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Gold(I) and Palladium(II) Thiolato Complexes Containing Water-Soluble Phosphane Ligands

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Water-soluble gold(I) and palladium(II) complexes containing different thiolates and the phosphanes 1,3,5-triaza-7-phosphaadamantane (PTA) and 3,7-diacetyl-1,3,7-triaza-5-phosphabicyclo[3.3.1]nonane (DAPTA) are described. The complexes were characterised by spectroscopic techniques including 2D NMR experiments, and the complexes $[Au(S_2CNEt_2)(PTA)]$, *trans*-$[Pd(SC_5H_4N)_2(PTA)_2]$ and *trans*-$[Pd(SC_5H_4N)_2(DAPTA)_2]$ were additionally characterised by X-ray crystallography; the latter complex is one of the few structurally characterised DAPTA complexes.
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Introduction

Water as a solvent for chemical transformations is experiencing a renaissance which has mainly been driven by environmental and, to some extent, economical concerns. The use of water as a solvent, however, requires the development of new catalysts or reagents that are compatible (stable) and soluble in water.[1,2] Gold thiolato complexes dispersed in different solvents, including natural resins, have been used as a gold source for decorating ceramic tiles and glasses after heating.[3] Because these dispersions are liquid, they are commonly referred to as "liquid gold" and, when other late transition metals are involved, the name "liquid precious metal" is used. To avoid the use of toxic and volatile solvents, there is an increasing interest in the development of water-soluble "liquid metals" and thus for water-soluble thiolato complexes.[4] The main strategy employed in this area is either the use of thiolato ligands with solubilising groups or the replacement of traditional phosphane ligands with other water-soluble analogues such as the mono-, di- and tri-sulfonated triphenylphosphanes.[4] Herein, we describe the use of the water-soluble phosphanes 1,3,5-triaza-7-phosphaadamantane (PTA) and 3,7-diacetyl-1,3,7-triaza-5-phosphabicyclo[3.3.1]nonane (DAPTA). PTA was first prepared about thirty years ago[5] and some gold complexes were studied by Fackler Jr.[6–9] and some of us.[10–13] A review and recent reports of new coordination modes of this ligand illustrate the rich and varied coordination chemistry displayed by this compound.[13–16] The diacetate derivative of PTA known as DAPTA has only been reported recently[17] and to date only a very limited number of complexes with this ligand have been described.[11,17]

In this paper we report the synthesis and structures of some water-soluble gold(I) and palladium(II) complexes containing PTA and DAPTA with various thiolato ligands.

Results and Discussion

Gold Complexes

The thiolato gold(I) complexes $[Au(SR)(PR'_3)]$ (SR = various thiolato derivatives as shown in Scheme 1; PR'_3 = PTA, DAPTA) were easily prepared in good yields by treating the complexes $[AuCl(PR'_3)]$ with the thiol derivatives in the presence of base (Scheme 1). The complexes [AuCl(PTA)][6] and [AuCl(DAPTA)] were prepared by replacement of tetrahydrothiophene (tht) from [AuCl(tht)] with the appropriate phosphane.

The thiolato complexes were characterised by spectroscopic techniques and in the case of $[Au(S_2CNEt_2)(PTA)]$ by X-ray diffraction. All of the $[Au(SR)(PR'_3)]$ complexes reported here show singlet resonances in their $^{31}P\{^1H\}$ NMR spectra displaced to a lower field relative to those of the free phosphanes.[5,17] The ^1H NMR spectra of the phosphane resonances merit some comments. The NCH_2P resonances appear as doublets in free PTA and as singlets in the thiolato derivatives, whilst the NCH_2N resonances appear as singlets in free PTA and as an AB system in the thiolato complexes. This behaviour has been observed in

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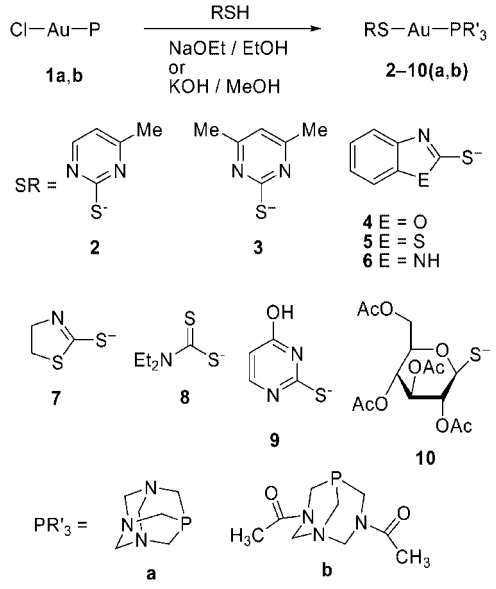

Scheme 1.

other PTA gold derivatives and was confirmed by 2D NMR spectroscopic techniques in the palladium complexes.[18] The ^{1}H NMR spectra of the DAPTA thiolato derivatives are much more complicated and show a similar pattern to that of the free ligand (Figure 1a). The assignment of the originally reported ^{1}H NMR spectrum of DAPTA[17] is incorrect so we provide a corrected assignment for all the signals on the basis of various 2D NMR methods here. The N*CH*$_2$P signals of DAPTA appear as five resonances, four of which integrate as one proton and the other as two protons, which is due to the nonsymmetry of the compound. Further assignment of these signals was conducted by ^{1}H-, ^{13}C- and ^{1}H–^{31}P{^{1}H} HSQC experiments. The latter, in addition to the ^{1}H{^{31}P} NMR spectrum (Figure 1b), show that all these protons are coupled with the phosphorus atom, although some of them with very small coupling constants.

The ^{1}H–^{13}C HSQC spectrum permits the assignment of the resonances of each of the diastereotopic methylene protons, one pair at δ = 5.25 (dd) and 3.20 (dt) ppm, the other at δ = 4.28 (d) and 3.79 (ddd) ppm. The third methylene N*CH*$_2$P is not diastereotopic, hence it appears as a doublet at δ = 3.51 ppm. In addition, ^{1}H–^{1}H homodecoupling experiments point to some coupling between protons of different methylene groups. The two N*CH*$_2$N methylene groups are diastereotopic and appear at δ = 5.79(d) and 3.95(d) ppm and the other at δ =4.93(d) and 4.53(d) ppm. The mass spectra of the gold(I) thiolato complexes show in all cases the parent peak, which confirms the proposed stoichiometry. In some cases higher mass adducts formed by the addition of Au(PTA) or Au(DAPTA) fragments can be observed, which is typical behaviour in mass spectra of thiolate gold(I) complexes.[19,20]

The water solubility of complexes **2** and **7** are quite high at 115 g/L for **2a**, 125 g/L for **2b**, 42 g/L for **7a** and 51 g/L for **7b**. The rest of complexes that are insoluble in water

