Diversity in the Structural Chemistry of (Phosphine)gold(I) 1,3,4-Thiadiazole-2,5-dithiolates (Bismuthiolates I)

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A series of dinuclear (phosphine)gold(I) complexes of the ambidentate 1,3,4-thiadiazoledithiolate ligand (SSS) were prepared in high yield from the corresponding (phosphine)gold(I) chlorides and $K_2(SSS)$ in methanol. While mononuclear components $(R_3P)AuCl$ with $R_3 = Ph_3$, Ph_2Py, or Me_3 (**1−3**) gave open-chain complexes, the dinuclear components $ClAu(Ph_2P-E-PPh_2)AuCl$ with $E = (CH_2)_6$, $(C_5H_4)Fe(C_5H_4)$, or $1,4-CH_2C_6H_4CH_2$ afforded cyclic complexes (**4−6**). The products have been characterized by analytical and spectroscopic methods, and the crystal structures of **1−4** have been determined by single-crystal X-ray techniques. Crystals of **1** $[(CH_2Cl_2)_2]$ and **2** (CH_2Cl_2) contain the molecules aggregated in strings with long and probably very weak intermolecular Au···S contacts. The P−Au−S groups are aligned parallel head-to-tail and shifted in opposite directions to reduce steric conflicts, thus ruling out aurophilic Au···Au bonding. By contrast, in crystals of **3** (CH_2Cl_2) with smaller tertiary phosphine ligands, the molecules are aggregated via short [3.0089(3) and 3.1048(5) Å] and probably strong aurophilic bonding to give a two-dimensional network with tetranuclear units formed from four $(Me_3P)AuS$ moieties of four different molecules as the connecting elements. In these tetranuclear units $[(Me_3P)AuS-]_4$, the P−Au−S axes are rotated against each other ("crossed swords") by 108.5° (P2−Au2···Au2′−P2′) or 116.9° (P2−Au2···Au1′−P1′), respectively, to minimize steric conflicts. There is also significant bending of the P−Au−S axes to bring the metal atoms closer together: P1−Au1−S1 = 171.88(8)° and P2−Au2−S2 = 165.52(8)°. In the crystals of the cyclic complex **4** which contain no solvent molecules, the molecular units are aggregated in strings with short closed-shell interactions between the gold atoms of neighboring molecules [3.1898(3) Å]. Because of the metallocyclic structure, the shielding of the gold atoms is reduced to allow aurophilic bonding as the P−Au−S groups are rotated against each other (crossed) by a dihedral angle P−Au···Au−P of 74.6°.

Introduction

Gold thiolates are by far the most important class of gold compounds. Complexes of the type AuSR or LAuSR (R = alkyl, aryl, etc.; L = neutral donor ligand) are the basis of most classical "liquid golds" for the glass and ceramics industry,[1,2] of gold pastes used in the electrical industry and in microelectronics,[3] and of gold drugs in chemotherapy.[4] Gold thiolate functions are the key connectivities between the surface of bulk gold and the substrate films in self-assembly monolayer nanotechnology.[3] The high affinity of gold for the heavy chalcogen elements (sulfur, selenium, and tellurium) allows the synthesis of many Au−S, −Se, and −Te preparations from gold salts and thiols or thiolates, although most of these compounds are thermodynamically unstable relative to gold metal and organic disulfides. The affinity of gold for thioethers is much lower, but $(R_2S)AuX$ complexes are, nevertheless, often very useful components in reactions with gold compounds.

In the present study, 1,3,4-thiadiazole-2,5-dithiol was chosen as a complexing agent for gold(I) because it offers both thiol and thioether functionalities in close proximity. It thus should be an ideal substrate for the construction of multinuclear complexes with metals attached to no less than three sulfur atoms. With the given ligand geometry, aurophilic bonding between these metal atoms could further improve the stability of the assembly. It could also give rise to interesting photophysical properties, as amply demonstrated for some related systems which exhibit intense photoluminescence.[5]

The rigid molecular geometry of the ligand as compared to flexible α,ω-dithiols[6] was expected to have a template function in the aggregation of the complexes in the solid state and to induce the formation of multidimensional patterns. It should also be instrumental in the construction of macrocycles with suitable wide-span difunctional auxiliary donor molecules.

