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New Pathways to Compact Tetragold(I) Bis(phenylene-1,2-dithiolate) Complexes with Tertiary Phosphine and Isonitrile Ligands

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Treatment of phenylene-1,2-dithiol (or its 4-methyl derivative) with equimolar quantities of tris[(triisopropylphosphine)gold]oxonium tetrafluoroborate under mild conditions (in dichloromethane, −20 to +20 °C) yields the trinuclear complex salts $\{[(^{i}Pr_3P)Au]_3[S_2C_6H_{4/3}(Me)]\}BF_4$ (**1**, **3**). From concentrated solutions warmed above 20 °C the neutral tetranuclear complexes $\{(^{i}Pr_3P)_2Au_4[S_2C_6H_{4/3}(Me)]_2\}$ (**2**, **4**) are crystallized in good yields. $[(^{i}Pr_3P)_2Au]BF_4$ (**6**) was identified as the byproduct of the ligand redistribution reaction which converts the tri- into the tetranuclear clusters. With $\{[(Ph_3P)Au]_3O\}BF_4$ no such ligand scrambling occurs and only the trinuclear complex salt $\{[(Ph_3P)Au]_3(S_2C_6H_4)\}BF_4$ (**5**) is formed. The structures of **2** and **4** have been determined by single-crystal X-ray diffraction studies. Although the crystals are not isomorphous, the molecules are almost superimposable. In the ligand framework, the four gold atoms form two edge-sharing, almost equilateral triangles which allow for tight aurophilic bonding. A similar tetranuclear cluster, $[(RNC)_2Au_4(S_2C_6H_4)_2]$ (**7**; R = cyclohexyl), is generated in low yield in the reaction of (RNC)AuCl with $C_6H_4(SNa)_2$. It has been isolated as a cocrystallizate with the (isocyanide)(carbene)gold(I) complex salt $\{(RNC)Au[C(NHR)_2]\}Cl$ (**8**) present in the reaction mixture, and the structure of the dichloromethane solvate has been determined. The components are aggregated in strings via aurophilic contacts following the sequence ...(**7**)(**8**)(**8**)(**7**)(**8**)(**8**)... The deep green gold(I)/gold(III) salt $[(RNC)_2Au][Au(S_2C_6H_4)_2]$ is the main product of the reaction.

Introduction

Gold thiolates and their complexes with donor ligands are the most widely used compounds in gold chemistry.[1] The commercial products include, inter alia, "liquid golds" for gilding in classical handicraft[2] and in modern surface technology,[3] self-assembled monolayers on surfaces,[4] and liquid crystal precursor molecules,[5] as well as gold drugs for chemotherapy.[6]

Many compounds of the gold(I) thiolate series show a surprisingly rich supramolecular chemistry owing to the aurophilicity phenomenon,[7−9] observed for all examples where a sufficiently open molecular structure gives free access to the gold atoms for metal−metal interactions.

For the design of multidimensional gold(I) thiolate complexes based on this novel type of intermolecular interaction, the introduction of polyfunctional thiols with template character is particularly promising. Phenylene-1,3-dithiol and phenylene-1,4-dithiol have recently been probed successfully for the construction of one-dimensional polymers.[10] Di-, tri-, and tetraauration leads to gold(I) thiolates, bis[gold(I)]sulfonium salts, or a combination of both bridged by the phenylene units. These end groups were found to be "sticky" at their metal atoms and to act like a metal solder for connecting the individual units into chains.

In previous work with the corresponding phenylene-1,2-dithiols or related dithiols it has been demonstrated that polyauration of these substrates leads to conventional di- and trinuclear complexes (**A** and **B**) if tri*aryl*phosphines are employed as ligands (Chart 1).[11−14] In the trinuclear complexes, the neighboring gold thi-

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[1] *Gold: Progress in Chemistry, Biochemistry and Technology*; Schmidbaur, H., Ed.; Wiley: Chichester, U.K., 1999.

[2] Landgraf, G. In ref 1, p 146.

[3] Puddephatt, R. J. In ref 1, p 239.

[4] Puddephatt, R. J. In ref 1, p 250.

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[11] (a) Gimeno, M. C.; Jones, P. G.; Laguna, A.; Laguna, M.; Terroba, R. *Inorg. Chem.* **1994**, *33*, 3932. (b) Sladek, A.; Schmidbaur, H. *Chem. Ber.* **1995**, *128*, 907. (c) Sladek, A.; Schmidbaur, H. *Inorg. Chem.* **1996**, *35*, 3268.

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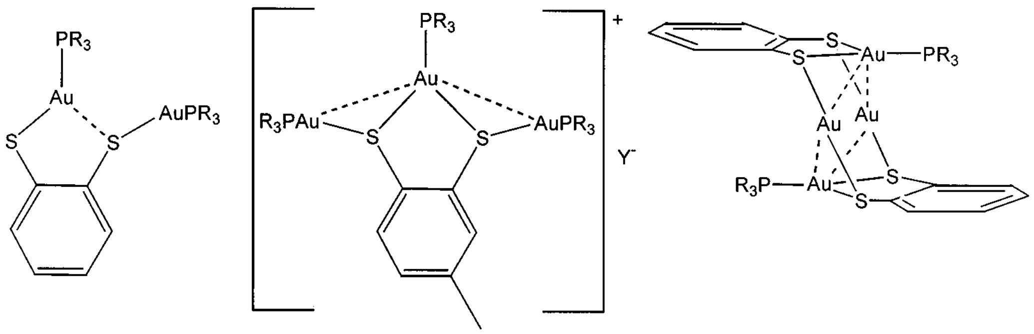
Chart 1. Gold(I) Complexes of Phenylene-1,2-dithiols



