

Theoretical Evidence for Transannular Metal–Metal Interactions in Dinuclear Coinage Metal Complexes[†]

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The dinuclear head-to-tail complexes $[M_2(\text{PPh}_2\text{CH}_2\text{SPh})_2]^{2+}$ ($M = \text{Cu}$ (**1**), Ag (**2a**, **2b**), Au (**4**)) are obtained either by reaction of $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{CF}_3\text{SO}_3$, AgClO_4 , AgCF_3SO_3 , with equimolecular amounts of $\text{PPh}_2\text{CH}_2\text{SPh}$ or of $[\text{AuCl}(\text{PPh}_2\text{CH}_2\text{SPh})]$ (**3**), prepared by reaction of $[\text{AuCl}(\text{tht})]$ and $\text{PPh}_2\text{CH}_2\text{SPh}$, with AgCF_3SO_3 . The crystal structures of complexes **2a** and **4** have been established by X-ray diffraction studies. Ab initio HF/II and MP2/II calculations have been performed on the $[M_2(\text{H}_2\text{PCH}_2\text{SH})_2]^{2+}$ model, indicating that metallophilic attraction is indeed present for all the coinage metals as a correlation effect and is strengthened in the case of gold by relativistic effects. Since experimental and theoretically predicted geometries are in close agreement, we assume that our calculations are accurate enough to obtain valid conclusions.

Introduction

Despite the fact that two closed-shell metal cations would normally be expected to repel each other, a large number of inorganic and organometallic compounds have been described whose structures indicate strong metal–metal attractions.¹ Particular evidence has now been accumulated for an attractive interaction between two d^{10} ions. Ab initio calculations indicate the attraction as a correlation effect but strengthened by the large relativistic effects for heavy elements, especially in the case of Au(I) .² Apart from its fundamental interest, this aurophilic attraction³ may play a role in the medical applications of gold compounds⁴ or be associated with useful optical properties.⁵ In contrast, the analogous cuprophilicity and argentophilicity of the lighter congeners is still a matter of controversy. Thus, the

short metal–metal distances observed for copper and silver dinuclear complexes have been attributed to the ligand architecture.⁶ Furthermore, the existence of a copper–copper bonding interaction to reflect the short contacts has both been supported⁷ and refuted⁸ at various levels of theory. To compare the metallophilicity of the three coinage metals, a set of complexes is required involving the same ligands, the same coordination number and geometry.⁹ There are few examples that would permit a clean comparison of $\text{Cu}\cdots\text{Cu}$, $\text{Ag}\cdots\text{Ag}$, and $\text{Au}\cdots\text{Au}$ metallophilic bonding.¹ We report here the first comparative study of the transannular $M^I\cdots M^I$ attraction for the three coinage metals.

In the course of our work on dinuclear complexes $[M_2L_2]^{2+}$,¹⁰ we decided to concentrate on P–S donor bidentate ligands, at least in part because the majority of coinage metal compounds used in modern technology and medicine or present in biological systems are based on phosphorus and/or sulfur donor ligands.^{11–15} Thus we chose the potentially bidentate ligand $\text{PPh}_2\text{CH}_2\text{SPh}$

[†] Dedicated to Professor Pascual Royo on the occasion of his 60th birthday.

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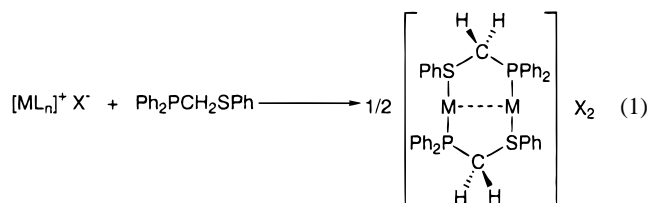
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and employed it in copper, silver or gold systems in order to compare the metal–metal interactions in the resulting complexes.