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Table 1. Crystal Data, Data Collection, and Structure Refinement of Compounds **1**−**4**

	[(Ph$_3$P)Au]$_2$(SSS)·2CH$_2$Cl$_2$ (**1**)	[(PyPh$_2$P)Au]$_2$(SSS)·CH$_2$Cl$_2$ (**2**)	[(Me$_3$P)Au]$_2$(SSS)·CH$_2$Cl$_2$ (**3**)	[(CH$_2$)$_3$PPh$_2$)Au]$_2$(SSS) (**4**)
		Crystal Data		
formula	C$_{40}$H$_{34}$Au$_2$Cl$_4$N$_2$P$_2$S$_3$	C$_{37}$H$_{30}$Au$_2$Cl$_2$N$_4$P$_2$S$_3$	C$_9$H$_{20}$Au$_2$Cl$_2$N$_2$P$_2$S$_3$	C$_{32}$H$_{32}$Au$_2$N$_2$P$_2$S$_3$
fw	1236.55	1153.60	779.22	996.65
crystal system	triclinic	monoclinic	orthorhombic	monoclinic
space group	$P\bar{1}$	$P2_1/c$	$P2_12_12$	Cc
a (Å)	9.2693(2)	18.1244(3)	19.6269(4)	16.3301(2)
b (Å)	13.4776(3)	14.9068(2)	9.8542(1)	11.3261(2)
c (Å)	18.4608(4)	15.2270(2)	10.5076(2)	18.3039(2)
α (deg)	103.874(1)	90	90	90
β (deg)	96.776(1)	113.801(1)	90	107.392(2)
γ (deg)	106.873(1)	90	90	90
V (Å^3)	2098.5(1)	3764.1(1)	2032.3(1)	3230.7(1)
ρ_{calc} (g cm^{-3})	1.957	2.036	2.547	2.049
Z	2	4	4	4
μ(Mo Kα) (cm^{-1})	74.96	82.14	151.14	93.90
abs correction/$T_{min/max}$	SCALEPACK[34]	DELABS/0.311/0.747	DELABS/0.211/0.678	DELABS/0.464/0.825
		Data Collection		
T (°C)	−120	−130	−130	−130
scan mode	φ rotation	φ rotation	φ rotation	φ rotation
measured reflns	73 330	86 251	40 295	37 623
unique reflns	10 383 [R_{int} = 0.0450]	12 549 [R_{int} = 0.0800]	6333 [R_{int} = 0.0677]	10 505 [R_{int} = 0.0606]
		Refinement		
refined params	615	451	182	370
final R values [$I > 2\sigma(I)$]				
R1^a	0.0431	0.0524	0.0479	0.0315
wR2^b	0.1216	0.1044	0.1245	0.0836
Flack parameter			0.07(1)	0.005(6)

^{a} R1 = $\sum(||F_o| - |F_c||)/\sum|F_o|$. ^{b} wR2 = $\{[\sum w(F_o{}^2 - F_c{}^2)^2]/\sum[w(F_o{}^2)^2]\}^{1/2}$; $w = 1/[\sigma^2 F_o{}^2 + (ap)^2 + bp]$; $p = (F_o{}^2 + 2F_c{}^2)/3$; a = 0.0797 (**1**), 0.0000 (**2**), 0.0678 (**3**), 0.0000 (**4**); b = 4.08 (**1**), 20.99 (**2**), 11.04 (**3**), 0.00 (**4**).

1,3,4-Thiadiazoledithiol has been used in the past as a ligand for many main-group and transition-metal cations from various parts of the periodic table,[7−11] but it appears that gold was included in these studies only in passing.[12] Because of the low solubility of the bismuth(III) salt, which makes the dithiol a specific reagent for Bi(III) in analytical chemistry, 1,3,4-thiadiazoledithiol has, for some time, been referred to as "Bismuthiol I"; however, this nomenclature has fallen out of use.

The work in this laboratory has also recently considered 2-amino-1,3,4-thiadiazole-5-thiol as a ligand for gold(I).[13] The results have shown that this closely related aminothiol can give rise to a variety of structural designs, including connectivities between the molecular units based on closed-shell Au−Au and Au−S interactions and hydrogen bonding.

Experimental Section

General Information. Experiments were carried out routinely in air. Instruments were an NMR JEOL GX 400 spectrometer using deuterated solvents with the usual standards at 25 °C and an MS Varian MAT311A instrument (FAB, *p*-nitrobenzyl alcohol). 2,5-Dimercapto-1,3,4-thiadiazole dipotassium salt (KSSSK) is commercially available. The complexes [R$_3$PAuCl] (R = Me or Ph),[14] [ClAuPPh$_2$(2-Py)],[15] and [PP(AuCl)$_2$] (PP = 1,6-bis(diphenylphosphino)hexane (dpph),[16] 1,1′-

bis(diphenylphosphino)ferrocene (dppf),[17] or α,α′-bis(diphenylphosphino)-*p*-xylene (dppx))[18] were prepared by following literature procedures.

