

Aurophilicity-Based One-Dimensional Arrays of Gold(I) Phenylene-1,3- and -1,4-dithiolates

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Phenylene-1,3-dithiol is converted into a trinuclear gold complex by treatment with 1 equiv of $\{[(\text{Ph}_3\text{P})\text{Au}_3\text{O}]^+\text{BF}_4^-\}$. In the product, the phenylene unit bears one gold thiolate and one di(gold)sulfonium function. These components aggregate into one-dimensional arrays through head-to-tail aurophilic contacts between the two functions. In the association process, the Au–S–Au angle of the sulfonium group is opened up to accommodate the incoming gold atom between its metal centers. A similar mode of aggregation is found for the triply aurophilic biphenylene-4,4'-dithiol obtained using the tri(gold)oxonium salt with tri(*p*-tolyl)phosphine ligands. Probably for steric reasons, in this oligomerization process, the gold(I) thiolate unit is attached side-on to the digold sulfonium unit with retention of the small Au–S–Au angle. Under similar reaction conditions, and with the same molar ratio of the components, phenylene-1,4-dithiol is converted into the bis-sulfonium salt: $1,4\text{-}\{[(\text{p-Tol})_3\text{PAu}]_2\text{S}\}_2\text{C}_6\text{H}_4(\text{BF}_4)_2$, the dication of which also associate into chains. Along the chains, the phenylene spacers alternate with tetranuclear gold clusters which arise from intimate aggregation of pairs of gold atoms. Together with previous findings, the present results show that gold thiolate (–SAuL) and digold sulfonium functions $[-\text{S}(\text{AuL})_2^+]$ in proper orientation at an arene unit ($\alpha\text{-}\omega$) can be considered as “soldering” points which can be used for joining up the molecular units into one-dimensional arrays solely through metal–metal contacts, which appear to be operative even against Coulomb repulsion between cations. The reaction of biphenylene-4,4'-dithiol with 2 equiv of sodium methoxide and [tri(*c*-hexyl)phosphine]gold chloride gives only neutral digold dithiolate complex **4** which is not associated owing to the steric bulk of the tri(*c*-hexyl)phosphine ligands.

Introduction

Gold(I) thiolates (RSAu) and their complexes (RSAuL) are well established as versatile precursors and reagents for a large variety of applications and represent a class of compounds in gold chemistry which has been studied most extensively for several decades.¹ The properties of the species are governed by the nature of the substituents R and the ligands L, and representative examples range from pastelike oligomeric thiolates $(\text{RSAu})_n$ as “liquid golds” for gilding² to crystalline monomeric complexes derived from tertiary phosphines and thioglucose for chrysotherapy.³

It is a specific feature of gold(I) complexes that oligomerization can not only be accomplished by conventional

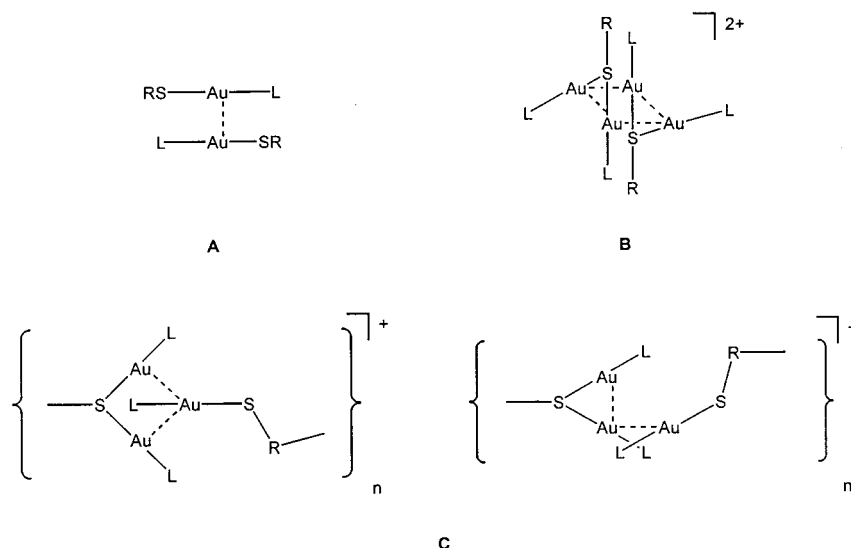
covalent or coordinative bonding but also through direct closed-shell interactions between the metal centers (“aurophilicity”).⁴ Even though this interaction is generally weak⁵ and comparable in its energy to hydrogen bonding,⁶ the effect is strong enough to have a marked influence on the configuration, conformation, and oligomerization of almost all gold(I) compounds.⁷

Coordinatively unsaturated gold(I) thiolates RSAu are known to aggregate into oligomers $(\text{RSAu})_n$ predominantly via conventional donor–acceptor bonding,⁸ but their coordinatively saturated complexes RSAuL still undergo association, which arises solely from aurophilic bonding (A, Scheme

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Scheme 1. Auophilic Interactions in Gold Thiolates **A**, Di(gold)sulfonium Salts **B** and Mixed Gold Thiolate/Di(gold)sulfonium Units **C**

1).⁹ In these aggregates, the gold atoms appear in pairs with intermolecular contacts typically in the range 2.9–3.2 Å. Note that these distances are close to the metal–metal separation in metallic gold and well below the sum of the van der Waals radii (3.65 Å).