Results and Discussion

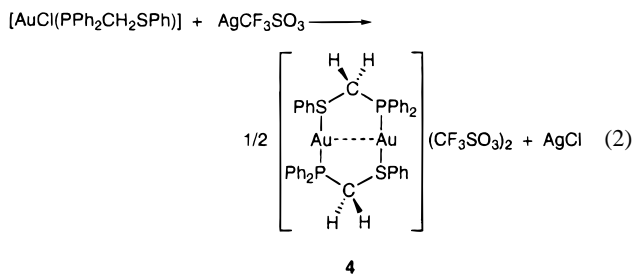
Synthesis. We have synthesized the head-to-tail complexes $[M_2(PPH_2CH_2SPh)_2]X_2$ ($M = Cu$, $X = CF_3SO_3$ (**1**); $M = Ag$, $X = ClO_4$ (**2a**), CF_3SO_3 (**2b**); $M = Au$, $X = CF_3SO_3$ (**4**)) by reaction of equimolar amounts of the phosphinothioether ligand and the appropriate metallic precursor for Cu and Ag (eq 1).



$M = Cu$; $L = CH_3CN$ ($n = 4$); $X = CF_3SO_3$ (**1**)

$M = Ag$; $X = ClO_4$ (**2a**), CF_3SO_3 (**2b**)

In case of the gold derivative a typical reaction between the gold precursor $[Au(tht)_2]CF_3SO_3$ ($tht =$ tetrahydrothiophene) and the phosphinothioether ligand in molar ratio 1:1 does not produce the expected product; only one tht ligand is substituted. This result differs from those previously described with diphosphines and even with a similar phosphine with three thioether functions.¹⁶ An alternative pathway consists of the reaction of $[AuCl(PPH_2CH_2SPh)]$ (**3**) (see Experimental Section) and $AgCF_3SO_3$ in equimolar amounts to give $[Au(PPH_2CH_2SPh)]CF_3SO_3$ "in situ", which dimerizes to the desired product in the crystallization process (eq 2). The analytical data and physical and spectroscopic properties of complexes **1–4** are as expected.



Crystal Structures. The crystal structure of $[Au_2(PPH_2CH_2SPh)_2](CF_3SO_3)_2$ (**4**) has been confirmed by X-ray diffraction studies and is shown in Figure 1. A selection of bond lengths and angles are collected in Table 1. The molecule has imposed crystallographic inversion symmetry and thus only half of it represents the asymmetric unit. Each gold atom is bonded to one sulfur and one phosphorus atom of the two different PPH_2-

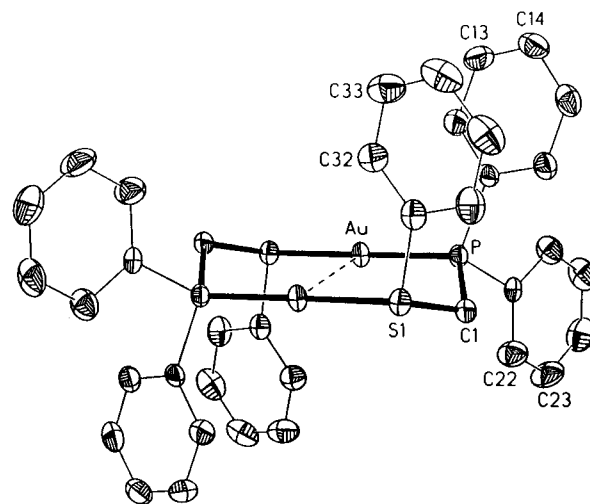


Figure 1. Structure of the cation of complex **4** in the crystal. Displacement parameter ellipsoids represent 50% probability surfaces. H atoms are omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for **4^a**