[(Ph$_3$P)Au]$_2$(SSS) (1). A solution of KSSSK (69 mg, 0.31 mmol) in methanol (5 mL) was added dropwise to a stirred solution of [Ph$_3$PAuCl] (300 mg, 0.61 mmol) in dichloromethane (20 mL). After being stirred for 2 h, all of the solvent was removed under vacuum. The residue was dissolved in dichloromethane (20 mL) and filtered through diatomaceous earth to remove KCl. Pentane (25 mL) was added to precipitate the colorless product in 95% (310 mg) yield. MS (FAB) *m/e*: 1066, 41% [M]$^+$, 720, 30% [Au(PPh$_3$)$_2$]$^+$, 459, 100% [AuPPh$_3$]$^+$. ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): 38.9 (s) ppm. ^{1}H NMR (CD$_2$Cl$_2$): 7.45−7.60 (m, C$_6$H$_5$) ppm. ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): 166.8 (s, N$_2$C$_2$S$_3$), 134.2 (d, *o/m*-C$_6$H$_5$, J_{CP} = 14.0 Hz), 131.8 (d, *p*-C$_6$H$_5$, J_{CP} = 2.6 Hz), 129.2 (d, *o/m*-C$_6$H$_5$, J_{CP} = 11.4 Hz), 129.1 (d, *ipso*-C$_6$H$_5$, J_{CP} = 58.1 Hz) ppm. Anal. Calcd for C$_{38}$H$_{30}$Au$_2$N$_2$P$_2$S$_3$: C, 42.79; H, 2.84; N, 2.63. Found: C, 42.32; H, 2.52; N, 2.39.

[(PyPh$_2$P)Au]$_2$(SSS) (2). A solution of KSSSK (46 mg, 0.20 mmol) in methanol (10 mL) was added dropwise to a stirred solution of [PyPh$_2$PAuCl] (200 mg, 0.40 mmol) in dichloromethane (20 mL). After being stirred for 2 h, all of the solvent was removed under vacuum. The residue was dissolved in dichloromethane (15 mL) and filtered through diatomaceous earth to remove KCl. Pentane (20 mL) was added to precipitate the colorless product in 83% (180 mg) yield. MS (FAB) *m/e*: 807, 19% [M − PPh$_2$Py]$^+$, 724, 30% [Au(PPh$_2$Py)$_2$]$^+$, 460, 100% [Au(PPh$_2$Py)]$^+$. ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): 37.5 (s) ppm. ^{1}H NMR (CDCl$_3$): 7.37−7.81 (m, C$_6$H$_5$), 8.06 (t, Py, J_{HH} = 7.7 Hz), 8.77 (d,

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Py, J_{HH} = 4.4 Hz) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$): 167.3 (s, N$_2$C$_2$S$_3$), 154.3 (d, C^{1}Py, J_{CP} = 81.5 Hz), 151.2 (d, C^{2}Py, J_{CP} = 15.4 Hz), 136.8 (d, C^{3}Py, J_{CP} = 10.8 Hz), 134.6 (d, o/m-C$_6$H$_5$, J_{CP} = 13.8 Hz), 131.9 (d, p-C$_6$H$_5$, J_{CP} = 2.3 Hz), 131.4 (d, ipso-C$_6$H$_5$, J_{CP} = 32.3 Hz), 129.1 (d, o/m-C$_6$H$_5$, J_{CP} = 12.3 Hz), 128.5 (s, C^{4}Py), 125.4 (d, C^{5}Py, J_{CP} = 2.3 Hz) ppm. Anal. Calcd for C$_{36}$H$_{28}$Au$_2$N$_4$P$_2$S$_3$·2CH$_2$Cl$_2$: C, 36.85; H, 2.60; N, 4.52. Found: C, 36.39; H, 2.44; N, 4.67.

[(Me$_3$P)Au]$_2$(SSS) (3) was prepared in an 84% yield in a similar manner using [Me$_3$PAuCl] instead of [Ph$_3$PAuCl]. MS (FAB) m/e: 694, 17% [M]$^+$. ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): 1.6 (s) ppm.^{1}H NMR (CD$_2$Cl$_2$): 1.59 (d, CH$_3$, J_{HP} = 11.0 Hz) ppm. Anal. Calcd for C$_8$H$_{18}$Au$_2$N$_2$P$_2$S$_3$: C, 13.84; H, 2.61; N, 4.03. Found: C, 13.70; H, 2.74; N, 3.95.

[(dpph)Au$_2$](SSS) (4). A solution of KSSSK (24 mg, 0.11 mmol) in methanol (5 mL) was added dropwise to a stirred solution of [dpph(AuCl)$_2$] (100 mg, 0.11 mmol) in dichloromethane (20 mL). After being stirred for 3 h, all of the solvent was removed under vacuum. The residue was dissolved in dichloromethane (20 mL) and filtered through diatomaceous earth to remove KCl. Pentane (25 mL) was added to precipitate the colorless product in 65% (70 mg) yield. MS (FAB) m/e: 996, 100% [M]$^+$, 651, 63% [Au(dpph)]$^+$. ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): 30.7 (s) ppm. ^{1}H NMR (CD$_2$Cl$_2$): 0.86, 1.25, 1.46, 1.58, 2.39 (s × 6, −CH$_2$−), 7.47−7.67 (m, C$_6$H$_5$) ppm. Anal. Calcd for C$_{32}$H$_{32}$Au$_2$N$_2$P$_2$S$_3$: C, 38.56; H, 3.24; N, 2.81. Found: C, 38.05; H, 3.32; N, 2.49.