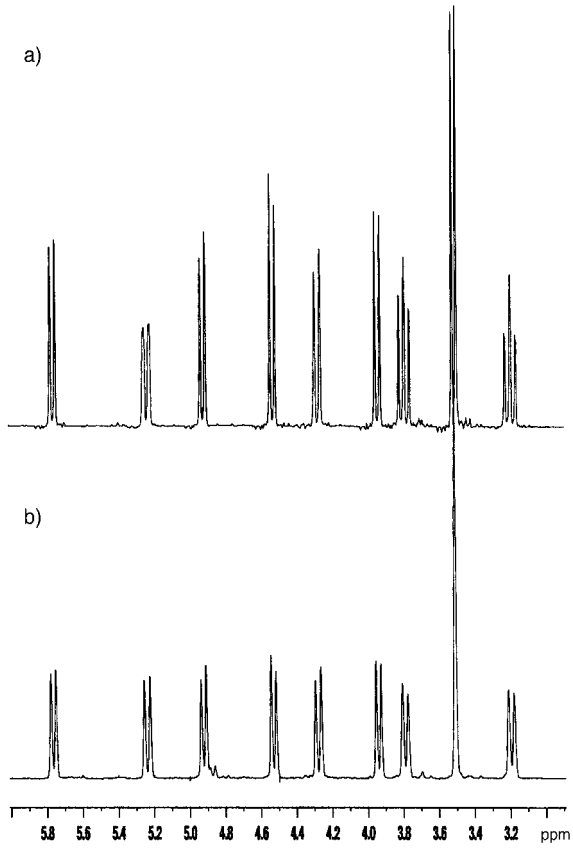

Figure 1. ^{1}H NMR spectrum showing the CH_2 region of DAPTA; a) P coupled spectrum, b) P decoupled spectrum.

tend to be quite soluble in MeOH or MeOH/H_2O mixtures. The solid gold(I) thiolato complexes are stable at room temperature but start to decompose around 200 °C and ultimately give metallic gold at ca. 750–800 °C as shown by thermal analysis experiments. Attempts to grow single crystals of any of the water-soluble complexes proved unsuccessful, in part owing to the decomposition of the solutions that occurred over a period of 1–2 weeks. However, we were successful in obtaining X-ray quality crystals of the *N*,*N*-diethyldithiocarbamate complex [Au(S_2CNEt_2)(PTA)], the molecular structure of which is shown in Figure 2.

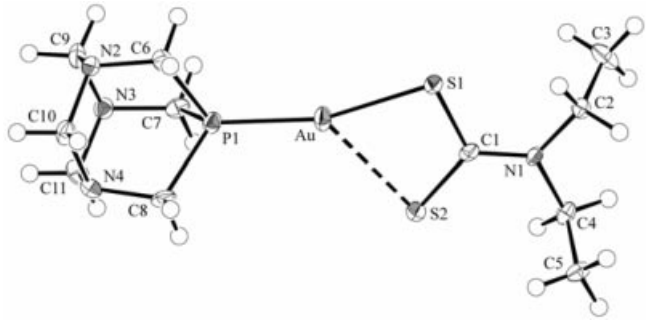

Figure 2. Molecular structure of [Au(S_2CNEt_2)(PTA)]. Ellipsoids show 50% probability levels. Bond lengths [Å] and angles [°]: Au–P1 2.2310(14), Au–S1 2.3840(13), Au···S2 2.7806(15); S1–Au–P1 163.54(5), S2···Au–P1 126.96(5).

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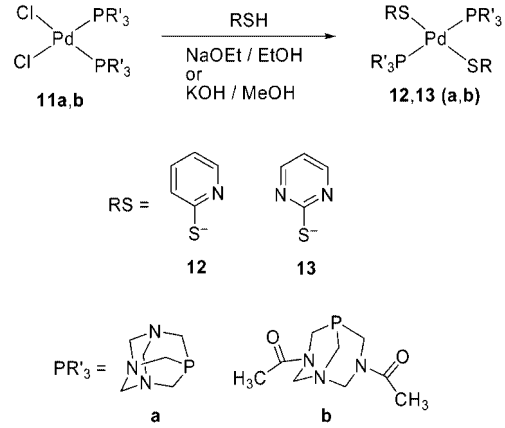
To a first approximation, the molecule of [Au(S_2CNEt_2)(PTA)] comprises a linear gold atom geometry defined by the S1 and P1 atoms. The relatively close approach of the S2 atom [Au–S2 2.7806(15) Å] is responsible for the significant distortion away from the ideal linear geometry, the angle P1–Au–S1 measures 163.54(5)°. There are several related monophosphane gold(I) dithiocarbamate structures available in the literature[21] and these, along with related xanthate (S_2COR)[22] and dithiocarboxylate (S_2CR)[23] structures, feature significantly more linear geometries at the gold atom as the S2 atom forms Au···S2 distances greater than 3.0 Å in these structure. Thus, the structure of [Au(S_2CNEt_2)(PTA)] is exceptional. For the dithiocarbamate structures,[21] the Au–S1, Au···S2 and Au–P1 distances fall in the ranges 2.3256(16)–2.3388(1), 3.0150(2)–3.1068(11) and 2.2430(14)–2.2600(4) Å, respectively. It is evident that the Au–P1 distance is significantly shorter in [Au(S_2CNEt_2)(PTA)], which is consistent with the strong σ bonding ability of this ligand. This interaction pushes the S1 atom away from the gold centre and allows close approach of the S2 atom.

Palladium Complexes

The chlorido palladium(II) complexes *cis*-[$PdCl_2$(PTA)$_2$] (**11a**) and *cis*-[$PdCl_2$(DAPTA)$_2$] (**11b**) were easily prepared by reacting $PdCl_2$ directly with stoichiometric quantities of the corresponding phosphanes. The *cis* geometry can be deduced from the presence of two ν(Pd–Cl) and ν(Pd–P) bands in the far-IR spectrum. This is consistent with the *cis* geometry of *cis*-[$PdCl_2$(PTA)$_2$], which was structurally characterised.[24,25] Thiolato palladium(II) complexes are easily prepared from the above dichlorido precursor complexes by reaction with the thiol derivatives in the presence of base. This synthetic approach was previously used by us[26] in the preparation of new palladium(II) and platinum(II) complexes showing novel thiolate coordination modes. The palladium thiolato complexes [Pd(SR)$_2$(PR′$_3$)$_2$] (SR = 2-SC_5H_4N, 2-$SC_4H_3N_2$ and PR′$_3$ = PTA, DAPTA) were prepared in good yields and were characterised by various spectroscopic techniques as well as X-ray crystallography (Scheme 2). The [Pd(SR)$_2$(PR′$_3$)$_2$] complexes show only one ν(Pd–P) and ν(Pd–S) band in the far-IR spectrum, which suggests a *trans* configuration about the palladium. This was indeed confirmed by an X-ray crystallographic study of *trans*-[Pd(2-SC_5H_4N)$_2$(PTA)$_2$] (**12a**) and *trans*-[Pd(2-SC_5H_4N)$_2$(DAPTA)$_2$] (**12b**). Molecular structures of these two complexes are shown in Figures 3 and 4, respectively.

The $^{31}P\{^1H\}$ NMR singlet resonances of the complexes are shifted to a higher field than those of the chlorido derivatives; furthermore, there is little difference in the chemical shift between the 2-pyridine and 2-pyrimidine derivatives. Like in the above-mentioned gold(I) complexes, the ^1H NMR spectra show singlet resonances due to equivalent NCH_2P protons of the PTA ligand as well as the AB system assigned to the NCH_2N protons. The DAPTA complexes show geminal H–H coupling for the NCH_2N and NCH_2P protons and, in addition, the P–H and H–H coupling patterns are identical to those observed in the free ligand. In addition, the mass spectra LSIMS+ agree with the mononuclear structures of the four thionate derivatives. No peaks due to any aggregation of metal–phosphane fragments comparable to gold(I) derivatives **1**–**10** are observed.



Scheme 2.

