Dithiophosphinates of gold (I); oxidative addition of Cl_2 to a neutral, dinuclear gold(I) dithiophosphinate complex, and X-ray crystal structures of $[AuS_2P(C_2H_5)_2]_2$, $[AuS_2PPh_2]_2$, $Au_2(CH_2)_2PMe_2(S_2PPh_2)$, and $Au_2Cl_2[(CH_2)_2PMe_2][S_2PPh_2]$

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Abstract: The formation and characterization of dinuclear gold(I) dialkyl- and diaryl-dithiophosphinate complexes of the type $[AuS_2PR_2]_2$ are described. The complexes are readily prepared from the reaction between a chloro–gold(I) starting material and the corresponding dithiophosphinate salt. The structures of the complexes show both the absence (R = Et, 1) and presence (R = Ph, 2a) of intermolecular Au···Au interactions as confirmed by X-ray crystallographic study in the solid state. Reaction between $[AuS_2PPh_2]_2$ and $[Au(CH_2)_2PMe_2]_2$ in CH_2Cl_2 solution leads to a ligand transfer reaction to form the hetero-bridged complex $[Au_2\{(CH_2)_2PMe_2\}\{S_2PPh_2\}]$ (3a) in high yield. Additionally, the latter complex reacts with Cl_2 to form the oxidative addition product $[Au_2Cl_2((CH_2)_2PMe_2)] (S_2PPh_2)]$ (4), the first gold(II) complex with a S-P-S bridging moiety. The X-ray crystal structure of both 3a and 4 exhibit rare boat conformations in the solid state, and 4 has a formal Au(II)—Au(II) single bond of 2.5611(5) Å. Reaction between $[AuS_2PPh_2]_2$ and dppm (dppm = $Ph_2PCH_2PPh_2$) leads to a sparsely soluble three-coordinate dinuclear gold(I) complex with the molecular formula $[Au_2\{dppm\}\{S_2PR_2\}_2]_n$ (n = 1 or ∞) (5).

Key words: dithiophosphinates, ylide, dithiols, gold-gold bond.

Résumé : On décrit la préparation et la caractérisation de complexes dinucléaires de dialkyl- et diaryldithiophosphinates d'or(I), du type $[AuS_2PR_2]_2$. Les complexes se forment facilement par réaction d'un produit de départ contenant du chloro-or(I) avec le sel de dithiophosphinate correspondant. Les structures des complexes montrent dans un cas l'absence (R = Et, 1) et dans l'autre la présence (R = Ph, 2a) d'interactions Au…Au intermoléculaires qui ont été confirmées par une étude cristallographique par diffraction des rayons X à l'état solide. La réaction entre le $[AuS_2PPh_2]_2$ et le $[Au(CH_2)_2PMe_2]_2$, en solution dans le CH_2Cl_2 , donne lieu à une réaction de transfert de ligand qui conduit à la formation, avec un rendement élevé, du complexe hétéroponté $[Au_2\{(CH_2)_2PMe_2\}\{S_2PPh_2\}]$, **3a**. De plus, ce dernier complexe réagit avec le Cl_2 pour former le produit d'addition oxydante $[Au_2Cl_2\{(CH_2)_2PMe_2\}\{S_2PPh_2\}]$, **4**, le premier complexe d'or(II) comportant un pont S-P-S. Les structures de diffraction des rayons X des produits **3a** et **4** montrent toutes les deux la présence de conformations bateaux, rares à l'état solide; de plus, le produit **4** comporte aussi une liaison simple Au(II)—Au(II) de 2,5611(5)Å. La réaction du $[AuS_2PPh_2]_2$ avec le dppm (dppm = $Ph_2PCH_2PPh_2$) conduit à la formation d'un complexe d'or(I) dinucléaire, tricoordiné et à peine soluble de formule moléculaire $[Au_2\{dppm]\{S_2PR_2\}_2]_n$ (n = 1 ou ∞), **5**.

Mots clés : dithiophosphinates, ylure, dithiols, liaison or-or.

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Best wishes to Professor Brian James on this occasion of his 65th birthday anniversary.