[(dppx)Au$_2$](SSS) (5). A solution of KSSSK (24 mg, 0.11 mmol) in methanol (5 mL) was added dropwise to a stirred solution of [dppx(AuCl)$_2$] (100 mg, 0.11 mmol) in dichloromethane (20 mL). After being stirred for 0.5 h, all of the solvent was removed under vacuum. The residue was dissolved in dichloromethane (20 mL) and filtered through diatomaceous earth to remove KCl. Pentane (25 mL) was added to precipitate the colorless product in 46% (50 mg) yield. MS (FAB) m/e: 1016, 9% [M]$^+$. ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): 31.0 (s) ppm. ^{1}H NMR (CD$_2$Cl$_2$): 3.56, 3.59 (s × 2, −CH$_2$−), 6.92 (s, C$_6$H$_4$), 7.39−7.66 (m, C$_6$H$_5$) ppm. Anal. Calcd for C$_{34}$H$_{28}$Au$_2$N$_2$P$_2$S$_3$: C, 40.17; H 2.78; N, 2.76. Found: C, 39.87; H, 2.90; N, 2.38.

[(dppf)Au$_2$](SSS) (6). A solution of KSSSK (22 mg, 0.10 mmol) in methanol (5 mL) was added dropwise to a stirred solution of [dppf(AuCl)$_2$] (100 mg, 0.10 mmol) in dichloromethane (20 mL). After being stirred for 2 h, all of the solvent was removed under vacuum. The residue was dissolved in dichloromethane (20 mL) and filtered through diatomaceous earth to remove KCl. Pentane (25 mL) was added to precipitate the pale-yellow product in 65% (70 mg) yield. MS (FAB) m/e: 1096, 39% [M]$^+$, 751, 22% [Au(dppf)]$^+$. ^{31}P{^{1}H} NMR (C$_6$D$_6$/CD$_2$Cl$_2$, 1:1): 33.3 ppm. ^{1}H NMR (C$_6$D$_6$/CD$_2$Cl$_2$, 1:1): 4.39, 4.79 (s(br) × 2, C$_5$H$_4$), 7.42−7.48 (m, C$_6$H$_5$) ppm. Anal. Calcd for C$_{36}$H$_{28}$Au$_2$FeN$_2$P$_2$S$_3$: C, 39.43; H, 2.57; N, 2.56. Found: C, 39.61; H, 3.04; N, 2.85.

X-ray Crystallography. Specimens of a suitable quality and size of compounds **1**−**4** were mounted on the ends of quartz fibers in F06206R oil and used for intensity data collection on a Nonius DIP2020 diffractometer, using graphite-monochromated Mo Kα radiation (Table 1). Intensity data of all of the compounds were corrected using the program SCALEPACK. Data of compounds **2**−**4** were further corrected for absorption effects (DELABS from PLATON). The structures were solved by a combination of direct methods (SHELXS-97) and difference Fourier syntheses and refined by full-matrix least-squares calculations on F^2 (SHELXL-97). The thermal motion was treated anisotropically for all of the non-hydrogen atoms. All of the hydrogen atoms were calculated and allowed to ride on their parent atoms with fixed isotropic contributions.

Preparative Results

The potassium salt of 1,3,4-thiadiazole-2,5-dithiol K$_2$(SSS) is commercially available. It is a convenient reagent for (phosphine)gold chlorides in methanol as a solvent. Mononuclear substrates LAuCl with L = triphenylphosphine, diphenyl(1-pyridyl)phosphine, or trimethylphosphine as the auxiliary ligands have been employed in the molar ratio 1:2 to give dinuclear complexes of the type LAu(SSS)AuL (**1**−**3**). Di-

