μ(MoKα) = 3.577 mm^{-1}, 59 074 reflections measured, 9883 independent reflections (R_{int} = 0.0632). The final R_1 values were 0.0464 ($I > 2\sigma(I)$). The final w$R(F^2)$ values were 0.1239 (all data). The goodness of fit on F^2 was 1.037.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as a supplementary publication no. 960836–960840.

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