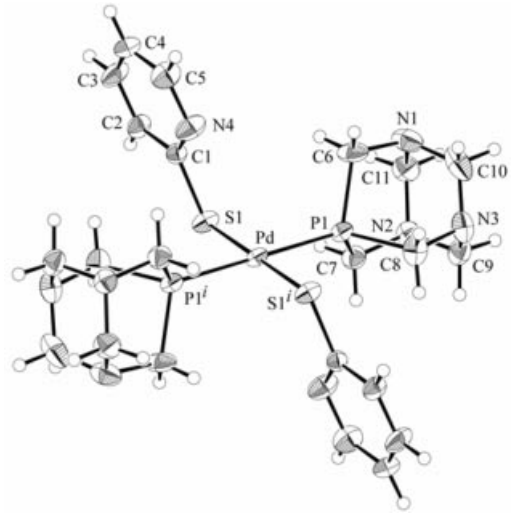


Figure 3. Molecular structure of *trans*-[Pd(SC_5H_4N)$_2$(PTA)$_2$]. Ellipsoids show 35% probability levels. Primed atom related by the symmetry operation *i*: 1 – *x*, 1 – *y*, 1 – *z*. Selected bond lengths [Å] and angles [°]: Pd–S1 2.3411(13), Pd–P1 2.2832(13), S1–C1 1.745(5); S1–Pd–P1 87.44(5).

Compounds **12**–**13** did not show any sign of decomposition even after several months at room temperature. They are insoluble in solvents such as methanol, ethanol, acetone and hexane, and they are partially soluble in CH_2Cl_2, $CHCl_3$, DMSO and H_2O. The solubility in H_2O is similar for all four complexes and is about 10 g/L. It is known that incorporation of the highly water-soluble DAPTA ligand into the coordination sphere of group 10 metal centres leads to water insoluble compounds.[17] We show here that the combination of thiolate and triazaphosphane ligands is a good ligand combination for the synthesis of water-soluble compounds of this group with attractive properties for new applications.

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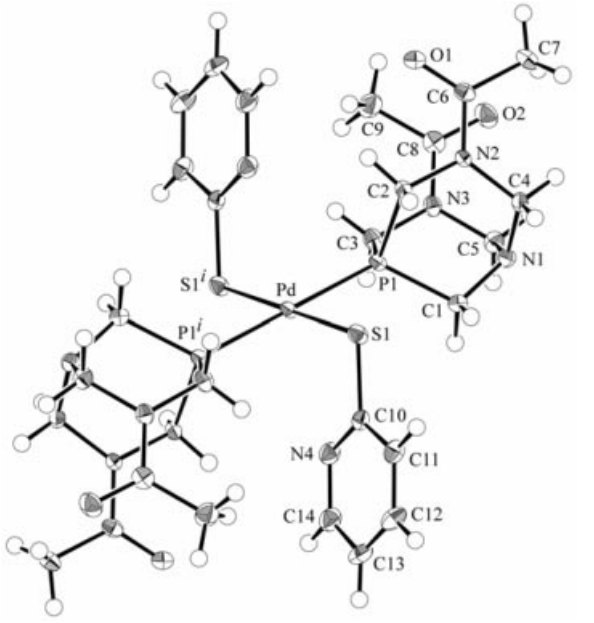

Figure 4. Molecular structure of *trans*-[Pd(SC_5H_4N)$_2$(DAPTA)$_2$]. Ellipsoids show 50% probability levels. Primed atom related by the symmetry operation *i*: 1 – *x*, 1 – *y*, 1 – *z*. Selected bond lengths [Å] and angles [°]: Pd–S1 2.3421(4), Pd–P1 2.2962(4), S1–C1 1.7536(18); S1–Pd–P1 87.092(16).

The palladium atom in *trans*-[Pd(SC_5H_4N)$_2$(PTA)$_2$] (**12a**) lies on a crystallographic centre of inversion and lies within a *trans* N_2S_2 donor set that defines a square-planar geometry. The structure of *trans*-[Pd(SC_5H_4N)$_2$(DAPTA)$_2$] (**12b**) is virtually identical to that just described, which allows the differences in chemistry, and shows virtually the same geometric parameters about the palladium save for the Pd–P1 bond length that is longer than that in *trans*-[Pd(SC_5H_4N)$_2$(PTA)$_2$]. In each case, the pyridine nitrogen atom is directed towards the central palladium atom but the Pd···N4 separations of 3.307(5) and 3.1564(16) Å are not considered to represent significant bonding interactions. Arguably, the most closely related complex in the literature available for comparison is that of *trans*-[Pd(SC_5H_5)$_2${P(H)Cy_2}$_2$][27] for which two independent centrosymmetric molecules comprise the asymmetric unit. Here, the two Pd–S bond lengths are 2.3366(2) and 2.3393(17) Å, with Pd–P of 2.3056(18) and 2.3121(18) Å. These distances are shorter and longer, respectively, than those found in each of *trans*-[Pd(SC_5H_4N)$_2$(PTA)$_2$] and *trans*-[Pd(SC_5H_4N)$_2$(DAPTA)$_2$]. There are no analogous *trans*-PdN_2S_2 structures containing either PTA or DAPTA in the crystallographic literature. However, a protonated form of PTA is found in the crystal structure of *trans*-[Pd(NCS)$_2$($PTAH$)$_2$](NCS)$_2$[28] with Pd–S and Pd–P distances of 2.3509(8) and 2.2940(8) Å, respectively, in the centrosymmetric molecule. Both of these distances are longer than the analogous bonds in *trans*-[Pd(SC_5H_4N)$_2$(PTA)$_2$]. In the crystal structure of *trans*-[Pd(SC_5H_4N)$_2$(PTA)$_2$], molecules associate through C–H···S interactions to form a chain motif along the *a* direction. From symmetry, each molecule forms two donor and two acceptor C–H···S interactions with geometric parameters: C7–H7a···S1^{ii} = 2.74 Å, C7···S1^{ii} = 3.663(5) Å and angle at H7a of 160°; *ii*: –*x*, 1 – *y*, 1 – *z*. By contrast, a three-dimensional architecture is found in the crystal structure of [Pd(SC_5H_4N)$_2$(DAPTA)$_2$] owing to the presence of C–H···O interactions. The O1 atom is bifurcated and forms interactions with the H1b and H5a atoms. The geometric parameters defining these interactions are C1–H1b···O1^{ii} = 2.47 Å, C1···O1^{ii} = 3.357(2) Å and angle at H1b of 152° for *ii*: *x*, 3/2 – *y*, –1/2 + *z*; the parameters for the C5–H5a···O1^{ii} interaction are 2.48 Å, 3.359(2) Å and 151°, respectively.

As commented for the gold complexes, the palladium derivatives were analysed by thermogravimetric analysis showing decomposition to metal (gold or palladium) around 750 °C. This behaviour permits their use as "liquid metal" when deposited on tiles and heated around 800 °C. The water solubility avoids the use of toxic organic solvents for this purpose. As an alternative to thermally induced decomposition, the use of a YAG laser beam focused on the complexes also leads to metal deposition as recently reported by some of us and others.[29,30] The development and optimisation of better metal deposition conditions are in progress.

Conclusions

We report here water-soluble thiolato complexes of gold(I) and palladium(II) that could be used for the preparation of "liquid metals" for metallic deposition. The structures of some derivatives were determined by X-ray crystallography and show a pseudolinear coordination of gold(I) in [Au(S_2CNEt_2)(PTA)] and *trans* square-planar coordination of palladium in *trans*-[Pd(SC_5H_4N)$_2$(PTA)$_2$] and *trans*-[Pd(SC_5H_4N)$_2$(DAPTA)$_2$]; the latter complex is one of the few structurally characterised examples of a compound containing DAPTA.

Experimental Section

General: NMR spectra were recorded with 400 MHz Varian Inova or 400 or 500 MHz Bruker Avance spectrometers. Chemical shifts are quoted relative to external TMS (^{1}H, ^{13}C) or 85% H_3PO_4 (^{31}P). FAB mass spectra were measured with a Micromass Autospec spectrometer in positive ion mode by using NBA as matrix. IR spectra were recorded as KBr or polyethylene disks with Nicolet Impact 410 or JASCO FTIR (far-IR) spectrometers. Elemental analyses were obtained in-house by using a LECO CHNS-932 microanalyser. The phosphanes PTA,[31] DAPTA[17] and [AuCl(tht)][32] as well as [AuCl(PTA)][6] were prepared according to published methods.