Auophilic bonding is even more efficient in groups with more than two gold atoms in close contact. Aggregation between two pairs of gold atoms thus leads to four-atom clusters in the form of a square, a rhombus, or even a tetrahedron. Representative examples in the gold(I) thiolate series are the cation aggregates of di(gold)sulfonium salts¹⁰ (**B**, Scheme 1). Note that this association occurs against Coulomb repulsion between cationic centers.

In the present account, we report on the preparation and structural characterization of novel oligomers based on interactions between mixed gold thiolate/di(gold)sulfonium units derived from phenylene-1,3/1,4- and biphenylene-4,4'-dithiols. For this particular combination (**C**, Scheme 1), the gold atoms are found to form closed triangles or V-shaped triatomic units, as shown by X-ray structure analysis of two representative examples. Owing to the absence of Coulomb repulsion, the auophilic bonding is particularly strong and determines the structure of the aggregates. Phenylene-4,4'-bis(digoldsulfonium) salts are shown to associate via tetra-

nuclear clusters as already described for the aliphatic analogues.¹⁰

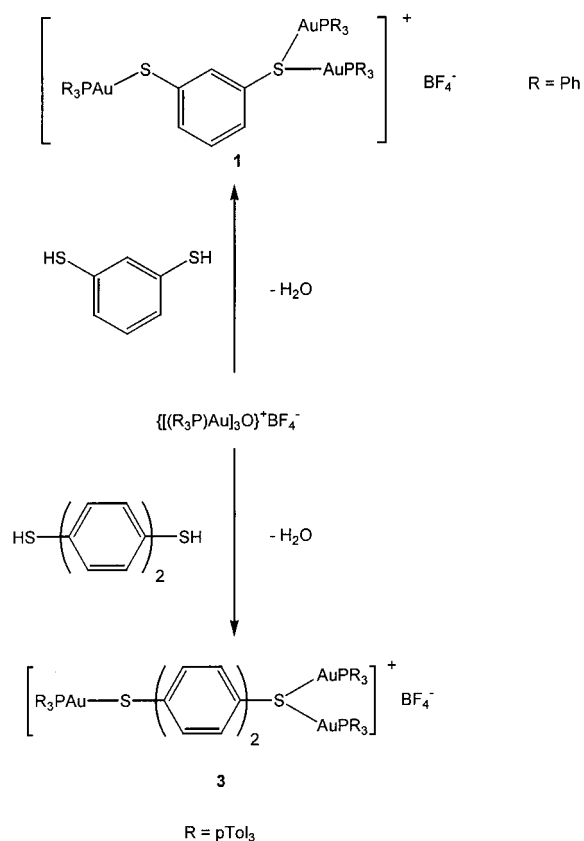
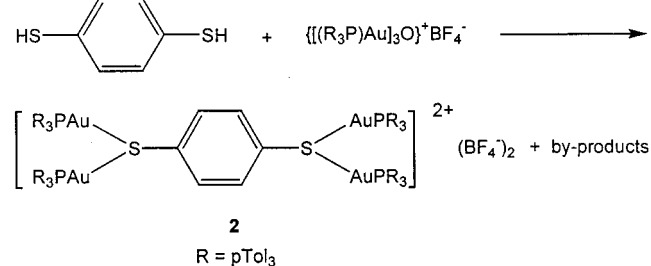
Preparative Studies

Phenylene-1,2-dithiol, its 4-methyl derivative, or related dithiols are known to react (as their alkali or ammonium salts) with aurating agents such as (R₃E)AuX (E = P, As; X = halogen) or {[(R₃P)Au]₃O}⁺BF₄⁻ to give dinuclear or trinuclear complexes with the gold atoms held in close (auophilic) proximity.^{11–14} Because of the internal (intramolecular) closed-shell interactions, no oligomerization is observed. It is only upon the loss of phosphine R₃P that further association into tetranuclear clusters takes place.^{11b,12} Phenylene-1,3-dithiol also affords a dinuclear gold(I) dithiolate, but with this substitution pattern, the metal atoms are separated and sterically protected such that no Au...Au contacts can be maintained.¹⁴ Furthermore, dinuclear complexes derived from phenylene-1,2-dithiol can be reacted with rhodium or iridium complexes to afford heterotrimeric compounds containing the (Au₂M) cores (M = Rh, Ir).¹⁵

The reaction of phenylene-1,3-dithiol with equimolar quantities of {[(Ph₃P)Au]₃O}⁺BF₄⁻ in dichloromethane affords high yields (92%) of a trinuclear complex (**1**, Scheme 2). The product can be crystallized from dichloromethane/pentane at –20 °C as pale yellow needles which give the correct elemental analysis. Solutions in CD₂Cl₂ show only one broad ³¹P resonance at 20 °C, but at –55 °C, this signal (br s 40.5 ppm) is split into two resonances in the intensity