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Introduction

The chemistry of gold-sulfur compounds finds significant application ranging from surface science (1) to medicine (2). The use of gold(I) dithiophosphates as sensitizers in photographic films is well established (3). Recently the luminescent properties of gold(I) dithiocarbamates and related materials has been suggested for possible use as photosensors (4). The organophosphor-1,1-dithiolato class of compounds (which includes the dithiophosphinates) have found widespread use as anti-oxidant additives in the oil and petroleum industry (5), insecticide derivatives (6), and metal ore extraction reagents (7). Although the dithiophosphinic acids, R₂P(S)SH, have been known for more than a century (8), gold(I) complexes of these ligands have not been studied extensively. In 1968, Kuchen et al. (9) reported the first examples of gold(I) dithiophosphinate complexes. The complexes were obtained by reduction of gold(III) and required the separation of several by-products. Dinuclearity was suggested for the majority of these compounds based on osmometric molecular weight determinations in chloroform. Further research remained dormant until 1995 when Siasios and Tiekink (10) reported the structure of [AuS₂PPh₂]₂ as the first diaryldithiophosphinate complex of gold. The complex was obtained as a decomposition product, a non-reproducible synthesis, and the structure was determined in the wrong space group, 14.

The first systematic study of gold(I) dithiophosphinate complexes was reported by Schmidbaur and co-workers (11). The main focus of their study was to use dithiophosphinic acid anions $[R_2PS_2]^-$ as potential bidentate ligands to form efficient clustering centers for gold(I) cations, as exemplified by complexes such as $[Ph_2P{Su(PR_3)}_2]^+$ and $Me_2P(S)SAuPR_3$.

As part of our ongoing studies of sulfur compounds of the Group 11 elements, the chemistry of the complexes of dithio-phosphorus ligands, $[AuS_2PR_2]_2$, sulfur analogs of the bis(ylide) complexes (for reviews of this chemistry see, ref. 12), is reported in this study. These materials show both the absence (R = Et) and the presence (R = Ph) of weak intermolecular Au···Au interactions in the solid state. The compound $[AuS_2PEt_2]_2$ was readily prepared from the so-

dium salt of the ligand, Na[S₂PEt₂], and shows a solution ¹H NMR with ${}^{3}J_{P,H}$ larger than ${}^{2}J_{P,H}$. The analog [AuS₂PPh₂]₂ was obtained by a direct synthesis and its structure redetermined. A ligand transfer reaction with an ylide has led to a new, mixed ligand ylide-dithiophosphinate product, which like the previously studied bis(ylide), methylene-thiophosphinate mixed and ligand dithiocarbamate-bis(ylide) products (12), form stable Au(II) derivatives upon oxidation with halogens.

Results and discussion

Preparative methods

The reaction between [Au(tht)Cl] (tht= tetrahydrothiophene) and Na[S₂PEt₂]·2H₂O in THF (molar ratio 1:1) leads to the cyclic dinuclear complex [AuS₂PEt₂]₂ (1). Following extraction of the product into CH₂Cl₂ solution and filtration through anhydrous MgSO₄ to remove water and NH₄Cl, complex 1 was isolated in >70% yield.

Different synthetic methodologies were investigated for the complex $[AuS_2PPh_2]_2$ (2a). Although 2a and its analog $[AuS_2P(C_6H_4-p-Me)_2]_2$ (2b) were isolated in a manner similar to 1, the yield for 2a was only ~50% because of the product's sparse solubility in organic solvents, which hampered an efficient separation from by-products. Significantly improved yields (>75%) were obtained by extraction with water (in which 2a remained stable) to remove NH₄Cl (from the ammonium salt of the ligand and the [Au(tht)Cl] and to obtain the product as a yellow paste, which was dried by consecutively washing with methanol and ether. A third method to prepare 2a was discovered by accident in a reaction shown in Scheme 1. In hot benzene the disulfide Ph₂P(S)S-SP(S)Ph₂ was reduced by cleavage of the S–S bond, in the presence of [(tht)Au(I)Cl], to form the dinuclear complex 2a in ~30% isolable yield. Organic by-products were not identified. Unlike the low thermal stability of the acid Ph₂P(S)SH, which decomposes through rapid elimination of hydrogen sulfide (11), the gold complex 2a appears to have remarkable thermal stability. It was recovered nearly quantitatively from a boiling benzene solution exposed to air for 3 days.

Fig. 1. Drawings of two reasonable structures for the complex $[Au_2\{dppm\}\{S_2PPh_2\}_2]_n$ where n = 1 (top) or $n = \infty$ (bottom) following the reaction between **2a** and dppm.