DAPTA: ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 2.03 (s, 3 H, CO*Me*), 2.02 (s, 3 H, CO*Me*), 3.20 (dt, $J_{H,H} \approx J_{P,H}$ = 15.2 Hz, $^4J_{H,H}$ = 2.5 Hz, 1 H, NCH_2P), 3.51 (d, $J_{P,H}$ = 11.4 Hz, 2 H, NCH_2P), 3.79 (ddd, $^2J_{H,H}$ = 15.4 Hz, $J_{P,H}$ = 14.7 Hz, $^4J_{H,H}$ = 2.8 Hz 1 H, NCH_2P), 3.95 (d, $J_{H,H}$ = 14.0 Hz, 1 H, NCH_2N), 4.28 (d, $J_{H,H}$ = 15.4 Hz, 1 H, NCH_2P), 4.53 (d, $J_{H,H}$ = 13.8 Hz, 1 H, NCH_2N), 4.93 (d, $J_{H,H}$ = 13.8 Hz, 1 H, NCH_2N), 5.25 (dd, $J_{H,H}$ = 15.2 Hz, J_{P-H} = 2.0 Hz, 1 H, NCH_2P), 5.79 (d, $J_{H,H}$ = 14.0 Hz, 1 H,

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NCH_2N) ppm. $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$, 25 °C): δ = –81.06 ppm. MS EI: *m/z* = 143 [M – 2CH_3CO]$^+$, 186 [M – CH_3CO]$^+$, 229 [M]$^+$, 230 [M + H]$^+$.

Preparation of [AuCl(DAPTA)] (1b): To a solution of [AuCl(tht)] (0.500 g, 1.56 mmol) in CH_2Cl_2 (ca. 50 mL) was added DAPTA (0.357 g, 1.56 mmol). After stirring the mixture for ca. 2 h, the solid products were isolated by filtration, washed with CH_2Cl_2 and Et_2O and dried in vacuo. Yield: 99%, colourless solid. ^1H NMR (400 MHz, [D$_6$]acetone, 25 °C): δ = 2.05 (s, 3 H, CO*Me*), 2.08 (s, 3 H, CO*Me*), 3.84 (d, *J* = 15.7 Hz, 1 H, NCH_2P), 4.12 (s, 2 H, NCH_2P), 4.24 (d, *J* = 14.1 Hz, 1 H, NCH_2N), 4.42 (dt, *J* = 15.7, 2.6 Hz, 1 H, NCH_2P), 4.79 (d, *J* = 14.2 Hz, 1 H, NCH_2N), 4.97 (dd, *J* = 15.2, 7.9 Hz, 1 H, NCH_2P), 5.05 (d, *J* = 14.2 Hz, 1 H, NCH_2N), 5.54 (dd, *J* = 15.6, 9.5 Hz, 1 H, NCH_2P), 5.63 (d, *J* = 14.0 Hz, 1 H, NCH_2N) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, [D$_6$]acetone, 25 °C): δ = –25.65 ppm. FAB MS: *m/z* = 426 [M – Cl]$^+$, 462 [M]$^+$, 655 [M – Cl + DAPTA]$^+$, 887 [M + AuDAPTA]$^+$. $C_9H_{16}AuClN_3O_2P$ (461.6): calcd. C 23.42, H 3.49, N 9.10; found C 24.01, H 3.31, N 9.21.

Preparation of [Au(SR)(PR′$_3$)] Complexes: To a solution of KOH (0.022 g, 0.385 mmol) in MeOH (ca. 10 mL) containing the thiol compound (0.308 mmol) was added [AuCl(PR′$_3$)] (PR′$_3$ = PTA, DAPTA) (0.100 g, 0.257 mmol). After stirring the mixture for ca. 20 h, the solid products were isolated by filtration, washed with H_2O, MeOH and Et_2O and dried in vacuo. In some cases, the [Au(SR)(P)] complexes were soluble in MeOH so a different work up procedure was used. The solution was evaporated to dryness in vacuo, and the residue was extracted with CH_2Cl_2 (3 × 10 mL). The combined extracts were passed through Celite and concentrated in vacuo to ca. 5 mL. Addition of pentane or Et_2O precipitated the products, which were isolated by filtration and dried in air.

[Au(SMepyrim)(PTA)] (2a): Yield: 49%, colourless solid. ^1H NMR (400 MHz, [D$_6$]DMSO, 25 °C): δ = 2.26 (s, 3 H, Me), 4.36 (s, 6 H, CH_2P), 4.40 (d, *J* = 13.1 Hz, 3 H, CH_2N), 4.50 (d, *J* = 13.1 Hz, 3 H, CH_2N), 6.85 (d, *J* = 5.3 Hz, 1 H, pyrim-H^5), 8.18 (d, *J* = 5.1 Hz, 1 H, pyrim-H^6) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, [D$_6$]DMSO, 25 °C): δ = –48.29 ppm. FAB MS: *m/z* = 480 [M]$^+$, 833 [M + AuPTA]$^+$. $C_{11}H_{17}AuN_5PS$ (479.3): calcd. C 27.57, H 3.58, N 14.61; found C 27.50, H 3.75, N 14.30.

[Au(SMepyrim)(DAPTA)] (2b): Yield: 63%, colourless solid. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 2.08, 2.09 (s, 3 H, DAPTA-Me), 2.39 (s, 3 H, Me), 3.75 (dd, *J* = 16.0, 6.3 Hz, 1 H, NCH_2P), 4.03 (s, 2 H, NCH_2P), 4.04 (d, *J* = 15.2 Hz, 1 H, NCH_2N), 4.35 (m, 1 H, NCH_2P), 4.64 (d, *J* = 14.1 Hz, 1 H, NCH_2N), 4.80 (m, 1 H, NCH_2P), 4.90 (d, *J* = 13.9 Hz, 1 H, NCH_2N), 5.64 (dd, *J* = 15.2, 7.4 Hz, 1 H, NCH_2P). 5.74 (d, *J* = 14.2 Hz, 1 H, NCH_2N), 6.75 (d, *J* = 5.3 Hz, 1 H, pyrim-H^5), 8.19 (d, *J* = 5.3 Hz, 1 H, pyrim-H^6) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, 25 °C): δ = –24.88 ppm. FAB MS: *m/z* = 552 [M]$^+$, 978 [M + AuDAPTA]$^+$. $C_{15}H_{24}AuN_5O_2PS$ (551.4): calcd. C 30.50, H 3.84, N 12.70; found C 30.41, H 3.79, N 12.64.

[Au(SMe$_2$pyrim)(PTA)] (3a): Yield: 89%, colourless solid. ^1H NMR (400 MHz, D_2O, 25 °C): δ = 2.50 (s, 6 H, Me), 4.55 (s, 6 H, CH_2P), 4.93 (d, *J* = 12.9 Hz, 3 H, CH_2N), 4.86 (d, *J* = 12.9 Hz, 3 H, CH_2N), 7.12 (s, 1 H, pyrim-H^5) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, D_2O, 25 °C): δ = –35.73 ppm. FAB MS: *m/z* = 494 [M]$^+$, 857 [M + AuPTA]$^+$. $C_{12}H_{19}AuN_5PS$ (493.3): calcd. C 29.22, H 3.88, N 14.20; found C 29.12, H 3.77, N 14.55.