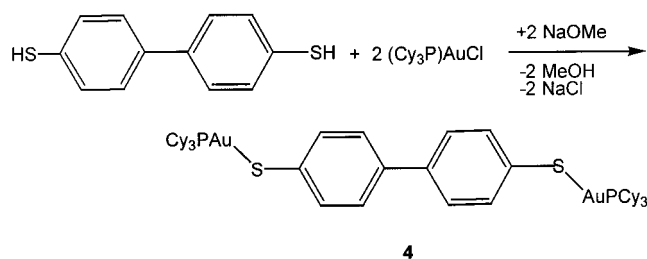
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Scheme 2. Preparation of Complexes 1 and 3

Scheme 3. Preparation of Complex 2


ratio 2:1 at 36.5 and 42.6 ppm, respectively. Likewise, the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra show the signals of virtually equivalent phenyl groups at room temperature, which are separated into two sets at -55°C . This finding suggests rapid scrambling of (Ph_3P) or (Ph_3PAu) units in solution at 20°C on the NMR time scale but long residence times of these units at the two different thiolate/sulfonium functions at low temperature. This structure has been confirmed in a single-crystal X-ray diffraction study.

Unexpectedly, treatment of phenylene-1,4-dithiol with tris- $\{[\text{tri}(p\text{-tolyl})\text{phosphine}]\text{-gold(I)}\}$ oxonium tetrafluoroborate under the conditions employed for **1** (molar ratio 1:1) gave mainly the tetranuclear bis-sulfonium salt (**2**, Scheme 3). Compound **2** could be crystallized in pure form. The analytical and spectroscopic data confirm the proposed composition, and the structure could be determined (see following paragraphs and the Experimental Section). The isolated yields of **2** are low (25%), and the nature of the byproducts is unclear. The trinuclear complex could not be isolated from, or detected in, the reaction mixture (Scheme 2).

Scheme 4. Preparation of Complex 4


Attempts to this end were successful, however, with biphenylene-4,4'-dithiol. A trinuclear product (**3**) was formed following the stoichiometry shown in Scheme 2. The NMR spectra show only one ^{31}P resonance at 20°C , but this signal (br s 43.2 ppm) also splits (as observed for **1**) into two components at -55°C (33.2 and 42.3 ppm, intensity ratio 1:2). The ^1H and $^{13}\text{C}\{^1\text{H}\}$ spectra are as expected (see Experimental Section).

The crystal structure of product **3** with tri(*p*-tolyl)phosphine ligands shows signs of steric crowding which alters the interaction between the individual units in the one-dimensional aggregates (see later). This steric crowding becomes even more important as the bulk of the phosphine is increased further. The reaction of biphenylene-4,4'-dithiol with 2 equiv of sodium methoxide and [tri(*c*-hexyl)phosphine]gold chloride gives only a dinuclear complex (**4**, Scheme 4), in which each sulfur atom is associated solely with one (phosphine)gold unit. The molecules are found to be monomers in the crystal with no discernible sub-van der Waals contacts.

Structural Studies

Crystals of complex **1** (from dichloromethane/pentane) are monoclinic, space group $P2_1/c$, with $Z = 4$ formula units and 12 dichloromethane molecules in the unit cell. The asymmetric unit contains one trinuclear cation (Figure 1), one BF_4^- counterion, and three solvent molecules [$1 \cdot 3\text{CH}_2\text{-Cl}_2$]. The cations are aggregated in parallel strings oriented along the *c*-axis as shown in Figure 2. In the individual cation, the 1,3-phenylene unit links a (phosphine)gold thiolate group and a bis[(phosphine)gold]sulfonium group. The three $\text{S}-\text{Au}-\text{P}$ units are quasilinear [$175.5(5)$, $171.12(4)$, and $168.39(4)^\circ$ for Au1, Au2, and Au3, respectively], while the valencies of the thiolate sulfur atom form an angle of $\text{Au1}-\text{S1}-\text{C1}$ $104.3(2)^\circ$ and the sulfonium group is pyramidal with angles $\text{Au2}-\text{S2}-\text{C5}$ $108.1(2)^\circ$, $\text{Au3}-\text{S2}-\text{C5}$ $103.3(1)^\circ$, and $\text{Au2}-\text{S2}-\text{Au3}$ $110.17(5)^\circ$. Only the latter of the three angles is surprising in that it is larger than in standard di(gold)sulfonium salts which are not associated into oligomers. In these standard cases $[\text{RS}(\text{AuL})_2]^+$, a small $\text{Au}-\text{S}-\text{Au}$ angle of less than 90° brings the gold atoms close together and allows for auophilic stabilization.¹⁰ (In this context, note also the small angles in compound **3** described later).