Au–P	2.2721(11)	Au–S(1)#1	2.3619(11)
Au–Au#1	2.9020(5)	P–C(11)	1.808(4)
P–C(21)	1.814(4)	P–C(1)	1.831(4)
S(1)–C(31)	1.783(5)	S(1)–C(1)	1.807(4)
P–Au–S(1)#1	175.07(4)	P–Au–Au#1	91.36(3)
S(1)#1–Au–Au#1	93.45(3)	C(11)–P–C(21)	106.8(2)
C(11)–P–C(1)	107.8(2)	C(21)–P–C(1)	104.8(2)
C(11)–P–Au	113.77(14)	C(21)–P–Au	110.50(14)
C(1)–P–Au	112.57(14)	C(31)–S(1)–C(1)	103.7(2)
C(31)–S(1)–Au#1	107.26(14)	C(1)–S(1)–Au#1	107.64(14)
S(1)–C(1)–P	116.9(2)		

^a Symmetry transformations used to generate equivalent atoms: #1, $-x + 1, -y + 1, -z$.

CH_2SPh ligands giving the head-to-tail isomer. The Au–P distance is 2.2721(11) Å and is very similar to those found in other dinuclear gold complexes with mixed sulfur–phosphorus ligands such as $[Au_2(\mu-S(CH_2)_3S)(\mu-dppm)]$ (2.259(3) and 2.266(3)¹⁷ Å) ($dppm =$ bis(diphenylphosphino)methane) or $[Au_2(\mu-SCH_2PEt_2)_2]$ (2.27 Å).¹⁸ However, the Au–S(1ⁱ) ($i = -x + 1, -y + 1, -z$) distance of 2.3619(11) Å is slightly longer than in the complexes mentioned above, perhaps because the uncharged sulfur donor in **4** leads to weaker Au–S bonds. The Au···Au distance is 2.9020(5) Å, a typical value for gold–gold interactions in dinuclear gold(I) complexes. There is a weak contact from gold to an oxygen atom of the triflate ligand: Au···O(2), 3.093(4) Å.

The crystal structure of the silver complex in the perchlorate salt (complex **2a**) has been confirmed by X-ray diffraction studies. The complex crystallizes with two independent molecules, each one associated with a symmetry center; the asymmetric unit thus consists of two-half molecules. One of the molecules is shown in Figure 2 and a selection of bond lengths and angles in Table 2. Each silver atom is bonded to one sulfur and one phosphorus atom of the different PPH_2CH_2SPh ligands giving (as in the gold compound) the head-to-tail isomer. The two independent silver atoms have a slightly distorted linear geometry, with angles P(1)–Ag(1)–S(1), 172.83(4)°, and P(2)–Ag(2)–S(2), 173.97(4)°. This distortion may arise from weak Ag···O contacts with the perchlorate

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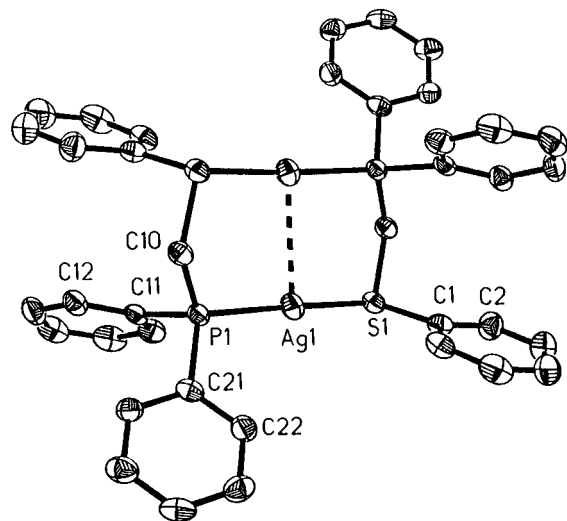


Figure 2. Perspective view of the cation of one of the molecules of complex **2a**. Displacement parameter ellipsoids represent 50% probability surfaces. H atoms are omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **2a**^a