[Au(SMe$_2$pyrim)(DAPTA)] (3b): Yield: 57%, colourless solid. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 2.10 (s, 6 H, DAPTA-Me), 2.35 (s, 6 H, Me), 3.72 (d, *J* = 15.4 Hz, 1 H, NCH_2P), 4.01 (s, 2 H, NCH_2P), 4.08 (d, *J* = 13.7 Hz, 1 H, NCH_2N), 4.32 (d, *J* = 15.4 Hz, 1 H, NCH_2P), 4.66 (d, *J* = 14.7 Hz, 1 H, NCH_2N), 4.75 (dd, *J* = 15.0, 9.5 Hz, 1 H, NCH_2P), 4.93 (d, *J* = 15.1 Hz, 1 H, NCH_2N), 5.65 (dd, *J* = 16.3, 7.3 Hz, 1 H, NCH_2P), 5.77 (d, *J* = 14.2 Hz, 1 H, NCH_2N), 6.60 (s, 1 H, pyrim-H^5) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, 25 °C): δ = –24.82 ppm. FAB MS: *m/z* = 566 [M]$^+$, 991 [M + AuDAPTA]$^+$. $C_{16}H_{26}AuN_5O_2PS$ (565.4): calcd. C 31.87, H 4.10, N 12.39; found C 31.82, H 3.99, N 12.18.

[Au(benzoxazole)(PTA)] (4a): Yield: 85%, pale yellow solid. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 4.37 (s, 6 H, CH_2P), 4.50 (d, *J* = 10.7 Hz, 3 H, CH_2N), 4.53 (d, *J* = 10.7 Hz, 3 H, CH_2N), 7.10 (m, 2 H, benzoxazole-H^2,H^3), 7.34 (d, *J* = 7.8 Hz, 1 H, benzoazole-H^1), 7.46 (d, *J* = 7.8 Hz, 1 H, benzoazole-H^4) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, 25 °C): δ = –52.00 ppm. FAB MS: *m/z* = 505 [M]$^+$, 858 [M + AuPTA]$^+$. $C_{13}H_{16}AuN_4OPS$ (504.3): calcd. C 30.96, H 3.20, N 11.11; found C 30.95, H 3.25, N 11.30.

[Au(benzoxazole)(DAPTA)] (4b): Yield: 60%, colourless solid. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 2.05 (s, 6 H, DAPTA-Me), 3.61 (d, *J* = 16.2 Hz, 1 H, NCH_2P), 3.91 (s, 2 H, NCH_2P), 4.01 (d, *J* = 14.3 Hz, 1 H, NCH_2N), 4.19 (d, *J* = 15.6 Hz, 1 H, NCH_2P), 4.58 (d, *J* = 14.3 Hz, 1 H, NCH_2N) ppm. 4.71 (dd, *J* = 15.9, 10.1 Hz, 1 H, NCH_2P), 4.88 (d, *J* = 14.1 Hz, 1 H, NCH_2N), 5.65 (dd, *J* = 15.7, 7.9 Hz, 1 H, NCH_2P), 5.72 (d, *J* = 14.4 Hz, 1 H, NCH_2N), 7.08–7.17 (m, 2 H, benzoxazole-H^2,H^3), 7.27–7.34 (m, 2 H, benzoazole-H^1,H^4) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, 25 °C): δ = –26.28 ppm. FAB MS: *m/z* = 577 [M]$^+$, 1003 [M + AuDAPTA]$^+$. $C_{16}H_{21}AuN_4O_3PS$ (576.4): calcd. C 33.28, H 3.67, N 9.70; found C 33.36, H 3.53, N 10.06.

[Au(Sbenzothiazole)(PTA)] (5a): Yield: 74%, pale yellow solid. ^1H NMR (400 MHz, [D$_6$]DMSO, 25 °C): δ = 4.42 (s, 6 H, CH_2P), 4.52 (d, *J* = 12.6 Hz, 3 H, CH_2N), 4.40 (d, *J* = 12.6 Hz, 3 H, CH_2N), 7.21 (dt, *J* = 7.1, 1.3 Hz, 1 H, benzothiaz-H^3), 7.33 (dt, *J* = 7.1, 1.3 Hz, 1 H, benzothiaz-H^2), 7.62 (dd, *J* = 8.1, 0.8 Hz, 1 H, benzothiaz-H^4), 7.76 (dd, *J* = 8.1, 0.8 Hz, 1 H, benzothiaz-H^1) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, [D$_6$]DMSO, 25 °C): δ = –48.23 ppm. FAB MS: *m/z* = 521 [M]$^+$, 874 [M + AuPTA]$^+$. $C_{13}H_{16}AuN_4PS_2$ (520.3): calcd. C 30.01, H 3.10, N 10.77; found C 29.99, H 2.90, N 11.11.

[Au(Sbenzothiazole)(DAPTA)] (5b): Yield: 68%, colourless solid. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 2.07 (s, 6 H, DAPTA-Me), 3.75 (d, *J* = 16.0 Hz, 1 H, NCH_2P), 3.99 (s, 2 H, NCH_2P), 4.03 (d, *J* = 14.4 Hz, 1 H, NCH_2N), 4.27 (d, *J* = 15.6 Hz, 1 H, NCH_2P), 4.57 (d, *J* = 14.0 Hz, 1 H, NCH_2N), 4.77 (dd, *J* = 15.6, 9.7 Hz, 1 H, NCH_2P), 4.87 (d, *J* = 14.0 Hz, 1 H, NCH_2N), 5.66 (dd, *J* = 16.0, 7.4 Hz, 1 H, NCH_2P), 5.73 (d, *J* = 14.0 Hz, 1 H, NCH_2N), 7.20 (dt, *J* = 8.2, 0.8 Hz, 1 H, benzothiaz-H^3), 7.32 (dt, *J* = 7.4, 1.2 Hz, 1 H, benzothiaz-H^2), 7.58 (d, *J* = 7.4 Hz, 1 H, benzothiaz-H^4), 7.71 (d, *J* = 8.2 Hz, 1 H, benzothiaz-H^1) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, 25 °C): δ = –28.76 ppm. FAB MS: *m/z* = 593 [M]$^+$, 1018 [M + AuDAPTA]$^+$. $C_{16}H_{20}AuN_4O_2PS_2$ (592.4): calcd. C 32.44, H 3.40, N 9.46; found C 31.94, H 3.40, N 9.46.

[Au(Sbenzimidazole)(PTA)] (6a): Yield: 81%, colourless solid. ^1H NMR (400 MHz, [D$_6$]DMSO, 25 °C): δ = 4.28 (s, 6 H, CH_2P), 4.45 (d, *J* = 12.9 Hz, 3 H, CH_2N), 4.35 (d, *J* = 12.9 Hz, 3 H, CH_2N), 6.98 (dd, *J* = 5.8, 3.0 Hz, 2 H, benzimidaz), 7.24 (br. s, 2 H, benzimidaz), 12.22 (br. s, 1 H, N*H*) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, [D$_6$]-DMSO, 25 °C): δ = –49.90 ppm. FAB MS: *m/z* = 405 [M]$^+$, 857 [M + AuPTA]$^+$. $C_{13}H_{17}AuN_5PS$ (503.3): calcd. C 31.02, H 3.40, N 13.91; found C 30.96, H 3.41, N 13.70.