Fig. 2. View of the molecular structure (50% thermal ellipsoids) of complex **1** showing the atomic labeling scheme. Selected bond lengths (Å) and angles (°): Au(1)-··Au(1A) 3.1822(13), Au(1)--S(1) 2.309(4), Au(1)--S(2) 2.310(4), S(1)--P(1) 2.035(5), P(1)--C(1) 1.780(14) Å; S(1)-Au(1)-S(2) 173.87(13), S(2)-Au(1)-Au(1A) 93.19(10), P(1)-S(1)-Au(1) 100.4(2), S(2A)-P(1)-S(1) 115.0(2)°.



Complexes **3a** and **3b** were formed in good yield (~80%) from the reaction between $[AuS_2PPh_2]$ (2a) and $[AuS_2PEt_2]$ (1), respectively, with $[Au(CH_2)_2PMe_2]_2$ (molar ratio 1:1) in a CH₂Cl₂ solution. The reaction was complete after 20 min. Complexes 3a and 3b are the first reported dinuclear gold(I) complexes with heterobridged phosphor-1,1-dithiolato moieties and bis(ylide) bridging ligands and show some unique structural features (vide infra). Laguna and co-workers (13) previously reported heterobridged complexes with dithiocarbamate $S_2CN(CH_2Ph)_2^-$, and xanthate S_2COR^- , along with bis(ylide) ligands bridging the two gold(I) centers.

Formation of the oxidative addition product $[Au_2Cl_2\{(CH_2)_2PMe_2\}\{S_2PPh_2\}]$ (4) was accomplished with Cl₂ in a CH₂Cl₂ solution. Upon Cl₂ addition the solution immediately turns from colorless to orange. Interestingly, following work-up and isolation of 4, this solid product slowly releases chlorine gas at 140-160°C. The material gradually changes color from orange to colorless without additional decomposition. The compound melts at ~205°C, which is in the same range as the expected reductive elimination product 3a. The elimination of chlorine gas was determined in a separate experiment wherein a saturated starch - NaI solution on filter paper was placed above ~100 mg of 4 that was heated. The chlorine released caused the filter paper to turn purple as expected for iodine formation. This apparently reversible reductive elimination appears related to the reversible CH₂Br addition-elimination observed with $[Au(CH_2)_2PPh_2]_2$ (12), but has not been observed previously with halogens.

The gold(I) complex $[Au_2\{dppm\}\{S_2PPh_2\}_2]_n$ ($n = 1 \text{ or }\infty$) (5) is formed from the reaction between **2a** and dppm (dppm = Ph_2PCH_2PPh_2) in CH_2Cl_2 in good yield. The complex is sparingly soluble in organic solvents, a result which hinders detailed spectroscopic investigation. However, based on limited ¹H NMR data and elemental analysis, two three-coordinate gold(I) structures are consistent with the available data. They are sketched in Fig. 1. Of these compounds, precedence exists for the molecular adduct with cationic complexes of dinuclear gold(I) dithiocarbamates, $[Au_2(\mu-S_2CNEt_2)\{\mu-PPh_2)_2C=CH_2\}_2]^+$, prepared and structurally established by X-ray crystallography (14). The limited solubility of **5** precluded ³¹P{¹H} NMR studies.

Solution ¹H and ³¹P NMR studies

All the complexes reported were studied in solution by ${}^{1}H$ and ${}^{31}P{}^{1}H$ NMR spectroscopy, except **5**. In several cases

Fig. 3. View of the molecular structure (50% thermal ellipsoids) of two adjacent units of the chain of complex **2a** showing the atom labeling scheme (determination 1). Atoms are shown as thermal ellipsoid plots at the 50% probability level. Selected bond lengths (Å) and angles (°): Au(1)—Au(1B) 2.9610(3), Au(1)—Au(1A) 3.0859(3), Au(1)—S(1) 2.3112(10), S(1)—P(1) 2.0265(11), P(1)—C(5) 1.817(6) Å; S(1C)-Au(1)-S(1) 171.29(4), P(1)-S(1)-Au(1) 100.84(5), C(1)-P(1)-C(5) 105.1(2), S(1)-P(1)-S(1A) 116.00(8)°.



interesting and somewhat unexpected NMR results were obtained. Due to the symmetry of **1**, the solution NMR spectrum is simple and consistent with the X-ray structure. Both CH₂ and CH₃ protons couple to the ³¹P nuclei (I = 1/2) giving a doublet of quartets and a doublet of triplets, respectively. The ³J_{P,H} coupling constant (21.78 Hz) is *larger* than the ²J_{P,H} coupling constant (10.98 Hz). This phenomenon is not uncommon in ethyl derivatives of four-coordinate P(V) compounds, which often show a similar behavior (15) with the extent of the three bond coupling depending primarily on the P-C-C-H dihedral angle (16). The same observation was made for the heterobridged complex **3b**. The ethyl groups show coupling constants of ³J_{P,H} = 21.3 Hz and ²J_{P,H} = 7.8 Hz for the CH₃ and CH₂ groups, respectively.