A R = Ph

B R = Ph, Y = ClO$_4$

C R = Et

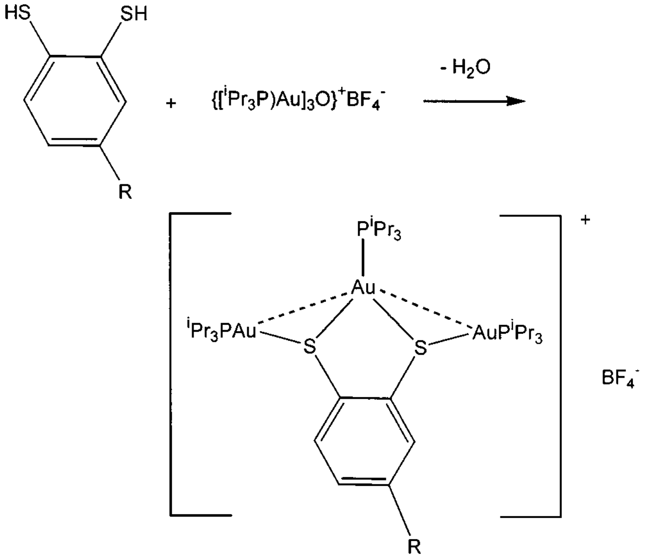
olate and bis(gold)sulfonium groups are intimately aggregated to give V-shaped triatomic gold units of high stability (**B**; Chart 1). The same observation is made when the *di*nuclear complexes derived from phenylene-1,2-dithiol are reacted with rhodium or iridium complexes to afford heterotrinuclear compounds containing the (Au$_2$M) cores (M = Rh, Ir).[14b] With triethylphosphine, however, the reactions are accompanied by an unprecedented partial loss of ligands, which leads to vacancies in the coordination sphere of the metal for more compact clustering.[13a,15] Tetranuclear dimers are obtained in which the metal atoms form rhombic units (**C**; Chart 1).

These investigations have now been extended to include other tertiary phosphines, as well as isonitriles, as auxiliary ligands, which were expected to enhance cluster formation owing to their smaller size. In particular, the opening of a "direct route" to the compounds (from only two components in the right stoichiometry) was desirable in order to test the ligand-dependent stability of the products. Previously employed multicomponent syntheses, even if carried out in the absence of oxidative agents, have the distinct disadvantage of the unexpected formation of gold(III) compounds, with salts of the bis(phenylene-1,2-dithiolato)gold(III) anion as the most common byproducts.[11a,12,16] This phenomenon is immediately obvious from the appearance of the deep green color of this anion.

Preparative Results

The reaction of phenylene-1,2-dithiol with an equimolar quantity of tris[(triisopropylphosphine)gold(I)]oxonium tetrafluoroborate in dichloromethane at ambient temperature was found to give two different products, depending on the workup procedure employed. Precipitation of the product directly from the reaction mixture by cooling to −20 °C and adding pentane gives the *tri*nuclear gold(I) phenylene-1,2-dithiolate tetrafluoroborate {[(i-Pr$_3$P)Au]$_3$S$_2$C$_6$H$_4$}$^+$BF$_4^-$ (**1**) in 83% yield as a colorless microcrystalline solid (Scheme 1) with only a few larger crystals of the byproduct **2**. This compound **2** crystallizes in almost 63% yield within 2 h if the reaction mixture is concentrated under vacuum to a small volume at 20 °C (Scheme 2). It has been identified as a *tetra*nuclear bis(phenylene-1,2-dithiolate) in which only two of the four phosphine ligands remain: [(^{i}Pr$_3$P)$_2$-Au$_4$(S$_2$C$_6$H$_4$)$_2$] (**2**).

Scheme 1. Preparation of Complexes 1 and 3



1 R = H
3 R = Me

The same results were obtained in experiments with 4-methylphenylene-1,2-dithiol and the oxonium salt bearing the triisopropylphosphine ligand. The analogous compounds **3** and **4** were isolated in 79 and 67% yields, respectively (Schemes 1 and 2).

In contrast, the reaction of {[(Ph$_3$P)Au]$_3$O}BF$_4$ with phenylene-1,2-dithiol gave only one product without loss of phosphine: {[(Ph$_3$P)Au]$_3$S$_2$C$_6$H$_4$}BF$_4$ (**5**), in 90% yield (Scheme 3).

Regarding the mechanism of formation of **1**/**3** or **2**/**4**, it appears that compounds **1** and **3** are first formed, as suggested by the stoichiometry of the reactants. The two initial products then undergo cleavage into the salt

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(13) (a) Davila, R. M.; Elduque, A.; Grant, T.; Staples, R. J.; Fackler, J. P., Jr. *Inorg. Chem.* **1993**, *32*, 1749. (b) Davila, R. M.; Staples, R. J.; Elduque, A.; Harlass, M. M.; Kyle, L.; Fackler, J. P., Jr. *Inorg. Chem.* **1994**, *33*, 5940.