Ag(1)–P(1)	2.3896(12)	Ag(1)–S(1)	2.4406(12)
Ag(1)–Ag(1)#1	2.9501(8)	P(1)–C(11)	1.807(4)
P(1)–C(21)	1.824(4)	P(1)–C(10)	1.831(4)
S(1)–C(1)	1.781(5)	S(1)–C(10)#1	1.807(4)
Ag(2)–P(2)	2.3931(13)	Ag(2)–S(2)	2.4519(13)
Ag(2)–Ag(2)#2	2.9732(9)	P(2)–C(41)	1.805(5)
P(2)–C(51)	1.821(4)	P(2)–C(40)	1.838(4)
S(2)–C(31)	1.790(4)	S(2)–C(40)#2	1.809(4)
P(1)–Ag(1)–S(1)	172.83(4)	P(1)–Ag(1)–Ag(1)#1	86.37(3)
S(1)–Ag(1)–Ag(1)#1	96.58(3)	C(11)–P(1)–C(21)	105.1(2)
C(11)–P(1)–C(10)	107.9(2)	C(21)–P(1)–C(10)	100.2(2)
C(11)–P(1)–Ag(1)	111.01(14)	C(21)–P(1)–Ag(1)	113.8(2)
C(10)–P(1)–Ag(1)	117.68(14)	C(1)–S(1)–C(10)#1	103.8(2)
C(1)–S(1)–Ag(1)	107.1(2)	C(10)#1–S(1)–Ag(1)	109.23(14)
P(2)–Ag(2)–S(2)	173.97(4)	P(2)–Ag(2)–Ag(2)#2	86.75(3)
S(2)–Ag(2)–Ag(2)#2	96.02(3)	C(41)–P(2)–C(51)	106.2(2)
C(41)–P(2)–C(40)	107.7(2)	C(51)–P(2)–C(40)	100.7(2)
C(41)–P(2)–Ag(2)	113.7(2)	C(51)–P(2)–Ag(2)	109.4(2)
C(40)–P(2)–Ag(2)	117.7(2)	C(31)–S(2)–C(40)#2	103.3(2)
C(31)–S(2)–Ag(2)	111.3(2)	C(40)#2–S(2)–Ag(2)	105.9(2)

^a Symmetry transformations used to generate equivalent atoms: #1, $-x + 1, -y, -z + 1$; #2, $-x + 2, -y, -z + 1$.

anion: Ag(2)···O(7), 2.640(3) Å; Ag(1)···O(5), 2.851(5) Å; and Ag1···O3, 2.988(4) Å (see Figure 3). The Ag–P distances are 2.3895(12) and 2.3932(13) Å, and the Ag–S bond lengths are 2.4406(12) and 2.4519(13) Å; these values are similar to those obtained in the complex [Ag{PPh₂(CH₂)₂SEt}]ClO₄.¹⁹ It is noteworthy to mention that both Ag–P and Ag–S distances are longer than the corresponding Au–P and Au–S distances, thus corroborating the observations made by Schmidbaur that the covalent radius of gold(I) is smaller than that of silver(I).⁹ Both dimers display Ag···Ag contacts of 2.9501(8) and 2.9732(9) Å, which are values close to the Ag–Ag distance in metallic silver, 2.89 Å, or in many silver(I) oxides.²⁰

The analogous complex of Cu was unfortunately too unstable to provide suitable single crystals for an X-ray structure determination.

Theoretical Calculations. The short distances observed for the Ag and Au derivatives indicate a feasible M···M interaction of great theoretical interest. The size of the molecule under