The homoleptic complexes 1, 2a, and 2b each show only a singlet in the ³¹P{¹H} NMR resonating at δ 82.5, 67.4, and 66.6 ppm respectively. The heterobridged complexes 3a and 3b show a doublet, a ⁴J_{P,P} coupling (8–11 Hz at 300 MHz) for each ³¹P nuclei. This coupling was not observed for the oxidative addition product 4 wherein each ³¹P appears as a single resonance. In complex 4 the chemical shift is down field with respect to the unoxidized precursor complex 3a.

Structural studies

The dinuclear gold(I) structures reported in the present study are all neutral eight-membered ring metallocycles in an elongated chair or boat conformation with short transannular Au…Au interactions. Complex 1 does not contain intermolecular Au…Au interactions, which is as observed for the previously reported methyl derivative (10). The molecule crystallizes in the monoclinic space group $P2_1/n$ with an inversion center between the two gold atoms. The structure is shown in Fig. 2.

The structure of 2a was previously reported (10), but several details raised suspicion causing us to further investigate the material. A significant concern was the absence of an inversion center (space group I4) for this molecularly symmetrical molecule. Other troublesome indicators were the unequally sized thermal ellipsoids reported for gold atoms (Z = 79) and large variations in the presumably equal Au—S bond lengths which range from 2.23(2) to 2.38(2) Å. Following a rational synthesis (vide supra), high quality single crystals of 2a were obtained, which allowed for successful structure refinement in the tetragonal space group I4/m. Unlike the methyl and ethyl derivatives which shows no intermolecular Au-Au interactions, the phenyl derivative shows short intermolecular Au. Au contacts of 2.9610(3) Å. This structure was determined at room temperature also for spectroscopic purposes. The results are statistically insignificant for the general structure but the intramolecular Au-Au distance is about 1% longer, and the intramolecular Au-Au distance about 1% shorter at room temperature than at -77°C. The structure of **2a** is shown in Fig. 3.

The complex **3a** crystallizes in the space group $P2_1/c$ with no intermolecular Au···Au interactions. An unusual feature of this structure is that the complex crystallizes in a boat conformation. Few examples of this form apparently exist for dimetallocycle Au(I) compounds (see Lin and co-workers (17)) when compared with the common chair conformation. The carbon atoms C(1) and C(2) were refined with some difficulty since the structure is close to that of a C-centered lattice, suggesting that the symmetry of the molecule is higher than the symmetry of the generated lattice. There also could be some ligand disorder, which would influence C(1) and C(2). The structure of **3a**, for which data was collected three times, is shown in Fig. 4.

Interestingly, the oxidative addition product of chlorine to **3a**, namely **4**, also crystallizes in a boat conformation. The single bond formed between the two Au(II) centers in **4** is clearly demonstrated by the crystallographic study. The intramolecular Au—Au distance decreases from 3.0966(7) Å (standard aurophilic bond) in **3a** to 2.5611(5) Å (single bond) in **4**. The structure is shown in Fig. 5. There is a significant twist of the two 5-membered rings in the molecule about the very short Au(II)–Au(II) bond which presumably arises from the constraints of the two different bridging ligands.

Experimental

General

All reactions and manipulations were carried out under an inert atmosphere with a positive nitrogen gas flow (pre-dried by two columns of Drierite) using standard Schlenk techniques. Solvents were distilled and kept under dinitrogen. The following chemicals were purchased from Aldrich: tetrahydrothiophene, aluminum trichloride, sodium sulfide nonahydrate, thiophosphoryl chloride, bis(diphenylphosphino)methane, ethylbromide. Elemental sulfur was obtained from J.T. Baker. The following compounds were prepared using literature procedures: $Et_2P(S)P(S)Et_2$ (18), $Na[S_2PEt_2]\cdot 2H_2O$ (19), $[NH_4][S_2PPh_2]$ (20),

Fig. 4. Thermal ellipsoid view (50%) of the boat form for the molecular structure of complex **3a** showing the atom labeling scheme. Atoms are represented by thermal ellipsoids at the 50% probability level. Selected bond lengths (Å) and angles (°): Au(1)—Au(2) 3.0966(7), Au(1)—S(1) 2.339(3), Au(2)—S(2) 2.317(3), Au(1)—C(1) 2.052(12),