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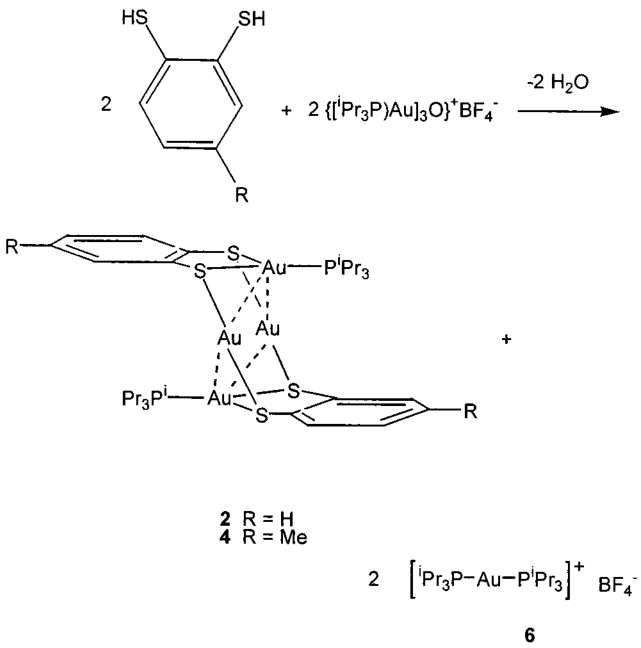
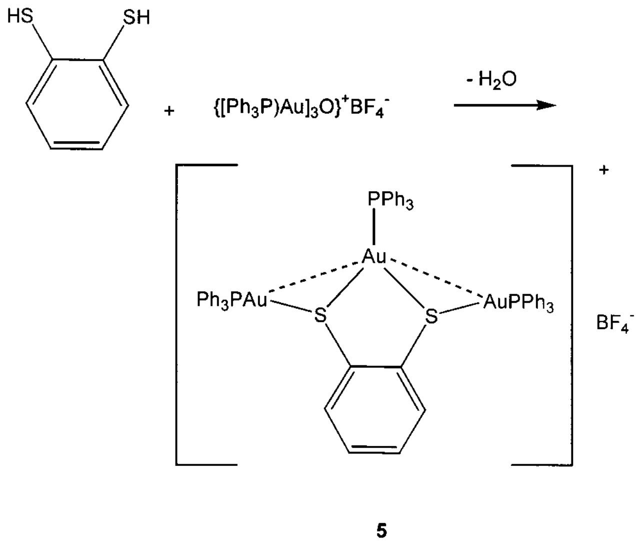
Scheme 2. Preparation of Complexes 2 and 4



Scheme 3. Preparation of Complex 5



[(^{i}Pr$_3$P)$_2$Au]$^+$BF$_4^-$ (**6**) (Scheme 2) and the secondary products **2** and **4**, respectively. Compound **6** could be detected in the mother liquor of the precipitates by ^{31}P (s, 74.4 ppm) and ^{1}H (dd, 1.34 ppm; dsep, 2.51 ppm) NMR spectroscopy. In the reaction with {[(Ph$_3$P)Au]$_3$O}-BF$_4$ no cleavage of the primary product (**5**) occurs which would give [(Ph$_3$P)$_2$Au]BF$_4$. Ph$_3$P may be classified as a poorer leaving group and may meet more or less ideal steric conditions in **5**, which make rearrangements thermodynamically unfavorable. It is probably no coincidence that the analogous reaction with 4-methylphenylene-1,2-dithiol also gives the analogous product *only*.

Two analogues of compounds **1** and **3** (with different dithiols and phosphines) have been structurally characterized.[11b,c] The analytical and spectroscopic data of the new compounds show no anomalies and suggest similar structural characteristics. The perchlorate salt of the cation present in compound **5** and the corresponding 4-methyl derivative have previously been reported, and the structure of the latter has been determined.[11] Similar characteristics are assumed for **5** on the basis of, for example, almost identical ^{31}P NMR spectroscopic data.

Compounds **2** and **4** are very different from complexes **1**, **3**, and **5** in that they are completely insoluble in both polar and nonpolar organic solvents. Therefore, no characterization by solution spectroscopy was possible, but the molecular structures were determined by single-crystal X-ray diffraction studies (below). Note that the low solubility of **2** and **4** may also be a driving force for the ligand redistribution of the precursor products **1** and **3**.

A cluster of the type **2**/**4** with cyclohexyl isocyanide as the ligand instead of triisopropylphosphine was obtained as one of several products of the reaction between (cyclohexyl isocyanide)gold(I) chloride and disodium phenylene-1,2-dithiolate in the molar ratio 2:1 in methanol. This product (**7**; Scheme 4) was detected in the reaction mixture by monitoring its spectroscopic data (Experimental Section). It could finally be cocrystallized serendipitously with [bis(cyclohexylamino)carbene](cyclohexyl isocyanide)gold(I) chloride (**8**; Scheme 4) and dichloromethane in the molar ratio 1:2:2 (see below). For this crystalline phase spectroscopic and elemental analysis data were also obtained.

The main product of the reaction in Scheme 4 is the deep green bis(cyclohexyl isocyanide)gold(I) bis(phenylene-1,2-dithiolato)aurate(III) (**9**), which will be presented in a more appropriate context.[17]

Structural Studies

Crystals of the compounds **2** and **4** are not isomorphous. The former are orthorhombic, space group *Pbca*, with $Z = 4$ formula units, while the latter are monoclinic, space group $P2_1/n$, with $Z = 2$ formula units in the unit cell. However, the structures of the individual molecules are very similar, as illustrated by the superposition shown in Figure 1. Note that the molecules differ only by the presence/absence of the 4-methyl group in the phenylene-1,2-dithiolate ligands.