Scheme 1
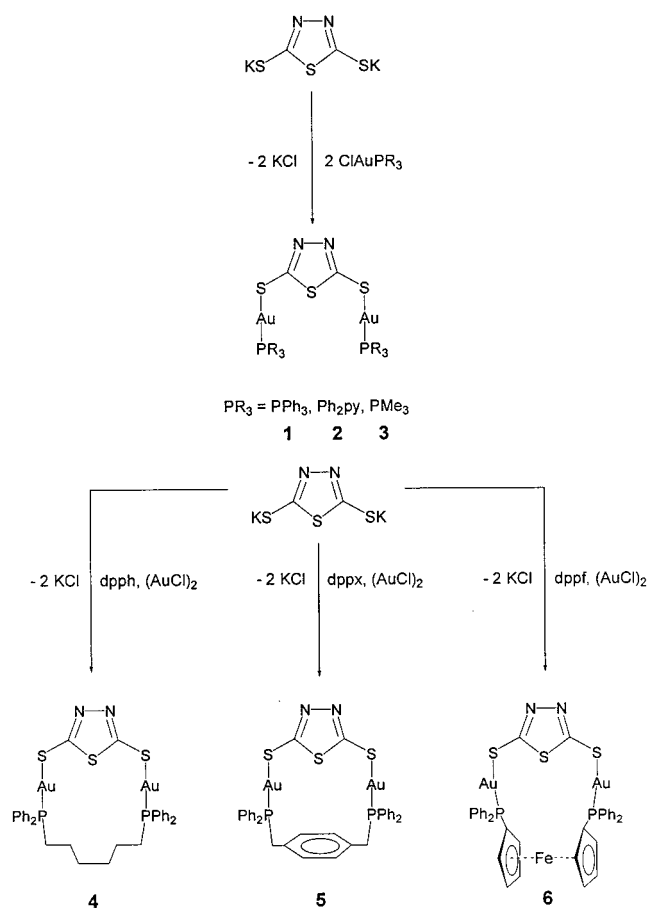
nuclear substrates ClAuL−LAuCl with difunctional ligands L−L = 1,6-bis(diphenylphosphino)hexane, α,α′-bis(diphenylphosphino)-p-xylene, and 1,1′-bis(diphenylphosphino)ferrocene were added in a 1:1 molar ratio to afford cyclic or oligomeric dinuclear products (**4**−**6**; Scheme 1).

Compounds **1**−**5** were generally obtained in high yields as colorless crystalline solids. The ferrocene derivative **6** is a pale-yellow solid. The composition of the compounds has been confirmed by microanalysis. The mass spectra of the complexes show the parent ion with high intensity, and the ^{1}H, ^{13}C, and ^{31}P NMR spectra are in agreement with the proposed structures. Only one set of resonances is obtained for the L−Au or Au−L−L−Au units, indicating the symmetrical bonding of these moieties at the five-membered ring. Compounds **1**−**4** could be obtained as single crystals, and their structures have been determined.

Crystal and Molecular Structures

Compound **1** [(Ph$_3$P)Au]$_2$(SSS) crystallizes (from dichloromethane layered with pentane) in the triclinic space group $P\bar{1}$ with two molecules of the complex and four molecules of dichloromethane in the unit cell. These molecules have no crystallographically imposed symmetry. The ring system and the thiolate sulfur atoms are coplanar, and one Ph$_3$PAu group is above and one below the ring plane (Figure 1), but as shown by the two dihedral angles Au1−S1−C1−S3 and Au2−S2−C2−S3 (144.8 and 46.4°, respectively), the two Ph$_3$PAu groups are folded away in opposite directions. Therefore, there is no approximation to point groups C_2 or C_s. The P−Au−S groups are close to linear, and the two Au−P and two Au−S distances are equivalent within the limits of standard deviations (see the
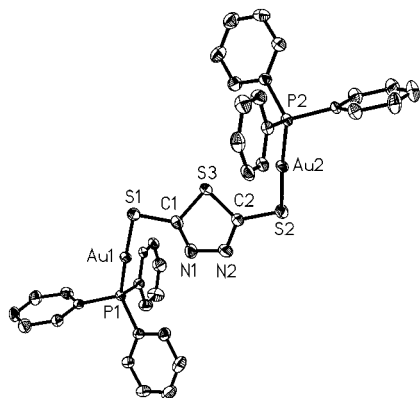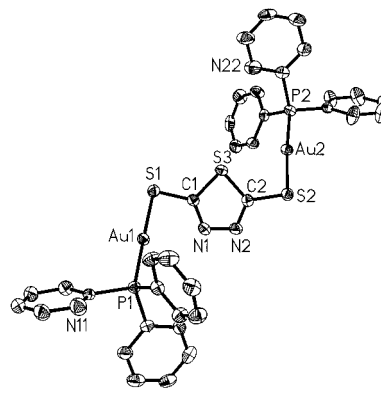
Figure 1. Molecular structure of [(Ph₃P)Au]₂(SSS) (**1**) (ORTEP drawing with 50% probability ellipsoids and H atoms omitted for clarity). Selected bond lengths [Å] and angles [deg]: Au1−P1 = 2.252(1), Au1−S1 = 2.314(1), Au2−P2 = 2.255(1), Au2−S2 = 2.304(1); P1−Au1−S1 = 176.18(4), P2−Au2−S2 = 176.18(4), Au1−S1−C1−S3 = 144.8, Au2−S2−C2−S3 = 46.4.
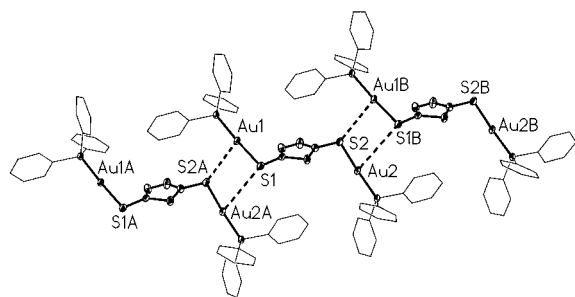