The reason for the opening of the $\text{Au2}-\text{S2}-\text{Au3}$ angle in complex **1** (by as much as ca. 25°) is immediately obvious from the structure of the polycationic chain (Figure 2). The gold atom Au1A of the thiolate function of a neighboring

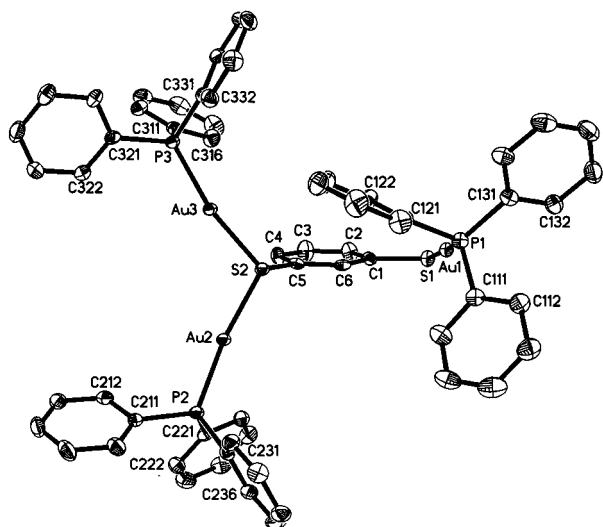


Figure 1. Cation of compound **1** with atomic numbering (ORTEP, 50% probability ellipsoids).

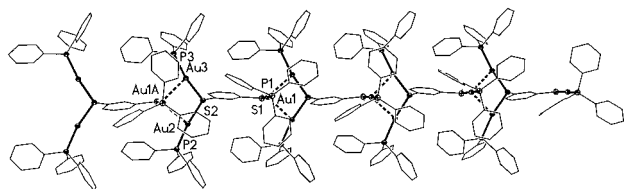


Figure 2. Arrangement of the cations of **1** in strings [Au2–Au1A 3.0602(2), Au3–Au1A 2.9983(2) Å].

molecule is inserted *between* the gold atoms Au2 and Au3 of the sulfonium group to give an isosceles triangle of gold atoms with two new short metal–metal contacts: Au2–Au1A 3.0602(2) and Au3–Au1A 2.9983(2) Å. The gold thiolate group S1A–Au1A is thus drawn into the wedge of the sulfonium group roughly bisecting the Au2–S2–Au3 angle. It appears that through this aggregation the energy gain from aurophilic bonds is doubled by replacing the single Au2–Au3 contact by the contacts of both Au2 and Au3 with the incoming Au1A. This is a new principle of aurophilicity-based oligomerization.^{4–7}

Crystals of compound **2** (from dichloromethane/pentane) contain 8 formula units and 8 molecules of dichloromethane in the unit cell (monoclinic, space group $C2/c$). The asymmetric unit therefore has one tetranuclear dication (Figure 3), two tetrafluoroborate counterions, and one solvent molecule [$2 \cdot \text{CH}_2\text{Cl}_2$]. The dications are aggregated into chains through intimate aurophilic bonding between the gold atoms of the sulfonium groups (Figure 4). At either end of the phenylene centerpiece, the gold atoms of two neighboring dications form tetranuclear units with short Au–Au distances:

Au1–Au2 3.2091(2), Au1–Au2A 3.1626(2), Au3–Au4 3.1607(2), Au3–Au3A 2.9684(3), and Au4–Au4A 3.0471(3) Å. At one end, the gold atoms are related by a center of inversion with complementary Au–Au–Au angles of 93.325(6)° (at Au1) and 86.675(6)° (at Au2), while the gold atoms at the other end are related by a 2-fold axis and form a trapezoid only slightly distorted from a rectangle with angles of 90.681(4)° at Au3 and 89.254(4)° at Au4.

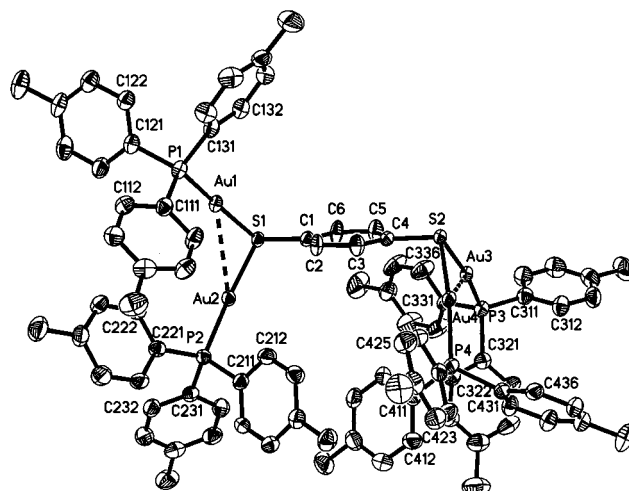


Figure 3. Dication of compound **2** with atomic numbering (ORTEP, 50% probability ellipsoids).

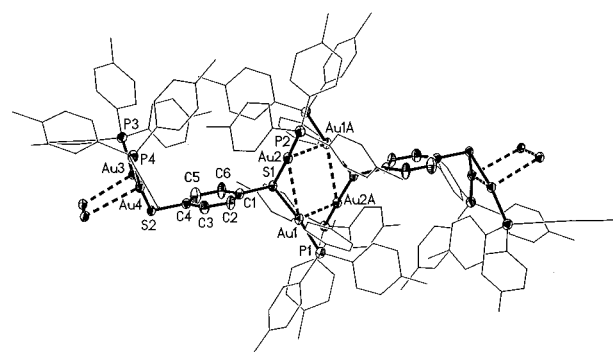


Figure 4. Aggregation of the cations of **2** into chains through intimate aurophilic bonding between the gold atoms of the sulfonium groups [Au1–Au2 3.2091(2), Au1–Au2A 3.1626(2), Au3–Au4 3.1607(2), Au3–Au3A 2.9684(3), Au4–Au4A 3.0471(3) Å; Au2–Au1–Au2A 93.325(6)°, Au1–Au2–Au1A 86.675(6)°, Au4–Au3–Au3A 90.681(4)°, Au3–Au4–Au4A 89.254(4)°].