In both **2** and **4** the atoms are related by a center of inversion located in the middle of the parallelogram formed by the four gold atoms (Figures 2 and 3). The two edges of these units are very similar: The distances Au1–Au2 and Au1–Au2A are 3.0398(3) and 3.0384(3) Å for **2** and 3.0667(7) and 3.0855(7) Å for **4**. Because of the acute angles Au1–Au2–Au1A of 63.653(8)° (**2**) and 62.54(2)° (**4**) the transannular distances Au1–Au1A are also short, at 3.2053(4) Å for **2** and at 3.193(1) Å for **4**, and thus are still in the range for significant aurophilic bonding. The parallelogram can be described as formed by two edge-sharing, almost equilateral triangles with the four peripheral edges bridged on different sides by the thiolate sulfur atoms. The gold atoms Au1 are linearly two-coordinated (S1A–Au1–S2 = 175.87(5)° in **2** and 175.4(1)° in **4**), while the gold atoms Au2 are planar three-coordinate (with sums of the angles at 359.7 and 359.9°). The alkylphosphine and dithiolate ligands show no anomalies. The structures of **2** and **4** will not be discussed any further, because there are

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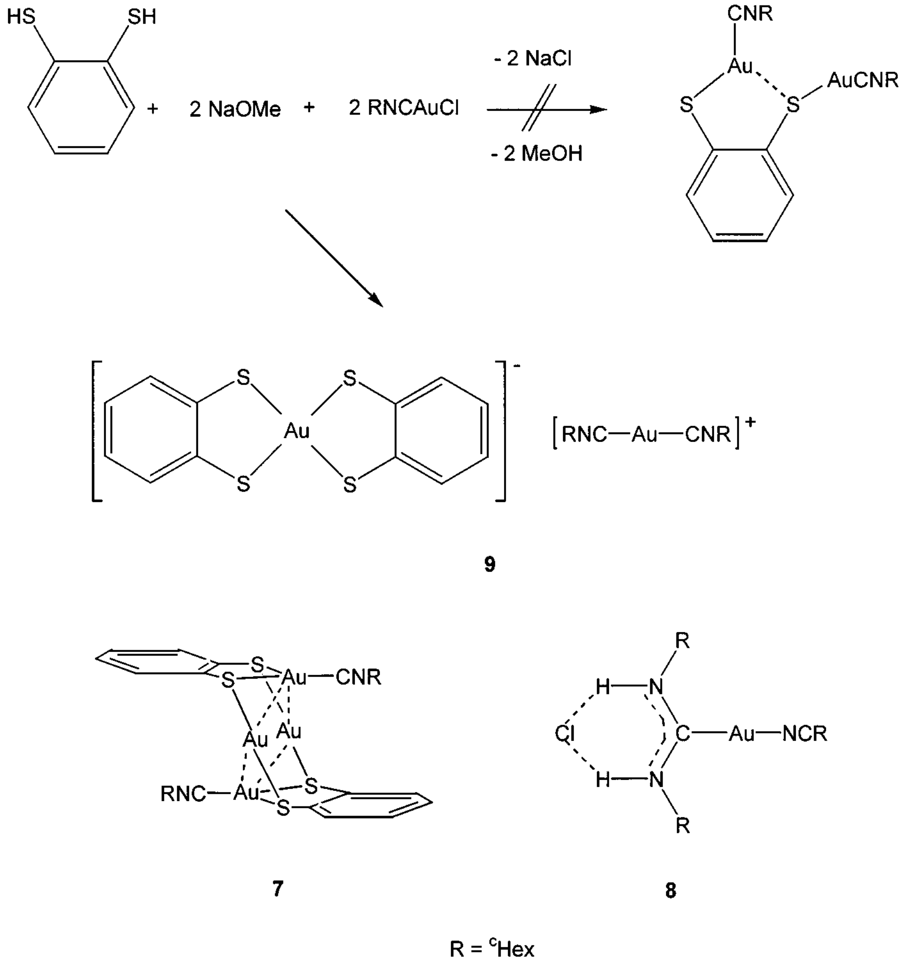
[17] Ehlich, H.; Schier, A.; Schmidbaur, H. To be submitted for publication.

Scheme 4. Preparation of Complexes 7−9



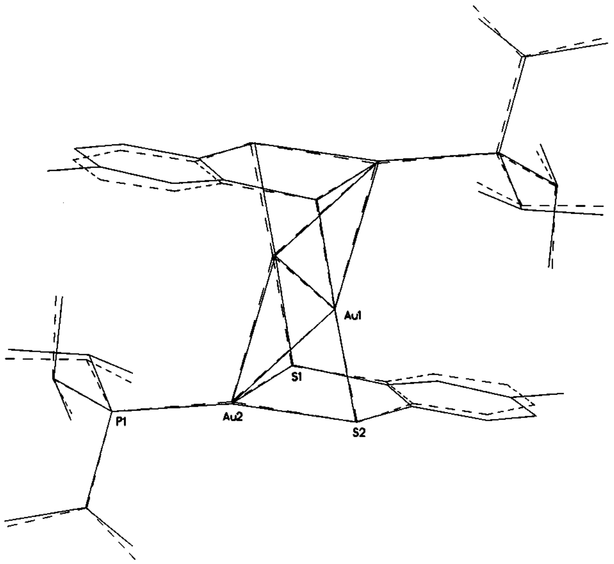


Figure 1. Superposition of the structures of compounds **2** and **4**.

many similarities with examples described previously.[13a,15]

Crystals of the composition $(\mathbf{7})(\mathbf{8})_2(CH_2Cl_2)_2$ are triclinic, space group $P\bar{1}$, with one cluster unit **7**, two carbene complex salts **8**, and two dichloromethane molecules in the unit cell. They appear as colorless needles together with the green needles of compound **9** when pentane is allowed to diffuse slowly into a dichloromethane solution of the products formed according to Scheme 4 and were separated mechanically. The structure consists of infinite chains of the components with the sequence ...**7**,**8**,**8**,**7**,**8**,**8**..., as shown in Figure 4. The tetranuclear cluster **7** and the pairs of the carbene complex salts **8** reside around centers of inversion. The chloride counterion is associated with the carbene part and with the dichloromethane solvate molecules via hydrogen bonding.