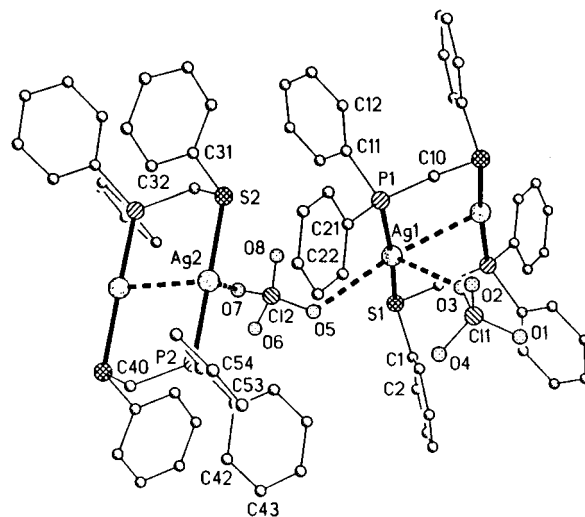


Figure 3. Structure of complex **2a** in the crystal. H atoms are omitted for clarity. There are no further contacts from the depicted perchlorates to other silver atoms.

study necessitates the use of [M₂(H₂PCH₂SH)₂]²⁺ as a model for the ab initio calculations. Any effect of the weak M···O contacts, which we assume to be minimal, is neglected. All calculations were carried out using the Gaussian94 program package.²¹ The molecular geometries were initially optimized, within appropriate molecular symmetry constraints (C_i), at the Hartree–Fock self-consistent field (HF) level of theory, and electron correlation, keeping the core orbitals frozen, was included in further optimizations by using Møller–Plesset perturbation theory²² with second-order corrections (MP2) employing Schlegel’s analytical gradient procedure.²³

The following basis set combination was employed. For C, S, P, and H, the standard split-valence 6-31G(d) basis set,^{24,25} and for Cu, Ag and Au, the pseudorelativistic Hay–Wadt small-core effective core potential,²⁶ where the minimal basis set has been split to [341/2111/41], [341/3111/31], and [341/3111/21], respectively.²⁷ This basis set combination will be hereafter referred to as II. The HF/II and MP2/II levels of theory have demonstrated their ability to calculate optimized geometries of transition metal complexes with good accuracy.²⁸

The absolute energies and the most relevant geometrical parameters of the [CH₂(SHMPH₂)₂CH₂]²⁺ optimized structures with the HF/II wave function are given in Figure 2. Several features are noteworthy. At this level of theory, the M–M

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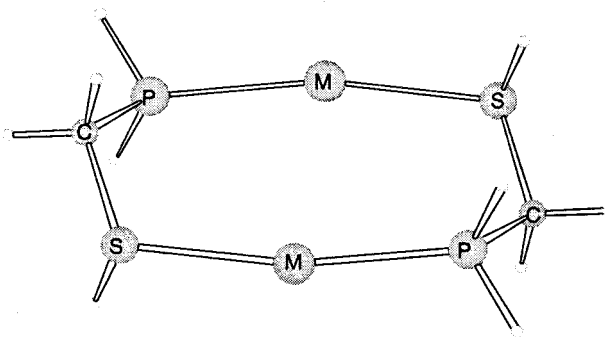
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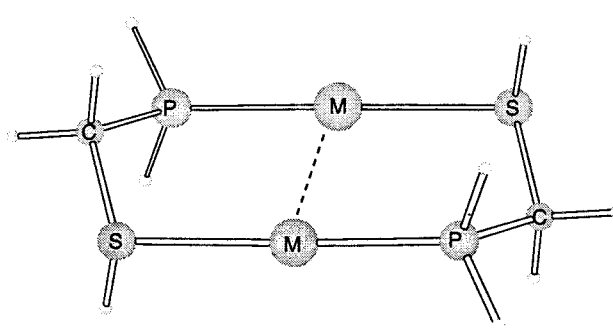
M	Cu	Ag	Au
Energy	-1947.572192	-1847.342735	-1826.626241
M-M	3.612	4.017	3.345
P-S	3.135	3.138	3.157
M-S	2.440	2.734	2.503
M-P	2.433	2.665	2.386
S-C	1.824	1.823	1.825
P-C	1.855	1.857	1.852
P-M-S	167.8	160.4	174.9
P-C-S	116.9	117.0	118.3