[Au(Sbenzimidazole)(DAPTA)] (6b): Yield: 58%, colourless solid. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 2.06 (s, 6 H, DAPTA-

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Me), 3.60 (d, *J* = 16.1 Hz, 1 H, NC*H*$_2$P), 3.85 (s, 2 H, NC*H*$_2$P), 4.02 (d, *J* = 14.3 Hz, 1 H, NC*H*$_2$N), 4.18 (d, *J* = 15.6 Hz, 1 H, NC*H*$_2$P), 4.60 (d, *J* = 14.3 Hz, 1 H, NC*H*$_2$N), 4.70 (dd, *J* = 15.9, 10.1 Hz, 1 H, NC*H*$_2$P), 4.89 (d, *J* = 14.1 Hz, 1 H, NC*H*$_2$N), 5.64 (dd, *J* = 15.7, 7.9 Hz, 1 H, NC*H*$_2$P), 5.71 (d, *J* = 14.4 Hz, 1 H, NC*H*$_2$N), 7.08–7.17 (m, 2 H, benzoimidazole-H^2,H^3), 7.27–7.34 (m, 2 H, benzoazole-H^1,H^4) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, 25 °C): δ = –27.26 ppm. FAB MS: *m*/*z* = 576 $[M]^+$, 1002 $[M + AuDAPTA]^+$. $C_{16}H_{21}AuN_5O_2PS$ (575.4): calcd. C 33.40, H 3.68, N 12.17; found C 33.57, H 3.85, N 12.35.

[Au(Sthiazoline)(PTA)] (7a): Yield: 63%, pale yellow solid. ^1H NMR (400 MHz, $[D_6]$DMSO, 25 °C): δ = 3.30 (t, *J* = 8.1 Hz, 2 H, thiazoline), 4.09 (t, *J* = 8.1 Hz, 2 H, thiazoline), 4.36 (s, 6 H, C*H*$_2$P), 4.53 (d, *J* = 12.9 Hz, 3 H, C*H*$_2$N), 4.37 (d, *J* = 12.9 Hz, 3 H, C*H*$_2$N) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $[D_6]$DMSO, 25 °C): δ = –48.62 ppm. FAB MS: *m*/*z* = 473 $[M]^+$, 826 $[M + AuPTA]^+$. $C_9H_{16}AuN_4PS_2$ (472.3): calcd. C 22.89, H 3.41, N 11.86; found C 22.95, H 3.27, N 12.25.

[Au(Sthiazoline)(DAPTA)] (7b): Yield: 65%, colourless solid. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 2.11, 2.12 (s, 3 H, DAPTA-Me), 3.43 (t, *J* = 7.8 Hz, 2 H, thiazoline), 3.72 (d, *J* = 14.4 Hz, 1 H, NC*H*$_2$P), 4.01 (s, 2 H, NC*H*$_2$P), 4.09 (d, *J* = 13.4 Hz, 1 H, NC*H*$_2$N), 4.20 (t, *J* = 8.1 Hz, 2 H, thiazoline), 4.30 (d, *J* = 16.2 Hz, 1 H, NC*H*$_2$P), 4.69 (d, *J* = 14.4 Hz, 1 H, NC*H*$_2$N), 4.76 (m, 1 H, NC*H*$_2$P), 4.94 (d, *J* = 14.1 Hz, 1 H, NC*H*$_2$N), 5.63 (dd, *J* = 15.2, 6.8 Hz, 1 H, NC*H*$_2$P), 5.77 (d, *J* = 14.1 Hz, 1 H, NC*H*$_2$N) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, 25 °C): δ = –32.74 ppm. FAB MS: *m*/*z* = 545 $[M]^+$, 970 $[M + AuDAPTA]^+$. $C_{12}H_{20}AuN_4O_2PS_2$ (544.4): calcd. C 26.48, H 3.70, N 10.29; found C 26.40, H 3.43, N 10.86.

[Au(Et$_2$dtc)(PTA)] (8a): Yield: 83%, pale yellow solid. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.29 (t, *J* = 9.1 Hz, 6 H, C*H*$_3$CH$_2$), 3.84 (q, *J* = 7.1 Hz, 4 H, CH$_3$C*H*$_2$), 4.27 (s, 6 H, C*H*$_2$P), 4.56 (d, *J* = 13.4 Hz, 3 H, C*H*$_2$N), 4.48 (d, *J* = 13.4 Hz, 3 H, C*H*$_2$N) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, 25 °C): δ = –52.92 ppm. FAB MS: *m*/*z* = 502 $[M]^+$, 856 $[M + AuPTA]^+$. $C_{11}H_{22}AuN_4PS_2$ (502.4): calcd. C 26.30, H 4.41, N 11.15; found C 26.24, H 4.16, N 11.35. X-ray quality crystals were obtained by slow diffusion of hexane into a CH_2Cl_2 solution of the complex.

[Au(Et$_2$dtc)(DAPTA)] (8b): Yield: 52%, yellow solid. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.30 (t, *J* = 9.1 Hz, 6 H, C*H*$_3$CH$_2$), 2.09 (s, 6 H, DAPTA-Me), 3.70 (d, *J* = 16.2 Hz, 1 H, NC*H*$_2$P), 3.85 (q, *J* = 7.1 Hz, 4 H, CH$_3$C*H*$_2$), 4.05 (s, 2 H, NC*H*$_2$P), 4.10 (d, *J* = 14.3 Hz, 1 H, NC*H*$_2$N), 4.32 (d, *J* = 15.6 Hz, 1 H, NC*H*$_2$P), 4.73 (d, *J* = 14.3 Hz, 1 H, NC*H*$_2$N), 4.80 (dd, *J* = 15.9, 10.1 Hz, 1 H, NC*H*$_2$P), 4.97 (d, *J* = 14.1 Hz, 1 H, NC*H*$_2$N), 5.60 (dd, *J* = 15.7, 7.9 Hz, 1 H, NC*H*$_2$P), 5.78 (d, *J* = 14.4 Hz, 1 H, NC*H*$_2$N) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, 25 °C): δ = –31.44 ppm. FAB MS: *m*/*z* = 574 $[M]^+$, 1000 $[M + AuDAPTA]^+$. $C_{14}H_{26}AuN_4O_2PS_2$ (574.5): calcd. C 29.27, H 4.56, N 9.75; found C 29.82, H 4.52, N 9.98.

[Au(thiouracil)(PTA)] (9a): Yield: 64%, colourless solid. ^1H NMR (400 MHz, $[D_6]$DMSO, 25 °C): δ = 4.36 (s, 6 H, C*H*$_2$P), 4.41 (d, *J* = 12.9 Hz, 3 H, C*H*$_2$N), 4.49 (d, *J* = 12.9 Hz, 3 H, C*H*$_2$N), 5.86 (d, *J* = 6.3 Hz, 1 H, thiouracil), 7.53 (d, *J* = 6.0 Hz, 1 H, thiouracil), 12.12 (br. s, 2 H, NH) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $[D_6]$DMSO, 25 °C): δ = –48.99 ppm. IR (KBr disk): $\tilde{\nu}$ = 3413 (N–H), 1688 (C=O) cm^{-1}. FAB MS: *m*/*z* = 482 $[M]^+$. $C_{10}H_{16}AuN_5OPS$ (482.3): calcd. C 24.90, H 3.34, N 14.52; found C 25.04, H 3.15, N 14.30.