It should be noted that, contrary to the situation found for **1**, the angles at the sulfonium centers [Au1–S1–Au2 86.66(4)°, Au3–S2–Au4 84.29(4)°] remain small upon aggregation because no insertion of gold atoms into the S(AuP)₂ wedges occurs. With the two angles significantly smaller than 90°, the Au–Au distances can be kept within the range of aurophilic bonding. A bending of all P–Au–S axes [with angles between 170.83(4)° and 174.60(4)°] also brings all gold atoms closer together.

Crystals of compound **3** (from dichloromethane/pentane) are monoclinic, space group $P2_1/n$ with $Z = 4$ formula units in the unit cell. One of the sulfur atoms (S2) at the ends of the biphenylene unit bears only one gold atom (Au3), while the other (S1) represents a sulfonium center bearing two gold atoms (Au1, Au2, Figure 5). Owing to the small angle Au1–S1–Au2 of only 79.83(3)° the two gold atoms are in close proximity [Au1–Au2 3.0039(2) Å] certainly associated with aurophilic bonding. The two phenylene rings are not coplanar and form a dihedral angle of 40.3(5)°.

These trinuclear units are lined up head-to-tail to form strings along the *b* axis as shown in Figure 6. The connectivity in the resulting polycation is solely based on aurophilic bonding between the gold atom Au3 of the thiolate group

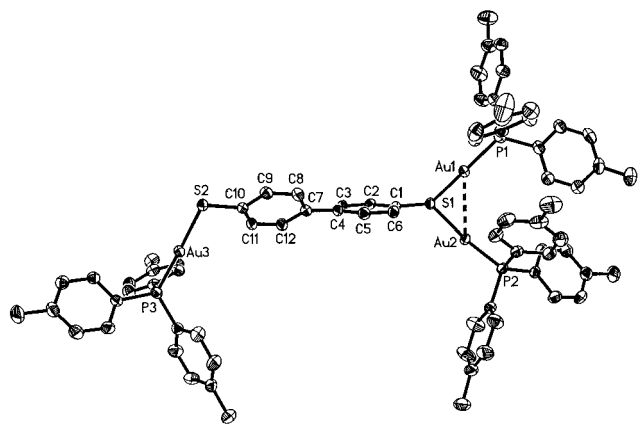


Figure 5. Structure of the cation of compound **3** [ORTEP drawing with 50% probability ellipsoids, H-atoms omitted for clarity; Au1–Au2 3.0039(2) Å].

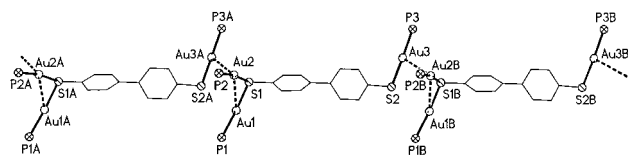


Figure 6. Head-to-tail alignment of trinuclear units of **3** [Au3–Au2B 3.2530(2) Å, S1B–Au2B–P2B 170.80(4)°, Au3–Au2B–Au1B 91.045(6)°].

and one of the two gold atoms (Au2B) of the sulfonium center of a neighboring molecule: Au3–Au2B 3.2530(2) Å. The two quasilinear triatomic units S2–Au3–P3 and S1B–Au2B–P2B form a dihedral angle of P3–Au3–Au2B–P2B = 88.7° representing a “crossed swords” orientation which is required to minimize steric repulsion between the bulky phosphine groups. There is also a significant bending of S1B–Au2B–P2B [170.80(4)°] assisting in the approach of Au2B and Au3. On the other hand, the angle Au3–Au2B–Au1B, although only 91.045(6)°, is too large to bring Au3 and Au1B close enough for a bonding interaction. The tetrafluoroborate counterions have no close contacts to atoms of the neighboring polycation strings.

Crystals of compound **4** are monoclinic, space group $P2_1/n$, with $Z = 2$ formula units and four molecules of dichloromethane in the unit cell. The two halves of the individual dinuclear molecules and the two solvent molecules are related by a center of inversion located in the middle of the C4–C4A linkage of the biphenylene unit (Figure 7). The two phenylene groups are coplanar with a dihedral angle of 180°. With standard bond distances and bond angles S1–Au1–P1 175.70(4)° and Au1–S1–C1 103.1(1)°, the molecular geometries show no anomalies.