Figure 2. Chain structure of compound **1** showing the shortest intermolecular contacts Au1···S2A (3.85 Å) and Au2···S1B (4.24 Å). The distance Au1···Au2A is 4.872 Å.

caption to Figure 1). The shortest intermolecular contacts are those between the gold and sulfur atoms of neighboring molecules [Au1···S2A = 3.850 Å] and not between the gold atoms (4.872 Å) (Figure 2). This is not really surprising because steric effects of the triphenylphosphine ligands can prevent a closer approach of metal atoms. The two neighboring P−Au−S axes are arranged parallel and head-to-tail, as in the crystals of many other (R₃P)AuX compounds, but the two triples are shifted either to minimize steric repulsion or to optimize crystal packing. This brings the gold and sulfur atoms closer together. An analogous packing (or no close contacts at all) has been observed with several other (Ph₃P)AuSR′ and (RNC)AuSR′ complexes, generally in dimers,[19−23] whereas, for compound **1**, strings of molecules are formed, owing to the dinuclearity of the complex.

Crystals of compound **2**, [(PyPh₂P)Au]₂(SSS) (also from dichloromethane/pentane), are not isomorphous with those of **1** but were found to be monoclinic of the space group $P2_1/c$ with $Z = 4$ molecules of the complex and four solvent molecules in the unit cell. Both the conformation of the individual molecules and their aggregation are similar to that of the Ph₃P analogue, and there are only very minor differences, even in the details. The dihedral angles Au1−S1−C1−S3 and
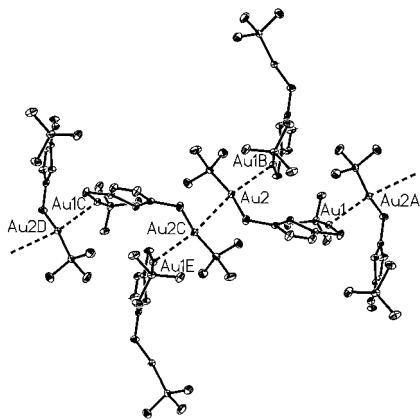
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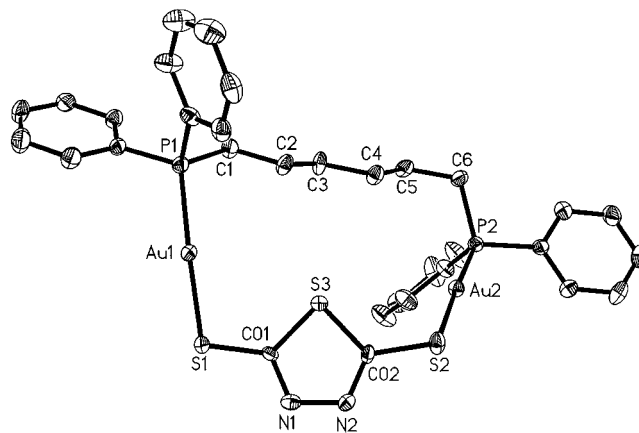

Figure 3. Molecular structure of compound [(PyPh₂P)Au]₂(SSS) (**2**) (ORTEP drawing with 50% probability ellipsoids and H atoms omitted for clarity). Selected bond lengths [Å] and angles [deg]: Au1−P1 = 2.255(2), Au1−S1 = 2.320(2), Au2−P2 = 2.264(2), Au2−S2 = 2.302(2); P1−Au1−S1 = 176.88(5), P2−Au2−S2 = 173.82(6), Au1−S1−C1−S3 = 145.7, Au2−S2−C2−S3 = 40.5.
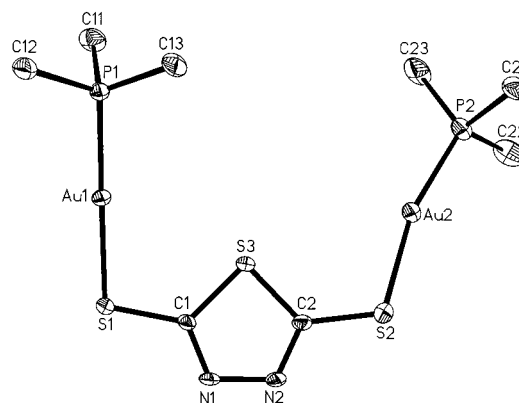
Figure 4. Molecular structure of compound [(Me₃P)Au]₂(SSS) (**3**) (ORTEP drawing with 50% probability ellipsoids and H atoms omitted for clarity). Selected bond lengths [Å] and angles [deg]: Au1−P1 = 2.265(2), Au1−S1 = 2.336(2) Au2−P2 = 2.277(2), Au2−S2 = 2.328(2); P1−Au1−S1 = 171.88(8), P2−Au2−S2 = 165.52(8), Au1−S1−C1−S3 = 8.2, Au2−S2−C2−S3 = 18.9.