[Au(thiouracil)(DAPTA)] (9b): Yield: 65%, colourless solid. ^1H NMR (400 MHz, D_2O, 25 °C): δ = 2.09 (s, 6 H, DAPTA-Me), 3.82 (d, *J* = 15.5 Hz, 1 H, NC*H*$_2$P), 4.01 (s, 2 H, NC*H*$_2$P), 4.25 (d, *J* = 14.1 Hz, 1 H, NC*H*$_2$N), 4.34 (d, *J* = 15.6 Hz, 1 H, NC*H*$_2$P), 5.10 (d, *J* = 14.2 Hz, 1 H, NC*H*$_2$N), 5.37 (dd, *J* = 15.9, 10.1 Hz, 1 H, NC*H*$_2$P), 5.49 (d, *J* = 14.1 Hz, 1 H, NC*H*$_2$N), 5.64 (dd, *J* = 15.7, 7.9 Hz, 1 H, NC*H*$_2$P), 5.71 (d, *J* = 14.4 Hz, 1 H, NC*H*$_2$N), 6.08 (d, *J* = 7.04 Hz, 1 H, thiouracil), 7.66 (d, *J* = 7.04 Hz, 1 H, thiouracil) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, D_2O, 25 °C): δ = –29.81 ppm. FAB MS: *m*/*z* = 556 $[M]^+$, 982 $[M + AuDAPTA]^+$. $C_{16}H_{21}AuN_5O_2PS$ (555.3): calcd. C 28.12, H 3.81, N 12.61; found C 28.30, H 3.85, N 12.35.

[Au(Sglucosetetraacetate)(PTA)] (10a): A mixture of [AuCl(PTA)] (0.100 g, mmol), 1-thio-β-D-glucose tetraacetate (0.094 g, mmol) and K_2CO_3 (0.036 g, mmol) in EtOH (10 mL) and water (10 mL) was stirred for ca. 18 h. The solvents were removed under reduced pressure, and the solid residue was extracted with acetone and filtered through Celite. The addition of pentane to the filtrate afforded the colourless product, which was isolated by filtration and dried in air. Yield: 79%, colourless solid. ^1H NMR (400 MHz, $[D_6]$-acetone, 25 °C): δ = 1.83, 1.88, 1.92, 1.94 (s, 3 H, Me), 3.80 (ddd, *J* = 9.8, 4.5, 2.3 Hz, 1 H, H^5), 4.00 (dd, *J* = 12.4, 2.4 Hz, 1 H, C*H*$_2$), 4.13 (dd, *J* = 12.1, 4.5 Hz, 1 H, C*H*$_2$), 4.38 (s, 6 H, C*H*$_2$P), 4.46 (d, *J* = 12.9 Hz, 3 H, C*H*$_2$N), 4.50 (d, *J* = 12.9 Hz, 3 H, C*H*$_2$N), 4.75 (t, *J* = 9.3 Hz, 1 H, H^2), 4.93 (t, *J* = 9.9 Hz, 1 H, H^4), 4.97–5.05 (m, 2 H, H^1, H^3) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $[D_6]$-acetone, 25 °C): δ = –49.18 ppm. $C_{20}H_{31}AuN_3O_9PS$ (717.5): calcd. C 33.48, H 4.35, N 5.86; found C 33.34, H 4.25, N 6.09.

***cis*-[PdCl$_2$(DAPTA)$_2$] and *cis*-[PdCl$_2$(DAPTA)$_2$]:** To a suspension of $[PdCl_2]$ (0.099 g, 0.56 mmol) in CH_2Cl_2 (ca. 20 mL) was added PR′$_3$ = PTA (0.177 g, 1.13 mmol) or DAPTA (0.259 g, 1.13 mmol). After stirring the mixture for ca. 24 h, the yellow solid products were isolated by filtration, washed with CH_2Cl_2 and dried in vacuo.

***cis*-[PdCl$_2$(PTA)$_2$] (11a):** Yield: 96%, yellow solid. ^1H NMR (400 MHz, D_2O, 25 °C): δ = 4.58 (s, 12 H, NC*H*$_2$P), 4.63 (d, *J* = 12 Hz, 6 H, NC*H*$_2$N), 4.57 (d, *J* = 12 Hz, 6 H, NC*H*$_2$N) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, D_2O, 25 °C): δ = –21.6 (s) ppm. IR (nujol): $\tilde{\nu}$ = 281, 271 (Pd–P), 307, 286 (Pd–Cl) cm^{-1}. FAB MS: *m*/*z* = 457 $[M – Cl]^+$. $C_{12}H_{24}Cl_2N_6P_2Pd$ (491.3): calcd. C 29.32, H 4.92, N 17.09; found C 29.73, H 4.76, N 16.85.

***cis*-[PdCl$_2$(DAPTA)$_2$] (11b):** Yield: 93%, yellow solid. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 2.08 (s, 3 H, DAPTA-Me), 2.09 (s, 3 H, DAPTA-Me), 2.39 (s, 6 H, DAPTA-Me), 3.75 (dd, *J* = 16.0, 6.3 Hz, 2 H, NC*H*$_2$P), 4.03 (s, 4 H, NC*H*$_2$P), 4.04 (d, *J* = 15.2 Hz, 2 H, NC*H*$_2$N), 4.35 (m, 2 H, NC*H*$_2$P), 4.64 (d, *J* = 14.1 Hz, 2 H, NC*H*$_2$N), 4.80 (m, 2 H, NC*H*$_2$P), 4.90 (d, *J* = 13.9 Hz, 2 H, NC*H*$_2$N), 5.64 (dd, *J* = 15.2, 7.4 Hz, 2 H, NC*H*$_2$P), 5.74 (d, *J* = 14.2 Hz, 2 H, NC*H*$_2$N) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, 25 °C): δ = –34.20 ppm. IR (nujol): $\tilde{\nu}$ = 277, 245 (Pd–P), 366, 311 (Pd–Cl) cm^{-1}. FAB MS: *m*/*z* = 601 $[M – Cl]^+$, 637 $[M]^+$. $C_{18}H_{32}Cl_2N_6O_4P_2Pd$ (635.8): calcd. C 34.01, H 5.07, N 13.22; found C 33.84, H 4.99, N 12.92.

Preparation of *trans*-[Pd(SR)$_2$(PR′$_3$)$_2$] Complexes: To a solution of the sodium salt of the thiol derivatives (prepared in situ from the thiol and NaOEt) in absolute EtOH was added *cis*-$[PdCl_2(PR'_3)_2]$ (PR′$_3$ = PTA, DAPTA). After stirring the mixture for ca. 24 h, the resulting precipitates were isolated by filtration and washed well with absolute EtOH and dried in air.

***trans*-[Pd(SPy)$_2$(PTA)$_2$] (12a):** Yield: 82%, yellow solid. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 4.14 (s, 12 H, C*H*$_2$P), 4.35 (m, 12 H, C*H*$_2$N), 6.85 (dt, *J* = 6.0, 1.0 Hz, 2 H, Py-H^5), 7.30 (dt, *J* = 7.7, 1.0 Hz, 2 H, Py-H^4), 7.56 (d, *J* = 8.0 Hz, 2 H, Py-H^3), 8.25 (d, *J* = 5.0 Hz, 2 H, Py-H^6) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$,

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Table 1. Crystallographic parameters and refinement details for [Au(S_2CNEt_2)(PTA)], *trans*-[Pd(SC_5H_4N)$_2$(PTA)$_2$] and *trans*-[Pd(SC_5H_4N)$_2$-(DAPTA)$_2$].