Au(2)—C(2) 2.080(12), C(1)—P(2) 1.756(14), P(1)—S(1) 2.031(4) Å; C(1)-Au(1)-S(1) 178.4(4),

C(2)-Au(2)-Au(1) 87.9(4), C(5)-P(1)-S(2) 110.2(4),



Instrumentation

Melting points were measured on a Unimelt (A.H. Thomas Co, Philadelphia, PA) capillary melting point apparatus and are uncorrected. Elemental analyses were performed at Desert Analytics Inc., Tucson AZ. ¹H NMR spectra were obtained on a Varian XL-200 spectrometer operating at 200 MHz, or a Varian UnityPlus-300 spectrometer operating at 299.9 MHz. ¹H NMR data are expressed in parts per million (ppm) downfield referenced internally to the residual proton impurity in the deuterated solvent, and are reported as: chemical shift position (¹H NMR (δ)), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constant (*J* (Hz)), relative integral, and assignment. All ³¹P{¹H} NMR spectra were obtained on either a Varian XL 200 MHz broadband spectrometer operating at 81 MHz, or a Varian UnityPlus-300 spectrometer operating at 121.4 MHz with chemical shifts reported relative to a 85% H₃PO₄ in D₂O external standard solution. Positive fast atom bombardment (+FAB-DIP) (DIP = direct insertion probe) mass spectra were acquired on a VG Analytical (Manchester, U.K.) 70S high resolution, double focusing mass spectrometer. Samples for analyses were prepared by dissolving the solid compound in appropriate solvent with a nitrobenzylalcohol (NBA) matrix added.

Fig. 5. Molecular structure of the Au(II)–Au(II) complex **4** showing the atom labeling scheme. Atoms are represented as thermal ellipsoids at the 50% probability level. There is a significant twist to the two chelate rings about the nearly linear Cl-Au-Au-Cl axis with the C(2)-Au(2)-S(2) axis offset by about 20° from the C(1)-Au(1)-S(1) axis. Selected bond lengths (Å) and angles (°): Au(1)—Au(2) 2.5611(5), Au(1)—C(1) 2.075(8), Au(2)—C(2) 2.063(8), Au(1)—Cl(1) 2.392(2), Au(1)—S(1) 2.401(2), Au(2)—S(2) 2.376(2) Å; C(1)-Au(1)-S(1) 177.8(3), Cl(1)-Au(1)-S(1) 91.05(7), S(1)-P(1)-S(2) 113.00(13)°.



X-ray crystallography

Crystals that were used in diffraction intensity measurements at room temperature were mounted on the tip of a quartz fiber with fast-adhesive glue. Single crystal diffraction analysis was carried out on complex 1 at Texas A&M using an automated Nicolet R3 four-circle diffractometer utilizing the Wyckoff scanning technique with graphite monochromated Mo K α ($\lambda = 0.71073$ Å) radiation. Refined cell parameters were determined from setting angles of 25 reflections with $20^{\circ} < 2\theta < 30^{\circ}$. The unit cell was determined using search, center, index, and least-squares refinement routine. The Laue class and lattice dimensions were verified by axial oscillation photography. The intensity data were corrected for absorption, Lorentz, and polarization effects. An empirical absorption correction was performed based on ψ scans of five strong reflections spanning a range of 20 values. All data processing were performed on a Data General Eclipse S140 minicomputer using the SHELXTL crystallographic package (version 5.1) and Siemens SHELXTL PLUS (Micro Vax II) (28). The systematic absences were consistent with the space group assigned. The structure was solved using direct-methods to determine the gold atom positions, while all other atoms were located with difference Fourier maps. Structure refinement was carried out using SHELX 93. The position of the hydrogen atoms were calculated by assuming idealized geometries, C-H = 0.93 Å.