Conclusions

The present study has shown that partial or complete auration of phenylene-1,3- and -1,4-dithiol or biphenylene-4,4'-dithiol leads to trinuclear mono- (**1**, **3**) or tetranuclear disulfonium salts (**2**). The cations of these salts are found to aggregate in one-dimensional coordination arrays through head-to-tail aurophilic bonding (Figures 2, 4, and 6). For the trinuclear units, the metal–metal contacts are established

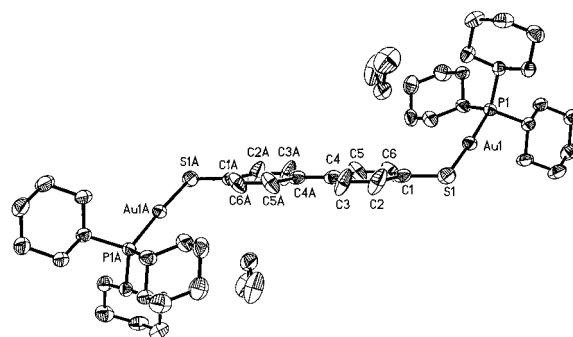


Figure 7. Structure of the cation of compound **4**. [ORTEP drawing with 50% probability ellipsoids, H-atoms omitted for clarity; Au1–P1 2.279(1), Au1–S1 2.310(1) Å, Au1–P1–S1 175.70(4)°].

between the neutral thiolate and the cationic sulfonium groups, while for the tetranuclear units the interaction relies on direct contacts between sulfonium groups overruling Coulomb repulsion. This Coulomb repulsion is avoided in the trinuclear complexes, like **1** or **3**, where each sulfonium function interacts with a thiolate function, suggesting that the sulfonium/sulfonium and thiolate/thiolate modes are the less favorable combinations as compared to two sulfonium/thiolate combinations.

A cartoon can be used to illustrate the overall structural pattern in compound **1**: a procession of animals (camels, donkeys, etc.) each of which holds on with his jaws to the tail of the preceding companion.

The molecular geometry of the components is readjusted such that an optimum of metal–metal contacts can be achieved. Compromises with steric effects of the ligands lead to specific preferences for either various Au–Au–Au isosceles triangles (V-shaped units) in the triatomic case (**1**, **3**) or square, rectangular, or rhombic arrangements in the tetra-atomic case (**2** and examples in the literature).

Solvation of the aggregates in polar solvents leads to disintegration to give ionic, monomeric units, for which ligand scrambling can be detected at room temperature by NMR methods. The process is reversible, and upon crystallization, the self-assembly of the cations leads to the formation of the one-dimensional systems.

Regardless of these structural details, and expressed in a simple picture, it appears that both gold thiolate and gold sulfonium functions are “sticky” and readily “glued” or “soldered” together through metal clustering.

Experimental Section

All experiments were routinely carried out in an atmosphere of dry and pure nitrogen. Solvents were dried and saturated with nitrogen, and glassware was oven-dried and filled with nitrogen. Standard equipment was used throughout. Sodium ethanethiolate,¹⁶ 1,4-bis(ethylsulfanyl)benzene,¹⁷ [tri(*c*-hexyl)phosphine]gold chloride,¹⁸ and tris[(triphenylphosphine)gold(I)]oxonium tetrafluoroborate and its tri(*p*-tolyl)phosphine analogue were obtained following literature procedures.¹⁹ Phenylene-1,4-dithiol and biphe-

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Table 1. Crystal Data, Data Collection, and Structure Refinement.

	1·3CH ₂ Cl ₂	2·CH ₂ Cl ₂	3	4·2CH ₂ Cl ₂
	Crystal Data			
formula	C ₆₃ H ₅₅ Au ₃ BCl ₆ F ₄ P ₃ S ₂	C ₉₁ H ₉₀ Au ₄ B ₂ Cl ₂ F ₈ P ₄ S ₂	C ₇₅ H ₇₁ Au ₃ BF ₄ P ₃ S ₂ ^b	C ₅₀ H ₇₈ Au ₂ Cl ₄ P ₂ S ₂
<i>M_r</i>	1859.51	2404.02	1807.06 ^b	1340.92
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic
space group	<i>P</i> 2 ₁ / <i>c</i>	<i>C</i> 2/ <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> (Å)	12.8733(1)	43.3854(3)	21.8506(2)	9.7574(1)
<i>b</i> (Å)	28.1979(3)	23.5896(1)	14.2848(1)	11.7033(1)
<i>c</i> (Å)	17.6585(1)	18.3088(1)	23.2992(2)	23.7344(3)
α (deg)	90	90	90	90
β (deg)	93.521(1)	108.309(1)	97.115(1)	101.336(1)
γ (deg)	90	90	90	90
<i>V</i> (Å ³)	6398.0(1)	17789.4(2)	7216.4(1)	2657.5(1)
ρ _{calcd} (g cm ⁻³)	1.930	1.795	1.663 ^b	1.676
<i>Z</i>	4	8	4	2
<i>F</i> (000)	3560	9280	3504 ^[b]	1332
μ(Mo Kα) (cm ⁻¹)	73.04	68.17	62.59 ^[b]	58.87
	Data Collection			
<i>T</i> (°C)	−130	−130	−130	−130
measured reflns	91405	228263	204962	79730
unique reflns	13154 [<i>R</i> _{int} = 0.0446]	19624 [<i>R</i> _{int} = 0.0440]	15702	5732 [<i>R</i> _{int} = 0.0370]
abs corr	DELABS	none	DELABS	none
<i>T</i> _{min} / <i>T</i> _{max}	0.385/0.788		0.356/0.772	
	Refinement			
refined params	739	1018	793	271
	Final <i>R</i> Values [<i>I</i> > 2σ(<i>I</i>)]			
<i>R</i> 1	0.0337	0.0360	0.0354	0.0302
w <i>R</i> 2 ^a	0.0796	0.0903	0.0801	0.0713
(shift/error) _{max}	<0.001	<0.001	<0.001	<0.001
ρ _{fin} (max/min) (e Å ⁻³)	2.177/−1661	1.620/−1.705	1.898/−1.322	0.909/−1.360