Figure 4. HF/II//HF/II absolute energies [hartrees] and optimized structural parameters [Å, deg] calculated for $[M_2(H_2PCH_2SH)_2]^{2+}$.

interatomic distances (3.612, 4.017, and 3.345 Å for Cu, Ag, and Au, respectively) are far removed from the experimental values (2.950 and 2.973 for Ag and 2.902 Å for Au). In contrast, the experimental radii observed for two- and four-coordinate M(I) compounds⁹ suggest that the calculated Au–Au distance should be intermediate between that of Cu–Cu and Ag–Ag when no interaction is present. However, the relatively short distance obtained at the HF/II level for the gold complex indicates an attraction that should be inherently relativistic since correlation is not included at the Hartree–Fock level. The same conclusion can be derived from the P–M–S angle (167.8, 160.4, and 174.9° for Cu, Ag, and Au, respectively).

The correlation was accounted for at the MP2/II level. Figure 5 shows the absolute energies and the most relevant geometrical parameters of the $[CH_2(SHMPH_2)_2CH_2]^{2+}$ optimized structures at this level. As can be observed, the calculated metal–metal interatomic distances are reduced to 3.089, 3.200, and 3.030 Å for Cu, Ag, and Au, respectively, which indicates that correlation effects are attractive in all coinage metals and that MP2 captures most of the physics of the $Cu^I \cdots Cu^I$ and $Ag^I \cdots Ag^I$ attraction. The Au–Au distance is still slightly shorter than Cu–Cu, which confirms the presence of both relativistic and correlation effects in the gold dimer. As expected from their experimental radii,⁹ the M–M distance is larger for silver than for copper or gold. The role of the correlation may also be deduced by the dramatic reduction of the P–M–S angle (from inner 167.8° to outer 179.7°, from 160.4° to 174.3°, and from inner 174.9° to outer 176.5° for Cu, Ag, and Au, respectively).

In summary, our calculations indicate that metallophilic attraction is indeed present for all the coinage metals as a correlation effect and that it is strengthened by the relativistic effect for gold. Since theoretically predicted geometries are in close agreement with the experimental ones, we can assume that our calculations are accurate enough to obtain valid conclusions.



M	Cu	Ag	Au
Energy	-1948.901446	-1848.295437	-1827.588416
M-M	3.089	3.200	3.030
P-S	3.096	3.111	3.123
M-S	2.279	2.557	2.427
M-P	2.259	2.510	2.315
S-C	1.822	1.821	1.825
P-C	1.850	1.853	1.849
P-M-S	179.7	174.3	176.5
P-C-S	115.0	115.8	116.5

Figure 5. MP2/II//MP2/II absolute energies [hartrees] and optimized structural parameters [Å, deg] calculated for $[M_2(H_2PCH_2SH)_2]^{2+}$.

Experimental Section

Instrumentation. Infrared spectra were recorded in the range 4000–200 cm^{-1} on a Perkin-Elmer 883 spectrophotometer and on a Perkin-Elmer FT-IR Spectrum 1000 spectrophotometer using Nujol mulls between polyethylene sheets. C, H, and S analyses were carried out with a Perkin-Elmer 240C microanalyzer. Mass spectra were recorded on a VG Autospec using the LSIMS techniques and nitrobenzyl alcohol as matrix and on a HP59987 A Electrospray. ¹H, ¹⁹F, and ³¹P NMR spectra were recorded on a Bruker ARX 300 in CDCl₃ and (CD₃)₂CO solutions. Chemical shifts are quoted relative to SiMe₄ (¹H, external), CFCl₃ (¹⁹F, external), and H₃PO₄ (85%) (³¹P, external).