X-ray data for complexes 2a, 3a, and 4 were collected at Harvard University on a Siemens (Bruker) SMART CCD (charge coupled device) based diffractometer equipped with a LT-2 low temperature apparatus operating at 213 K. Data for 2a was collected three times including once at room temperature. A suitable crystal was chosen in each case and mounted on a glass fiber using grease. Data were measured

	1	2a	3a	4
Empirical formula	$C_8H_{20}Au_2P_2S_4$	$C_{24}H_{20}Au_2P_2S_4$	$C_{16}H_{20}Au_2P_2S_4$	$C_{16}H_{20}Au_2Cl_2P_2S_4$
FW	700.35	892.51	732.31	803.21
Crystal system	Monoclinic	Tetragonal	Monoclinic	Triclinic
Space group	$P2_1/n$	I4/m	$P2_{1}/c$	$P\overline{1}$
a (Å)	6.5660(10)	15.8963(4)	7.5146(6)	9.1519(9)
<i>b</i> (Å)	15.606(3)	15.8963(4)	9.0287(7)	9.669(1)
c (Å)	8.338(2)	12.0938(4)	28.734(2)	18.419(1)
α (°)	90	90	90	106.193(2)
β (°)	94.69(3)	90	97.346(2)	95.353(2)
γ (°)	90	90	90	102.084(2)
U (Å ³)	851.5(3)	3056.0(2)	1933.5(3)	1100(2)
$D_{\rm c}~({\rm g}~{\rm cm}^{-1})$	2.731	1.940	2.516	2.424
Z	2	4	4	2
<i>F</i> (000)	640	1664	1344	740
μ (Mo K α) (mm ⁻¹)	17.863	9.979	15.532	13.893
<i>T</i> (K)	293(2)	213(2)	213(2)	213(2)
Theta range (°)	2.61-22.48	1.81-27.62	2.37-22.50	2.26-23.27
Reflections collected	1201	7028	5844	5638
Unique reflections	1093	1709	2508	3145
GoF on F^2	1.073	1.076	1.013	1.098
Final $R[I > 2\sigma(I)]/R_1$, wR_2	0.0389, 0.0973	0.0243, 0.0633	0.0421, 0.0967	0.0384, 0.1086
R (all data)/ R_1 , wR_2	0.0475, 0.1006	0.0305, 0.0683	0.0527, 0.1006	0.0411, 0.1130
$\rho(\text{max. min.})$ (e Å ⁻³)	1.651 and -1.267	0.761 and -0.696	1.999 and -2.194	1.932 and -2.409

Table 1. Crystal data and structure refinement for compounds 1, 2a, 3a, and 4.

using omega scans of 0.3° per frame for 30 s, such that a hemisphere was collected. A total of 1271 frames were collected. The first 50 frames were collected again at the end of the data collection to monitor for decay. Cell parameters were retrieved using SMART software (29) and refined using SAINT on all observed reflections. Data reduction were performed using SAINT software (30) which corrects for Lp and decay. Absorption corrections were applied (semi-empirical from psi-scans) using SADABS (31) supplied by G. Sheldrick. The structures were solved by direct methods using the SHELXS 97 (32) program and refined by least-squares method on F^2 , SHELXL 97 (33). The structures were solved in space groups consistent with analysis of systematic absences. All non-hydrogen atoms were refined anisotropically. The crystals used for diffraction showed no decomposition during data collection. Crystallographic data and structure refinement results are listed in Table 1. Bond lengths and angles are reported in the appropriate figure captions.

Preparation of compounds

$[AuS_2PEt_2]_2$ (1) (9)

A 50-mL Schlenk tube was charged with a solution of $Na[S_2PEt_2]\cdot 2H_2O$ (0.16 g, 0.72 mmol) and [Au(tht)Cl] (0.22 g, 0.70 mmol) in THF (35 mL) and stirred for 1 h at room temperature. The solvent was subsequently evaporated under reduced pressure, the crude mixture was extracted with CH₂Cl₂ (30 mL), active charcoal was added, and the mixture filtered through anhydrous MgSO₄ to remove water and NaCl. The volume of the filtrate was reduced in vacuo to 5 mL, and the clear solution transferred to a 10 mL test-tube, which was transferred to a larger vial that contained hexane. The larger vial was corked and after three

days in the closed system the CH₂Cl₂ solvent diffused into the hexane yielding crystals and trace amounts of dark brown decomposition product (Au₂S?). Crystals of **1** suitable for X-ray crystallographic studies were obtained as colorless plates, yield 0.36 g (73%), mp 153°C. +FAB-MS (NBA/CH₂Cl₂) *m/z*: 701 ([M + 1]⁺). ¹H NMR (200 MHz, CDCl₃, 19°C) & 1.36 (dt, $J_{P,H} = 21.78$ Hz, 12H, 4CH₃), 2.33 (dq, $J_{P,H} = 10.98$ Hz, 8H, 4CH₂). ³¹P NMR (CH₂Cl₂ with 85% H₃PO₄ insert in 85% D₂O, 200 MHz, 20°C) & 82.59 (s). Anal. calcd. for C₈H₂₀P₂S₄Au₂: C 13.72, H 2.88; found: C 13.62, H 2.81.