^a w*R*2 = { $\sum w(F_o^2 - F_c^2)^2$ }/ $\sum [w(F_o^2)^2]$ ^{1/2}; $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]$; $p = (F_o^2 + 2F_c^2)/3$; $a = 0.0260$ (1·3CH₂Cl₂), 0.0518 (2·CH₂Cl₂), 0.340 (3), 0.0250 (4·2CH₂Cl₂); $b = 32.60$ (1·3CH₂Cl₂), 88.03 (2·CH₂Cl₂), 15.51 (3), 6.87 (4·2CH₂Cl₂). ^b Values correspond to solvent free unit (see Experimental Section).

nylene-4,4'-dithiol²⁰ were prepared in modified procedures as described. Phenylene-1,3-dithiol and all other reagents are commercially available.

Phenylene-1,4-dithiol. A solution of 1,4-bis(ethylsulfanyl)-benzene (0.85 g, 4.29 mmol) in HMPA (7.5 mL) is treated with sodium (0.51 g, 22.0 mmol) at room temperature for 24 h. After separation from the remaining sodium the reaction mixture is poured into ice water (50 mL) containing concentrated hydrochloric acid (5 mL). After extracting twice with diethyl ether (each 25 mL), the united organic extracts are washed twice with water (each 100 mL) and dried with sodium sulfate. The diethyl ether is removed in vacuo to leave the phenylene-1,4-dithiol as a pale yellow solid (372 mg, 61%). The analytical data agree with those given in the literature.^{20a}

Biphenylene-4, 4'-dithiol. Biphenylene-4,4'-disulfonyl dichloride (5.96 g, 16.97 mmol) is dissolved in a hot toluene–water mixture (70 and 48 mL, respectively). Then, at 70 °C and with vigorous stirring, 16.10 g (0.136 mol) of tin filings is added, followed by dropwise addition of concentrated hydrochloric acid (27 mL, 0.27 mol) within 0.5 h while increasing the temperature to 85 °C. After the addition of the acid, the mixture is kept at 85 °C for an additional 2 h. Subsequently, more toluene is added to improve phase separation. After cooling to room temperature, the toluene layer

containing the dithiol is separated and dried with sodium sulfate. Toluene is distilled off in vacuo, and the product is obtained as a pale yellow solid (2.88 g, 78%). The analytical results are in agreement with the data given in the literature.^{20d}

Phenylene-1-bis[(triphenylphosphine)gold(I)]sulfonio-3-[(triphenylphosphine)gold(I)]thiolate Tetrafluoroborate, 1. A solution of tris[(triphenylphosphine)gold(I)]oxonium tetrafluoroborate (281 mg, 0.19 mmol) in dichloromethane (5 mL) is treated with a solution of phenylene-1,3-dithiol (27 mg, 0.19 mmol) in CH₂Cl₂ (2 mL) and a small quantity of NaBF₄ at 20 °C for 1 h. The precipitate is filtered off, and the product is crystallized from the filtrate upon addition of pentane and cooling to −20 °C; the pale yellow crystals are dried in a vacuum (280 mg, 92% yield). C₆₀H₄₉Au₃BF₄P₃S₂ (1604.80) Calcd: C, 44.91; H, 3.08; Au, 36.82%. Found: C, 44.80; H, 3.48; Au, 37.40%. NMR (CD₂Cl₂, 20 °C): ³¹P{¹H} 40.5, br s (−55 °C: 36.5, s, 2 P; 42.6, s, 1 P); ¹H 7.27–7.84, m, 45 H, Ph; 7.88, t, *J* = 1.73 Hz, 1 H, C₆H₄; 7.23, dd, *J* = 7.92, and 1.73 Hz, 2 H, C₆H₄; 6.85, t, *J* = 7.92 Hz, 1 H, C₆H₄; ¹³C{¹H} 129.1, 129.9, 132.7, and 134.5, with *J* = 7.3, 11.9, 0, and 14.5 Hz, respectively, for C₆H₅; 128.2, 128.4, 136.4, and 139.8, all s, for C₆H₄(S)₂.

Phenylene-1,4-bis{bis[(tri(*p*-tolyl)phosphine)gold(I)]sulfonium} Bis(tetrafluoroborate), 2. Following the procedure described for **1**, the product is obtained from the oxonium salt (138 mg, 0.086 mmol) and phenylene-1,4-dithiol (12.2 mg, 0.086 mmol) in a total of 7 mL of CH₂Cl₂ as colorless crystals (50 mg, 25% yield).