The components **7** and **8** (and **8** with **8**) are associated through aurophilic bonding which extends along the chain axis with a slight puckering as shown by the following *inter*molecular bond lengths and angles: Au1−Au3 = 3.2925(6) Å, Au1−Au1B = 3.466(1) Å, Au1B−Au1−Au3 = 162.2(1)°, Au1−Au3−Au2 = 163.46(2)°. Note that the aurophilic contact Au1−Au1B connects two cations and is thus maintained against Coulomb repulsion.

The cluster **7** with the composition $[(^{c}HexNC)_2Au_4(S_2C_6H_4)_2]$ has a core structure similar to that known from previous examples with trialkylphosphine ligands,[13a,15] including the compounds **2** and **4** (see above). The four gold atoms form a parallelogram (planar by crystallographic inversion symmetry) with the edges Au2−Au3 = 3.0466(6) Å and Au2−Au3′ = 3.0984(6) Å. Together with the shorter of the two diagonals, Au2−Au2′ = 3.1588(7) Å, these data show that the tetranuclear unit is again formed from two

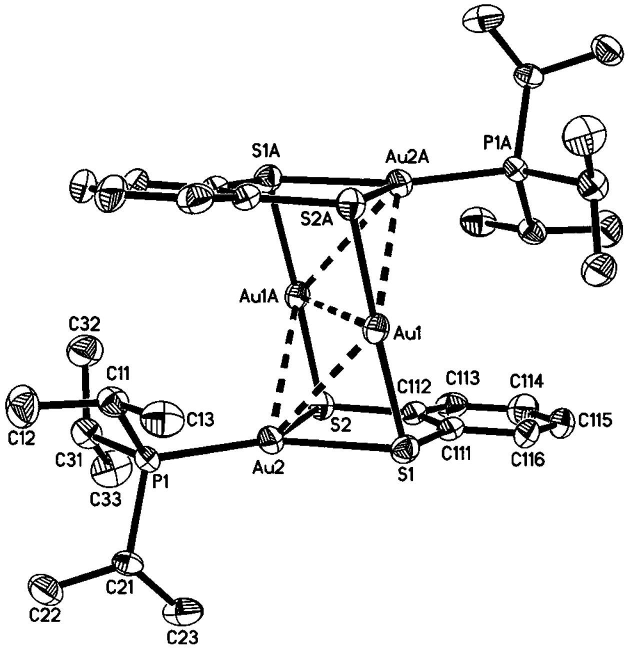


Figure 2. Structure of compound **2** (ORTEP drawing with 50% probability ellipsoids, H atoms omitted for clarity). Selected distances (Å) and angles (deg): Au1−S1 = 2.318(2), Au1−S2A = 2.320(2), Au1−Au2 = 3.0398(3), Au1−Au1A = 3.2053(4), Au1−Au2A = 3.0384(3); S1−Au1−S2A = 175.87(5), Au2−Au1−Au2A = 116.347(8), Au2A−Au1−Au1A = 58.194(8), Au2−Au1−Au1A = 58.153(8).

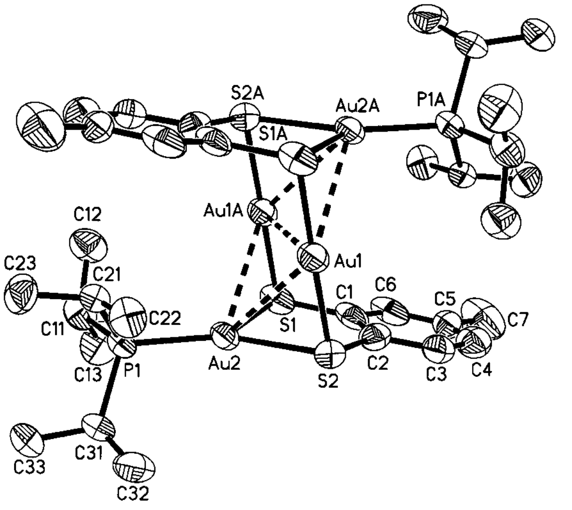


Figure 3. Structure of compound **4** (ORTEP drawing with 50% probability ellipsoids, H atoms omitted for clarity). Selected distances (Å) and angles (deg): Au1−S2 = 2.305(3), Au1−S1A = 2.306(3), Au1−Au2 = 3.0667(7) Au1−Au1A = 3.193(1), Au1−Au2A = 3.0857(7); S2−Au1−S1A = 175.4(1), Au2−Au1−Au2A = 117.47(2), Au2A−Au1−Au1A = 58.44(2), Au2−Au1−Au1A = 59.02(2).

edge-sharing, almost equilateral triangles. The three endocyclic Au−Au−Au angles are all close to 60°: Au2′−Au2−Au3′ = 58.26(1)°, Au2−Au3−Au2′ = 61.86(1)°, Au2−Au2′−Au3 = 59.88(1)°. With these dimensions of the Au_4 unit, compound **7** is another classical example for tight aurophilic bonding. The short Au−Au contacts are associated with small Au−S−Au angles of only 77.89(8)° at S1 and 81.93(8)° at S2.