$[AuS_2PPh_2]_2$ (2a) (9)

Method A: A 50-mL Schlenk tube was charged with a solution of $[NH_4][S_2PPh_2]$ (0.11 g, 0.415 mmol) in THF (40 mL) at room temperature. Upon dissolution, [Au(tht)Cl] (0.131 g, 0.408 mmol) was added in one portion. The solution immediately afforded a white precipitate (NH₄Cl). The mixture was stirred for 1 hour at room temperature. The solvent was removed in vacuo, and CH₂Cl₂ (40 mL) was added to extract the product. The mixture was filtered through anhydrous MgSO₄ (3 mm). The solvent was evaporated under reduced pressure, washed with dry ether, and vacuum dried for 1 hour.

Method B: Similar to Method A, but after THF was removed in vacuo, water (40 mL) was added to dissolve the NH_4Cl . The product (a wet yellow paste, stable in water) was filtered and washed consecutively with methanol and ether. The yellow product was dried in the air.

Method C: To a 100-mL beaker was added a solution of $Ph_2P(S)S-SP(S)Ph_2$ (0.2 g, 0.40 mmol) and [Au(tht)Cl] (0.26 g, 0.80 mmol) in benzene (40 mL) at room tempera-

ture. The mixture was heated to boiling for 20 min, which yielded a clear solution. Upon cooling, a yellow microcrystalline powder was obtained, which was filtered on a frit and washed with ether. Yields: Method A: 55% (some loss occurs due to the limited solubility of the product in CH₂Cl₂.); Method B: 78% (this was our best method); Method C: 28% (as crystallized product), mp 295°C (dec.). +FAB-MS (insolubility of product prevented satisfactory spectrum to be obtained). The complex is partially soluble in chlorinated solvents and THF, and insoluble in ether and hexane. ¹H NMR (300 MHz, CDCl₃, 20°C) & 8.06–7.92 (m, 8H, Ph), 7.58–7.38 (m, 12H, Ph). ³¹P NMR (200 MHz, CDCl₃, 19°C) & 67.43 (s). Anal. calcd. for C₂₄H₂₀P₂S₄Au₂: C 32.32, H 2.24, S 14.33; found: C 32.92, H 2.13, S 13.86.

$[AuS_2P(C_6H_4-p-Me)_2]_2$ (2b)

Starting from $[NH_4][S_2P(C_6H_4-p-Me)_2]$ the toluene derivative was obtained in the same manner as described in Method A for **2a**, yield 77%, mp 275°C. ¹H NMR (200 MHz, CDCl₃, 20°C) δ : 7.90–7.78 (m, 8H, Ph), 7.22–7.12 (m, 8H, Ph), 2.37 (br s, 12H, 4Me). ³¹P NMR (200 MHz, CDCl₃, 20°C) δ : 66.62 (s). Anal. calcd. for C₂₈H₂₈P₂S₄Au₂: C 35.45, H 2.97; found: C 35.62, H 3.08.

$Au_2[(CH_2)_2PMe_2](S_2PPh_2)$ (3a)

A 50-mL Schlenk tube was charged with a solution of 2a (75.8 mg, 0.085 mmol) and [Au(CH₂)₂PMe₂]₂ (48 mg, 0.085 mmol) in CH₂Cl₂ (10 mL) at room temperature. An orange-yellow colored suspension was initially obtained since both starting materials are sparingly soluble in CH₂Cl₂. After the reaction mixture had been stirred for 10 min, a clear orange solution was obtained, and stirring was continued for an additional 20 min, followed by filtration through anhydrous MgSO₄. The filtrate solution was concentrated by evaporation of the solvent under reduced pressure, and ether was added to precipitate the product, which was filtered on a frit and air dried. Colorless blocky crystals suitable for X-ray studies were obtained from a concentrated CH₂Cl₂ solution layered with either ether or hexane, yield 52.3 mg (84%), mp 208°C (dec.). +FAB-MS (NBA/CHCl₃) *m/z*: 733 $([M + 1]^{+})$. ¹H NMR (300 MHz, CDCl₃, 20°C) δ : 8.22–8.08 (m, 4H, Ph), 7.48–7.35 (m, 6H, Ph), 1.24 (d, $J_{PH} = 13.2$ Hz, 4H, 2CH₂), 1.10 (d, $J_{P,H} = 12.6$ Hz, 6H, 2CH₃). ³¹P NMR (300 MHz, CDCl₃, 20°C) & 68.52 (d, $J_{P,P} = 11.9$ Hz, PPh₂), 34.78 (d, $J_{P,P} = 11.9$ Hz, PMe₂). Anal. calcd. for C₁₆H₂₀P₂S₂Au₂: C 26.24, H 2.75; found: C 26.32, H 2.81.