Au2−S2−C2−S3 are 145.7 and 40.5°, respectively, and thus, close to those in complex **1**.

The nitrogen atoms of the pyridine rings have been located, but there is no special orientation of these ring systems which would indicate intra- or intermolecular coordination (Figure 3). The main crystallographic difference between **1** and **2** is, thus, the presence of fewer CH₂Cl₂ molecules in the latter. Clearly, the steric effects of the phenyl and pyridyl substituents are similar; therefore, the supramolecular association pattern is largely the same, including even sensitive parameters such as the dihedral angles (previously discussed). The higher polarity of the pyridyl groups appears to play no significant role in the packing.

Compound **3**, [(Me₃P)Au]₂(SSS), crystallizes (from CH₂Cl₂/pentane) in the orthorhombic space group $P2_12_12$ with $Z = 4$ formula units and four dichloromethane molecules in the unit cell. Crystallographically, the molecules have no symmetry; however, the geometry is reminiscent of the requirements of point group C_2, with the 2-fold axis passing through both S3 and the middle of the N=N bond (Figure 4). The deviations of the gold atoms from the ring plane are much smaller than those for **1** and **2**, and the dihedral angles are similar because of the folding of the Me₃PAu groups in the same direction (toward sulfur atom S3): Au1−S1−C1−S3 = 8.2° and Au2−S2−C2−S3 = 18.9°.

Figure 5. Two-dimensional network of compound **3** (Au2···Au1B = 3.0089(3) Å, Au···Au2C = 3.1048(5) Å).

The molecules are aggregated into a novel two-dimensional network via close Au···Au bonding. Four Me₃PAuS groups of four different molecules are grouped together in tetranuclear units with distances Au2···Au1B = 3.0089(3) and Au2···Au2C = 3.1048(5) Å. The neighboring Me₃PAuS groups are not parallel (head-to-head) or antiparallel (head-to-tail) but crossed with dihedral angles P2−Au2···Au2′−P2′ = 116.0° and P2−Au2···Au1′−P1′ = 108.5°. The aggregation of independent LAuX molecules into isolated tetramers or as parts of chainlike formations has been observed previously, [23−33] and the conformation of these aggregates is similar to that found in compound **3**. The present case is unique, however, in that the tetranuclear units are part of a two-dimensional structure connecting difunctional components into a network (Figure 5).

In the absence of any steric crowding by the tertiary phosphine group, the aurophilic interaction is clearly the dominating supramolecular force which overrules Au···S interactions or other van der Waals-type bonding. It should be noted that the gold atoms appear to be drawn together quite strongly, leading to a very significant bending of the P−Au−S angles which are already 171.88(8)° for P1−Au1−S1 and as small as 165.52(8)° for P2−Au2−S2.

Crystals of **4**, [(CH₂)₃PPh₂Au]₂(SSS) (from dichloromethane/pentane), are monoclinic of the space group *Cc* with *Z* = 4 formula units in the unit cell. There are no solvent molecules in the crystal lattice. The dinuclear complex is a 14-membered heterocycle. The two PAuS units are folded toward the central sulfur atom (S3) on the same side of the thiodiazole ring with quite different dihedral angles: Au1−S1−C01−S3 and Au2−S2−C02−S3 of 11.8 and 52.7°, respectively (Figure 6). The hexanediyl chain bridging the two phosphorus atoms is in a stretched all-trans configuration. The closest approximation to

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Figure 6. Molecular structure of compound [(CH₂)₃PPh₂Au]₂(SSS) (**4**) (ORTEP drawing with 50% probability ellipsoids and H atoms omitted for clarity). Selected bond lengths [Å] and angles [deg]: Au1−P1 = 2.265(1), Au1−S1 = 2.310(1) Au2−P2 = 2.275(1), Au2−S2 = 2.320(1); P1−Au1−S1 = 169.91(6), P2−Au2−S2 = 176.19(6), Au1−S1−C01−S3 = 11.8, Au2−S2−C02−S3 = 52.7.
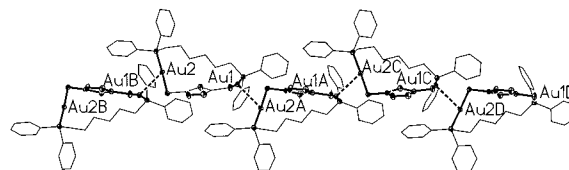
Figure 7. Formation of aggregates via Au···Au contacts in compound **4** (Au1···Au2A = 3.1898(14) Å).

a symmetry operation is to a 2-fold axis passing through both S3 and the middle of the C3−C4 bond.