C₉₀H₈₈Au₄B₂F₈P₄S₂ (2319.20) Calcd: C, 46.61; H, 3.82; Au, 33.97%. Found: C, 47.55; H, 4.01; Au, 34.11%. NMR (CD₂Cl₂, 20 °C): ³¹P{¹H} 35.9, s; ¹H 2.37, 36 H, Me; 7.19–7.36, m, 52 H, C₆H₄; ¹³C{¹H} 21.6, s, Me; 126.0, 130.6, 134.4, and 143.4, with *J* = 60.7, 12.3, 13.8, and 0 Hz, respectively, for C₆H₄(Tol); 133.0,

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s, 4 C; 135.0, s, 2 C, for $C_6H_4(S)_2$. MS (FAB) m/z 1144.7 (18.7%) [$M - 2(AuPTol_3)$].

Biphenylene-4-{bis[(tri(*p*-tolyl)phosphine)gold(I)]sulfonio}-4'-[(tri(*p*-tolyl)phosphine)gold(I)thiolate] Tetrafluoroborate, 3. A solution of the oxonium salt (100 mg, 0.062 mmol) in dichloromethane (5 mL) is treated with a solution of the dithiol (13.6 mg, 0.062 mmol) in 2 mL of CH_2Cl_2 and a small amount of $NaBF_4$ with stirring at 20 °C for 1 h. The precipitate is filtered off, and the product is crystallized from dichloromethane/pentane at -20 °C (57 mg, 51% yield).

$C_{75}H_{71}Au_3BF_4P_3S_2$ (1807.14) Calcd: C, 49.85; H, 3.96; Au, 32.70%. Found: C, 51.06; H, 4.13; Au, 32.12%. NMR (CD_2Cl_2 , 20 °C): $^31P\{^1H\}$ 43.2, br s; [-55 °C: 33.2 (s, 1 P) and 42.3 (s, 2 P)]; 1H 2.39, s, 27 H, Me; 7.10–7.80, m, 44 H, C_6H_4 ; $^{13}C\{^1H\}$ 21.25, s, Me; 125.8, 130.5, 134.3, and 143.5, with $J = 58.6, 8.3, 10.9$, and 0 Hz, respectively, for $C_6H_4(Tol)$; 126.7, 133.1, 137.1, and 138.6, all s, for $(C_6H_4)_2(S)_2$. MS(FAB): $m/e = 1219.6$ (12.0%) [$M - Au(PTol_3)$] $^+$.

Biphenylene-4,4'-bis{[tri(*c*-hexyl)phosphine]gold(I)}-thiolate, 4. A solution of the biphenylene-4, 4'-dithiol (11 mg, 0.049 mmol) in dichloromethane (2 mL) is treated with a solution of sodium methoxide (6 mg, 0.098 mmol) in 2 mL of methanol. The resulting solution is united with a solution of [tri(*c*-hexyl)phosphine]gold chloride (50 mg, 0.098 mmol) in dichloromethane (2 mL) with stirring at 20 °C for 1 h. The volatiles are removed in vacuo, and the residue is extracted with 4 mL of dichloromethane. The product crystallizes upon addition of pentane and cooling to -20 °C (50 mg, 88% yield).

$C_{48}H_{74}Au_2P_2S_2$ (1171.12) Calcd: C, 49.23; H, 6.37; Au, 33.64%. Found: C, 48.72; H, 6.23; Au, 33.37%. NMR (CD_2Cl_2 , 20 °C): $^31P\{^1H\}$ 57.9, s; 1H 1.10–2.70, m, 66 H, C_6H_{11} , 7.25 and 7.47, d, $J = 8.38, 8$ H, $(C_6H_4)_2S_2$; $^{13}C\{^1H\}$ 30.83, s; 25.96, 27.07, and 33.35, with $J = 1.6, 11.9$, and 28.0 Hz, C_6H_{11} ; 125.7, 132.3, 135.5, and 142.0, all s, for $(C_6H_4)_2(S)_2$. MS(FAB): $m/e = 1170.7$ (37.1%) [M] $^+$.

Structure Determinations. Specimens of suitable quality and size were mounted on the ends of quartz fibers in F06206R oil and used for intensity data collection on a Nonius DIP2020 diffractometer, employing graphite-monochromated Mo $K\alpha$ radiation. 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 non-hydrogen atoms. All hydrogen atoms were placed in idealized calculated positions and allowed to ride on their corresponding carbon atoms with fixed isotropic contributions. Crystals of compound **3** contained some additional disordered and unidentified solvent in the lattice, which was not included in the refinement but was taken care of by the "SQUEEZE" procedure (from PLATON). The volume occupied by the solvent is 677 Å³; the number of electrons per unit cell deduced by SQUEEZE is 14. Further information on crystal data, data collection, and structure refinement are summarized in Table 1. Important interatomic distances and angles are shown in the corresponding figure captions. Thermal parameters and tables of interatomic distances and angles have been deposited with the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K. The data are available on request on quoting CCDS 183445-183448.

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Supporting Information Available: Atomic coordinates, bond lengths and angles, atomic displacement parameters, hydrogen coordinates, and torsion angles (CIF).

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