$[Au_2\{(CH_2)_2PMe_2\}\{S_2PEt_2\}]$ (3b)

Prepared in the same fashion as **3a**, but **1** was used as a starting material instead of **2a**, yield 78%. ¹H NMR (300 MHz, CDCl₃, 20°C) & 2.30 (dq, $J_{P,H} = 7.8$ Hz, 4H, 2CH₂CH₃), 1.60 (d, $J_{P,H} = 12.3$ Hz, 6H, 2P-CH₃), 1.38 (dt, $J_{P,H} = 21.3$ Hz, 6H, 2CH₂CH₃), 1.23 (d, $J_{P,H} = 12.3$ Hz, 4H, 2P-CH₂-Au). ³¹P NMR (300 MHz, CDCl₃, 20°C) & 81.93 (d, $J_{P,P} = 7.9$ Hz, PEt₂), 34.20 (d, $J_{P,P} = 7.9$ Hz, PMe₂).

$Au_2Cl_2[(CH_2)_2PMe_2][S_2PPh_2]$ (4)

A 50-mL Schlenk tube was charged with a solution of **3a** (60 mg, 0.082 mmol) in CH_2Cl_2 (8 mL) at room temperature. The solution was cooled to 0°C and PhI·Cl₂ (26 mg, 0.095 mmol) was added in one portion. The solution imme-

diately turned deep orange. The reaction mixture was stirred for 30 min with a gradual increase of temperature until room temperature was reached. The solvent was partially removed under reduced pressure, and subsequently ether was added when the solution became sufficiently concentrated to induce precipitation of the product. The product was filtered, dried under vacuum for 2 h, and stored in a refrigerator, yield 78%, mp at ~ 205°C. +FAB-MS (NBA/CHCl₃) m/z: is similar to 3a, ([M - Cl₂]⁺). ¹H NMR (CDCl₃, 300 MHz, 20°C) δ: 8.05-7.90 (m, 4H, Ph), 7.60-7.40 (m, 6H, Ph), 2.05 (d, $J_{P,H} = 7.79$ Hz, 4H, 2CH₂), 1.81 (d, $J_{P,H} = 8.19$ Hz, 6H, 2CH₃). ³¹P NMR (300 MHz, CDCl₃, 20°C) &: 70.06 (s, no ${}^{4}J_{P,P}$ coupling detected, PPh₂), 42.02 (s, no ${}^{4}J_{P,P}$ coupling detected, PMe₂). Anal. calcd. for C₁₆H₂₀Cl₂P₂S₂Au₂: C 23.92, H 2.51; found: C 22.84, H 2.49 (some loss of Cl₂ is expected). Orange needles suitable for X-ray crystallographic studies were obtained from a concentrated CH₂Cl₂ solution layered with hexane.

$[Au_{2}\{dppm\}\{S_{2}PPh_{2}\}_{2}]_{n}$ (5)

A 50-mL Schlenk tube was charged with a solution of 2a (0.1 g, 0.11 mmol) in CH₂Cl₂ (10 mL) at room temperature. To the yellow suspension was added dppm (0.043 g, 0.11 mmol) in one portion. The initial suspension became a clear solution after a few minutes, followed by formation of a white precipitate that emerged after 30–40 min. The solvent was subsequently removed under reduced pressure until a concentrated solution was obtained. Ether was added in excess to precipitate and consolidate the solid. The product was filtered on a frit and washed with ether. The product is a white solid and is sparingly soluble in polar and non-polar solvents, yield 72%, mp 227°C. ¹H NMR (300 MHz, CDCl₃, 20° C) δ : 8.28–8.12 (m, 8H, Ph), 7.80–7.62 (m, 12H, Ph), 7.50-7.35 (m, 8H, Ph), 7.26-7.10 (m, 12H, Ph), 4.26 (br s, 2H, PCH₂P). Anal. calcd. for C₄₉H₄₂P₄S₄Au₂: C 46.09, H 3.32, S 10.04; found: C 45.07, H 3.42, S 8.83.

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