Parameter	[Au(S_2CNEt_2)(PTA)]	*trans*-[Pd(SC_5H_4N)$_2$(PTA)$_2$]	*trans*-[Pd(SC_5H_4N)$_2$(DAPTA)$_2$]
Formula	$C_{11}H_{22}AuN_4PS_2$	$C_{22}H_{32}N_8P_2PdS_2$	$C_{28}H_{40}N_8O_4P_2PdS_2$
Fw	502.38	641.02	785.14
Crystal system	orthorhombic	triclinic	monoclinic
Space group	$P2_12_12_1$	$P\bar{1}$	$P2/_1c$
a [Å]	7.2450(3)	6.3722(14)	9.9858(2)
b [Å]	7.9897(4)	10.393(2)	10.4425(2)
c [Å]	27.1870(13)	11.117(2)	15.5161(3)
α [°]	90	65.422(3)	90
β [°]	90	78.909(4)	100.468(2)
γ [°]	90	72.698(3)	90
V [Å^3]	1573.73(13)	637.2(2)	1591.04(5)
Z	4	1 (dimer)	2 (dimer)
μ [cm^{-1}]	9.708	1.047	0.865
D_X [g/cm^3]	2.120	1.670	1.639
No. indep. reflns	3742	2222	5133
No obs. reflns with $I>2\sigma(I)$	3304	1816	3913
R (obs. data)	0.034	0.035	0.025
a in weighting scheme	0.030	0.057	0.040
R_w (all data)	0.068	0.114	0.072
CCDC No.	634748	634749	634750

25 °C): δ = –57.20 ppm. IR (nujol): $\tilde{\nu}$ = 392 (Pd–S), 254 (Pd–P) cm^{-1}. FAB MS: m/z = 530 [M – SPy]$^+$, 484 [M – PTA]$^+$. $C_{22}H_{33}N_8P_2PdS_2$ (641.0): calcd. C 41.22, H 5.03, N 17.48; found C 40.77, H 4.91, N 17.04.

***trans*-[Pd(SPy)$_2$(DAPTA)$_2$] (12b):** Yield: 66%, pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.84 (s, 6 H, DAPTA-Me), 2.05 (s, 6 H, DAPTA-Me), 3.66 (d, *J* = 15.7 Hz, 2 H, NCH_2P), 3.73 (d, *J* = 15.1 Hz, 2 H, NCH_2P), 3.88 (d, *J* = 14.1 Hz, 2 H, NCH_2N), 3.94 (d, *J* = 15.7 Hz, 2 H, NCH_2P), 4.17 (d, *J* = 15.4 Hz, 2 H, NCH_2P), 4.50 (d, *J* = 13.8 Hz, 2 H, NCH_2N), 4.59 (d, *J* = 15.6 Hz, 2 H, NCH_2P), 4.87 (d, *J* = 13.9 Hz, 2 H, NCH_2N), 5.63 (d, *J* = 15.6 Hz, 2 H, NCH_2P), 5.71 (d, *J* = 14.1 Hz, 2 H, NCH_2N), 6.92 (t, *J* = 6.0 Hz, 2 H, SPy-H^5), 7.35 (dt, *J* = 7.8, 1.3 Hz, 2 H, Py-H^4), 7.52 (d, *J* = 7.8, 1.3 Hz, 4 H, SPy-H^3), 8.32 (d, *J* = 4.3 Hz, 2 H, Py-H^6) ppm. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 25 °C): δ = –35.60 ppm. IR (nujol): $\tilde{\nu}$ = 364 (Pd–S), 271 (Pd–P) cm^{-1}. FAB MS: *m/z* = 556 [M – DAPTA]$^+$, 674 [M – SPy]$^+$, 785 [M]$^+$. $C_{28}H_{40}N_8O_4P_2PdS_2$ (785.2): calcd. C 42.83, H 5.14, N 14.27; found C 42.82, H 5.18, N 13.74.

***trans*-[Pd(SPyrim)$_2$(PTA)$_2$] (13a):** Yield: 75%, cream coloured solid. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 4.22 (s, 12 H, CH_2P), 4.41 (m, 12 H, CH_2N), 6.85 (t, *J* = 4.5 Hz, 2 H, pyrim-H^5), 8.35 (d, *J* = 4.5 Hz, 4 H, pyrim-H^4, H^6) ppm. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 25 °C): δ = –57.13 ppm. IR (nujol): $\tilde{\nu}$ = 392 (Pd–S), 256 (Pd–P) cm^{-1}. FAB MS: m/z = 374 [M – PTA – SPyrim]$^+$, 486 [M – PTA]$^+$, 531 [M – SPyrim]$^+$. $C_{20}H_{30}N_{10}P_2PdS_2$ (643.0): calcd. C 37.36, H 4.70, N 21.78; found C 37.20, H 4.88, N 21.52.

***trans*-[Pd(SPyrim)$_2$(DAPTA)$_2$] (13b):** Yield: 80%, pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.74 (s, 6 H, DAPTA-Me), 2.05 (s, 6 H, DAPTA-Me), 3.72 (dd, *J* = 15.4, 2.5 Hz, 2 H, NCH_2P), 3.76 (d, *J* = 15.4 Hz, 2 H, NCH_2P), 3.93 (d, *J* = 14.1 Hz, 2 H, NCH_2N), 4.09 (d, *J* = 15.4 Hz, 2 H, NCH_2P), 4.26 (dd, *J* = 15.7, 2.2 Hz, 2 H, NCH_2P), 4.58 (d, *J* = 14.1 Hz, 2 H, NCH_2N), 4.62 (d, *J* = 15.7 Hz, 2 H, NCH_2P), 4.89 (d, *J* = 14.0 Hz, 2 H, NCH_2N), 5.66 (d, *J* = 15.7 Hz, 2 H, NCH_2P), 5.73 (d, *J* = 13.9 Hz, 2 H, NCH_2N), 6.93 (t, *J* = 4.8 Hz, 2 H, Spyrim-H^5), 8.47 (d, *J* = 4.8 Hz, 4 H, Spyrim-H^4,H^6) ppm. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 25 °C): δ = –37.10 ppm. IR (nujol): $\tilde{\nu}$ = 370 (Pd–S), 262 (Pd–P) cm^{-1}. FAB MS: m/z = 446 [M – SPyrim – DAPTA]$^+$, 558 [M – DAPTA]$^+$, 675 [M – SPyrim]$^+$. $C_{26}H_{38}N_{10}O_4P_2PdS_2$ (787.1): calcd. C 39.67, H 4.87, N 17.79; found C 39.13, H 5.01, N 17.87.

Crystallography: Intensity data for [Au(S_2CNEt_2)(PTA)] (**8a**), *trans*-[Pd(SC_5H_4N)$_2$(PTA)$_2$] (**12a**) and *trans*-[Pd(SC_5H_4N)$_2$-(DAPTA)$_2$] (**12b**) were measured at 293, 230 and 293 K, respectively, with a Xcalibur Oxford Diffraction in the case of **12b** and on a Bruker CCD for **8a** and **12a** fitted with Mo-K_α radiation so that σ_{max} was 28.4, 25.0 and 32.2°, respectively. The structures were solved by heavy-atom methods (SHELXS97) [33] and refinement was on F^2 (SHELXL97)[33] with the use of data that was corrected for absorption effects with an empirical procedure,[34] with non-hydrogen atoms modelled with anisotropic displacement parameters, with hydrogen atoms in their calculated positions, and by using a weighting scheme of the form $w = 1/[\sigma^2(F_o^2) + (aP)^2]$ where $P = (F_o^2 + 2F_c^2)/3$. Disorder was noted in the structure of [Au(S_2CNEt_2)(PTA)] so that two distinct positions were determined for the gold atom. Refinement showed that the major component had a site occupancy factor = 0.807(3). The absolute configuration of [Au(S_2CNEt_2)(PTA)] was determined on the basis of differences in Friedel pairs included in the data sets and confirmed by the near zero value of the Flack parameter [i.e. –0.003(7)].[35] A residual electron density peak of 1.12 e/Å^3 was noted in the final difference map for *trans*-[Pd(SC_5H_4N)$_2$(DAPTA)$_2$], this was located between the Pd and S1 atoms. Molecular structures are shown in Figures 1, 2 and 3 and were generated with ORTEP.[36] Data analyses were performed with PLATON.[37] Crystallographic data and refinement details are given in Table 1. 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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