The heterocycles are arranged in strings with the individual molecular units tied together solely via aurophilic bonding. The distances Au1···Au2A are 3.1898(14) Å, and the P−Au−S units are bent with angles P1−Au1−S1 = 169.91(6) and P2−Au2−S2 = 176.19(6)°. The dihedral angle P1−Au1···Au2′−P2′ is 76.4°, indicating, again, a crossing of the two P−Au−S units (Figure 7).
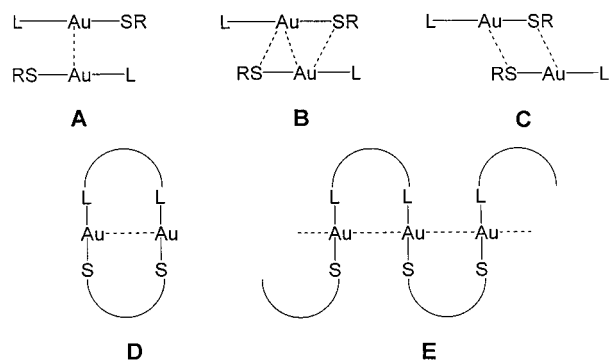
Conclusions

At first glance, the series of (phosphine)gold(I) thiolates presented here appears to be just another group of representatives of this perhaps most common class of gold compounds. However, an inspection of the structural details and a comparison with the existing wealth of data support some concepts emerging recently in the interpretation of bonding between closed-shell atoms.

The first point is the dominating influence of steric effects exerted by neighboring ligands. The bulk of a triphenylphosphine ligand can be sufficient to prevent Au···Au bonding, particularly in cases where the packing is more favorable for monomers than for dimers. Perhaps not surprising, this is also true for the diphenyl(1-pyridyl)phosphine ligand, which is isoelectronic and equally space-filling. It should be noted that there is no evidence for a special orientation of the pyridyl nitrogen donor atom toward a metal center of the same or a neighboring molecule. The conformation of the Ph₂PyP group appears to be determined only by general packing forces. Nevertheless, the exchange of a Ph₃P for a Ph₂PyP ligand leads to different solvation: the crystal of the Ph₃P complex contains two CH₂Cl₂ molecules, while that of Ph₂PyP has only one per molecule of complex. This observation illustrates the delicate balance of weak packing forces in the crystals.

Scheme 2

Even if Au···Au bonding is ruled out by steric effects, the complexes show a clear preference for aggregation (head-to-tail) through contacts between the diatomic Au−S units over other types of contacts. As a result of a shift of these units along two parallel lines, the shortest distance between the two components is the Au···S contact as an edge of an Au_2S_2 parallelogram (Scheme 2, **B** and **C**), whereas, in aurophilicity-determined patterns, the Au···Au contacts are the shortest (Scheme 2, **A**). This mode has been observed as a recurrent motif in several gold−sulfur compounds recently and seems to be of a more general significance.[19−21]

If reduced ligand bulk is the factor permitting aurophilic bonding, as detected for the Me_3P complex **3**, the aggregation may go well beyond simple dinuclear units and reach higher nuclearity. Tri- and, in particular, tetranuclear units appear to be the most efficient mode in which the most intimate bonding can be realized as reflected by short Au···Au distances, by extensive bending of the P−Au−S units, and by a crossed arrangement instead of a parallel head-to-tail association.

Metallocyclic compounds of the type **4−6** show reduced shielding of the gold atoms, even though the substituent pattern is similar to that of the Ph_3P and Ph_2PyPp complexes. Steric crowding is less in the periphery of rings as compared to chainlike molecules; therefore, compound **4**, with two exocyclic phenyl groups at the neighboring phosphorus atom, can still form short intermolecular Au···Au bonds (Scheme 2, **D**). It should be pointed out that the system could be based on an isomeric structure (Scheme 2, **E**) with alternating ligand bridges and that there should even be a mechanism to transform the two isomers into each other. We are presently engaged in studies of such interconversions.

Supporting Information Available: Details of crystal data, data collection, and structure refinement and tables of atomic coordinates, isotropic and anisotropic thermal parameters, and all of the bond lengths and angles are deposited as CIF. This material is available free of charge via the Internet at http://pubs.acs.org.

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