While the cluster atoms Au2/Au2′ are linearly two-coordinated (S1′−Au2−S2 = 175.0(1)°), the cluster atoms Au3/Au3′ are three-coordinated with the atoms C3, Au3, S1, and S2 all in one plane (sum of the valence angles at Au3 359.7(1)°). The small angle S1−Au3−S2 (85.49(9)°) imposed by the ligand span of the phenylene-1,2-dithiolate unit, and by the optimization of the aurophilic Au2−Au2′ contacts, means an unusually large distortion away from the ideal 120°. This is probably the reason why the two bond lengths Au3−S1 = 2.528(3) Å and Au3−S2 = 2.421(3) Å and the two angles C3−Au3−S1/S2 (130.2(3)/144.0(3)°) are significantly different. The isocyanide ligand is "leaning over" toward S1 in order to somewhat straighten the axis N3−C3−Au3−S2. A similar distortion has also been observed for **2** and **4** (P1 closer to S1 than to S2 in Figures 2 and 3).

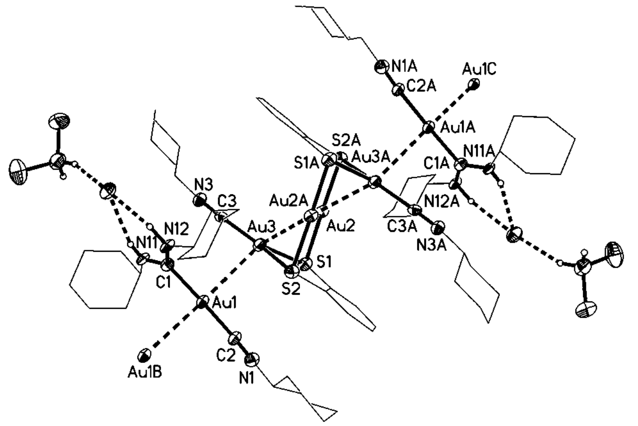


Figure 4. Infinite chains in the structure of crystals of the composition $(\mathbf{7})(\mathbf{8})_2(CH_2Cl_2)_2$ (ORTEP drawing with 50% probability ellipsoids). Selected distances (Å) and angles (deg): Au1−Au3 = 3.2965(6), Au1−Au1B = 3.466(1), Au3−Au2 = 3.0466(6), Au3−Au2A = 3.0984(6), Au2−Au2A = 3.1588(7), Au1−C1 = 2.03(1), Au1−C2 = 1.98(1), Au2−S1 = 2.312(3), Au2−S2A = 2.303(3), Au3−C3 = 1.95(1), Au3−S1 = 2.528(3), Au3−S2 = 2.421(3); Au1B−Au1−Au3 = 162.2(1), Au1−Au3−Au2 = 163.46(2), Au1−Au3−Au2A = 119.60(2), C1−Au1−C2 = 177.9(4) S1−Au2−S2A = 175.0(1).

The carbene complex unit **8** has linearly two-coordinated gold atoms (Au1) with conventional isocyanide bonding (N1−C2−Au1) and "Fischer carbene" coordination (N11/N12−C1−Au1). The C1 atom is in a trigonal-planar environment (sum of the angles 359.9°). Since there is precedent for this type of coordination, the structure of component **8** is not discussed in detail.[18] The dimensions of the hydrogen bonding of the chloride anion are summarized in Table 1.

Discussion and Conclusion

The present work has shown that the reaction of equimolar quantities of tris[(trialkylphosphine)gold(I)]oxonium tetrafluoroborates and phenylene-1,2-dithiols is a convenient, high-yield, one-step route to compact bis(phosphine)tetragold bis(phenylene-1,2-dithiolate) clusters (**2** and **4**; Scheme 2). These tetranuclear compounds are formed in a ligand redistribution process from tris(phosphine)(phenylene-1,2-dithiolato)trigold tetrafluoroborate intermediates, with bis(phosphine)gold tet-

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(18) Raubenheimer, H. G.; Cronje, S. In *Gold: Progress in Chemistry, Biochemistry and Technology*; Schmidbaur, H., Ed.; Wiley: Chichester, U.K., 1999; p 608 ff.

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

	2	**4**	**7**(**8**)$_2$(CH$_2$Cl$_2$)$_2$
Crystal Data			
formula	$C_{30}H_{50}Au_4P_2S_4$	$C_{32}H_{54}Au_4P_2S_4$	$C_{68}H_{104}Au_6Cl_6N_8S_4$
M_r	1388.75	1416.80	2556.33
cryst syst	orthorhombic	monoclinic	triclinic
space group	*Pbca*	$P2_1/n$	$P\bar{1}$
a (Å)	13.5964(1)	11.3630(4)	12.2612(4)
b (Å)	15.3692(2)	14.6980(6)	12.3935(3)
c (Å)	17.7202(2)	12.4590(4)	14.2413(5)
α (deg)	90	90	78.193(1)
β (deg)	90	110.982(2)	87.988(1)
γ (deg)	90	90	72.019(1)
V (Å^3)	3702.9(1)	1942.9(1)	2013.9(1)
ρ_{calcd} (g cm^{-3})	2.491	2.422	2.103
Z	4	2	1
F(000)	2560	1312	1208
μ(Mo Kα) (cm^{-1})	161.30	153.37	112.32
Data Collection			
T (°C)	−130	−130	−130
no. of measd rflns	98 026	87 126	72 102
no. of unique rflns	4098 ($R_{int} = 0.059$)	4288 ($R_{int} = 0.050$)	8400 ($R_{int} = 0.096$)
abs cor	DELABS	DELABS	DELABS
T_{min}/T_{max}	0.195/0.665	0.131/0.602	0.143/0.615
Refinement			
no. of refined params	181	190	421
final *R* values ($I \geq 2\sigma(I)$)			
R1	0.0308	0.0596	0.0546
wR2[a]	0.0803	0.1157	0.1266
a/*b*	0.0000/17.72	0.0007/44.48	0.0000/0.000

[a] $wR2 = \{[\sum w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]$; $p = (F_o^2 + 2F_c^2)/3$.

rafluoroborates as the byproducts (Scheme 2). With oxonium salts bearing triarylphosphine ligands, no such ligand redistribution occurs and the trinuclear salts are the sole products (**5**; Scheme 3).

Tetranuclear clusters of the type obtained with trialkylphosphines are also generated in the reaction of (isocyanide)gold(I) chlorides (RNC)AuCl with alkali-metal phenylene-1,2-dithiolates. However, the resulting bis(isocyanide)tetragold bis(phenylene-1,2-dithiolate) (**7**; Scheme 4) is only a minor byproduct in this reaction and was isolated as a cocrystallizate with (isocyanide)(diaminocarbene)gold(I) chloride in a dichloromethane solvate, (**7**)(**8**)$_2$(CH$_2$Cl$_2$)$_2$. Component **8** of the type (RNC)Au[C(NHR)$_2$]$^+$Cl$^-$ (Scheme 4) is probably formed from the bis(isocyanide)gold chloride byproduct [(RNC)$_2$Au]$^+$Cl$^-$ upon addition of the alkylamine RNH$_2$ present in the reaction mixture owing to trace hydrolysis of the isocyanide (R = cyclohexyl).

The main product of the reaction between (RNC)AuCl and $C_6H_4(SNa)_2$ is a deep green salt of the composition [(RNC)$_2$Au]$^+$[Au(S$_2$C$_6$H$_4$)]$^-$ containing gold in two oxidation states (Au(I) in the cation and Au(III) in the anion) (Scheme 4). Similar redox products have been observed in analogous reactions with (R$_3$P)AuCl compounds in several laboratories and are not fully understood, because the oxidizing agent (and its reduction product) have not yet been identified.[11a,12,16] Further work is necessary to clarify this point.

The structures of the new tetranuclear compounds (**2**, **4**, and **7**) are very similar and have been shown to contain the neutral cluster [Au$_4$(S$_2$C$_6$H$_3$R)$_2$] (R = H, Me) stabilized by either two trialkylphosphine or two isocyanide ligands. The cluster geometry is indicative of intimate aurophilic bonding which supports the exceedingly compact arrangement of the four metal atoms at the corners of two coplanar, edge-sharing, almost equilateral triangles. There is precedent for this type of aggregation, which appears to be one of the most favorable supramolecular aggregation modes in gold(I) chemistry.[1]

Experimental Section

All experiments were carried out under an atmosphere of dry, pure nitrogen. Solvents were dried and saturated with nitrogen, and glassware was oven-dried and filled with nitrogen. Standard equipment was used throughout. The tris(gold)oxonium salts (LAu)$_3$O$^+$BF$_4^-$ (L = ^{i}Pr$_3$P, Ph$_3$P) and (cyclohexyl isocyanide)gold chloride were prepared by following established procedures.[19,20] The phenylenedithiols and all other reagents are commercially available.

Tris[(triisopropylphosphine)gold](phenylene-1,2-dithiolate) Tetrafluoroborate (1) and Its 4-Methyl Analogue (3). A solution of {[(^{i}Pr$_3$P)Au]$_3$O}BF$_4$ (150 mg, 0.13 mmol, for **1**; 100 mg, 0.085 mmol, for **3**) in dichloromethane (5 mL) is treated with a solution of 1,2-C$_6$H$_4$(SH)$_2$ (18 mg, 0.13 mmol) or 1,2,4-C$_6$H$_3$(SH)$_2$(Me) (13 mg, 0.085 mmol) in 2 mL of the same solvent and a small quantity of NaBF$_4$ for 1 h at 0 °C with stirring. The precipitate is filtered off and the product precipitated from the filtrate by layering with pentane at −20 °C. Colorless solids were obtained (**1**, 140 mg, 83% yield; **3**, 88 mg, 79% yield). A few large crystals of **2**/**4** may also be formed, which should be separated in order to obtain pure products. Anal. Calcd for **1**, $C_{33}H_{67}Au_3BF_4P_3S_2$: C, 30.52; H, 5.20. Found: C, 31.07; H, 5.36. Anal. Calcd for **3**, $C_{34}H_{69}Au_3BF_4P_3S_2$: C, 31.11; H, 5.30. Found: C, 32.30; H, 5.73. ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 20 °C; δ): **1**, 69.0 (s); **3**, 68.5 (s). ^{1}H NMR (CD$_2$Cl$_2$, 20 °C; δ): **1**, 1.26 (dd, *J* = 7.0 and 16.1 Hz, 54 H, Me), 2.28 (dsep, *J* = 7.0 and 7.3 Hz, 9 H, C*H*(Me)$_2$), 7.01 and 7.86

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(dd, $J = 5.9$ and 3.3 Hz, 4 H, C_6H_4); **3**, 1.25 (dd, $J = 7.2$ and 16.1 Hz, 54 H, (*Me*)$_2$CH), 2.27 (dsep, $J = 7.2$ and 6.9 Hz, 9 H, C*H*(Me)$_2$), 2.25 (s, 3 H, *Me*(Ph)), 7.69, 7.70, and 6.82 (m, 3 × 1 H, C_6H_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C; δ): **1**, 20.65 (d, $J =$ 6.9 Hz, Me), 24.9 (d, $J = 29.2$ Hz, CH), 125.8, 135.1, and 138.9 (s, C_6H_4); **3**, 20.47 (d, $J = 1.6$ Hz, (*Me*)$_2$CH), 24.40 (d, $J = 28.5$ Hz, *C*H(Me)$_2$), 20.58 (s, *Me*(Ph)), 126.8, 134.6, 134.8, 135.3, 135.8, and 138.7 (all s, *C*$_6$H$_3$(Me)).

Bis(triisopropylphosphine)tetragold Bis(phenylene-1,2-dithiolate) (2) and Its 4-Methyl Analogue (4). The reactions described for the preparation of **1**/**3** give a reaction mixture which upon a different workup yields products **2** and **4** instead. To this end, the filtrate is concentrated under vacuum at room temperature to a volume of 1 mL and the residue kept at this temperature for prolonged time. After 2 h the products begin to separate as large crystals, which cannot be redissolved in dichloromethane: **2**, 112 mg, 63% yield; **4**, 81 mg, 67% yield.

Anal. Calcd for **2**, $C_{30}H_{50}Au_4P_2S_4$: C, 25.95; H, 3.63; Au, 56.73. Found: C, 26.23; H, 3.77; Au, 55.60. Calcd for **4**, $C_{32}H_{54}Au_4P_2S_4$: C, 27.13; H, 3.84; Au, 55.61. Found: C, 25.56; H, 3.73; Au, 54.60.

Tris[(triphenylphosphine)gold](phenylene-1,2-dithiolate) Tetrafluoroborate (5). A 281 g amount (0.19 mmol) of $\{[(Ph_3P)Au]_3O\}BF_4$ dissolved in 5 mL of CH_2Cl_2 is reacted for 1 h at 20 °C with a small amount of $NaBF_4$ and a solution of 1,2-$C_6H_4(SH)_2$ (27 mg, 0.19 mmol) in 2 mL of the same solvent with stirring. After filtration the product is precipitated by careful layering with pentane at −20 °C. The colorless solid (270 mg, 89% yield) is soluble in di- and trichloromethane but insoluble in pentane and diethyl ether. Anal. Calcd for $C_{60}H_{49}Au_3BF_4P_3S_2$: C, 44.91; H, 3.08; Au, 36.82. Found: C, 44.73; H, 2.76; Au, 37.04. The NMR data are in agreement with those reported for the perchlorate salt, including the temperature dependence of the ^{31}P resonance (δ); 20 °C, 35.41; −50 °C, 44.9 (1 P), 34.1 (2 P).

Reaction of (Cyclohexyl isocyanide)gold Chloride with Disodium Phenylene-1,2-dithiolate. (^{c}HexNC)AuCl (100 mg, 0.293 mmol) is reacted with NaOMe (16 mg, 0.293 mmol) and $C_6H_4(SH)_2$ (21 mg, 0.147 mmol) in a mixture of methanol (2 mL) and dichloromethane (2 mL) at 20 °C for 1 h with stirring. The reaction mixture is evaporated to dryness under vacuum, and the residue is extracted with 4 mL of CH_2Cl_2. Upon careful layering with pentane a mixture of crystals is formed, consisting mainly of the green needles of $[(^cHexNC)_2Au][Au(S_2C_6H_4)_2]$ (41 mg, 31% yield after mechanical separation). MS (FAB): cations, *m/z* 415.6 (99%) $[(^cHexNC)_2Au]^+$; anions, *m/z* 477.2 (4.4%) $[Au(S_2C_6H_4)_2]^-$. The crystal structure has been determined.[17]

The colorless needles separated from the green needles were subjected to a single-crystal X-ray diffraction study and shown to have the composition (**7**)(**8**)$_2$(CH_2Cl_2)$_2$ (Scheme 4, Figure 4).

Anal. Calcd for $C_{66}H_{100}Au_6Cl_2N_8S_4 + C_5H_{12}$: C, 34.68; H, 4.59; N, 4.56. Found: C, 35.63; H, 4.38; N, 4.60. The cocrystallizate is soluble in chloroform (at 20 °C) and shows the following NMR signals. ^1H NMR (δ): **7** + **8**, 1.38, 1.68, 1.91, and 3.84/3.57 (m, rel intens 4:4:2:1 H, C_6H_{11}), 7.33 and 7.65 (dd, $J = 1.5$ and 4.7 Hz, rel int.ens 2:2 H, C_6H_4); **8**, 9.12 (br s, NH). $^{13}C\{^1H\}$ NMR (δ): **7** + **8**, 23.1, 24.5/24.9, 31.3/31.9, and 51.6/55.2 (s, C_6H_{11}); **8**, 195.5 (s, CN_2), *C*N-^{c}Hex not observed; **7**, 126.0, 129.4, 142.3 (s, C_6H_4).

Crystal Structure Determinations. Specimens of suitable quality and size of compounds **2**, **4**, and **7**(**8**)$_2$(CH_2Cl_2)$_2$ 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 Kα 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 calculated and allowed to ride on their parent atoms with fixed isotropic contributions. Important interatomic distances and angles are given in the corresponding figure captions. Anisotropic thermal parameters and complete lists 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 CCDC−184333−184335.

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

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