Solvent and Reagent Pretreatment. Dichloromethane and hexane were distilled from CaH₂ and diethyl ether from sodium, under nitrogen atmosphere. $[Cu(CH_3CN)_4]CF_3SO_3$ was prepared as described²⁸ using triflic acid instead of tetrafluoroboric acid or perchloric acid; $[AuCl(tht)]^{29}$ and PPh_2CH_2SPh ³⁰ were prepared by reported literature methods.

Caution! Perchlorate salts with organic cations may be explosive.

Synthetic Procedures. Preparation of $[Cu_2(PPh_2CH_2SPh)_2](CF_3SO_3)_2$ (1**).** To a solution of $[Cu(CH_3CN)_4]CF_3SO_3$ (0.122 g, 0.32 mmol) in CH₂Cl₂ (20 mL) was added PPh_2CH_2SPh (0.100 g, 0.32 mmol). The reaction mixture was stirred for 1 h at room temperature, and then the solvent was removed by reduced pressure to leave **1** as a white solid. Yield: 90%. Mass spectra: $[CuPPh_2CH_2SPh]^+$ at m/z 371 (100%); $[M + CF_3SO_3]^+$ at m/z 893 (7%). Anal. Calcd for C₄₀H₃₄Cu₂F₆O₆P₂S₄, **1**: C, 46.1; H, 3.3; S, 12.3. Found: C, 45.8; H, 3.2; S, 11.8. ³¹P{¹H} NMR (CDCl₃), δ: –8.7 (s). ¹⁹F NMR (CDCl₃), δ: –77.97 (s). ¹H NMR (CDCl₃), δ: 7.62–7.19 (m, 30H, Ph), 3.99 (m, 4H, CH₂).

Preparation of $[Ag_2(PPh_2CH_2SPh)_2](X)_2$ (X = ClO₄ (2a**), CF₃SO₃ (**2b**)).** PPh_2CH_2SPh (0.100 g, 0.32 mmol) was added to a solution of AgClO₄ (0.067 g, 0.32 mmol of **2a**) or AgCF₃SO₃ (0.083 g, 0.32 mmol of **2b**) in 20 mL of Et₂O. After stirring for 1 h a white precipitate of **2a** or **2b** was filtered off. Yield: 83% **2a**, 70% **2b**. Mass spectra: $[AgPPh_2CH_2SPh]^+$ at m/z 417 (100%, **2a**, **2b**); $[M + ClO_4]^+$ at m/z 930 (6%, **2a**); $[M + CF_3SO_3]^+$ at m/z 981 (15%, **2b**). Anal. Calcd

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Table 3. Details of Data Collection and Structure Refinement for Complexes **2a** and **4**

	2a	4
empirical formula	C ₃₈ H ₃₄ Ag ₂ Cl ₂ O ₈ P ₂ S ₂	C ₄₀ H ₃₄ Au ₂ F ₆ O ₃ P ₂ S ₄
crystal habit	colorless prism	colorless prism
crystal size/mm	0.75 × 0.50 × 0.40	0.30 × 0.30 × 0.20
crystal system	monoclinic	triclinic
space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 1̄
<i>a</i> /Å	16.801(3)	9.5174(14)
<i>b</i> /Å	15.618(4)	10.2427(8)
<i>c</i> /Å	16.994(4)	11.8853(14)
α /deg	90	79.785(8)
β /deg	119.08(2)	75.068(10)
γ /deg	90	80.246(8)
<i>U</i> /Å ³	3897.0(15)	1092.4(2)
<i>Z</i>	4	1
<i>D_c</i> /Mg m ⁻³	1.758	1.917
<i>M</i>	1031.36	1260.79
<i>F</i> (000)	2064	604
<i>T</i> /°C	-130	-100
2 θ _{max} /deg	50	50
μ (Mo K α)/mm ⁻¹	1.383	7.034
transmission	0.839–0.956	0.784–0.963
no. of reflns measd	9549	4081
no. of unique reflns	6876	3832
<i>R</i> _{int}	0.0215	0.0139
<i>R</i> (<i>F</i> , <i>F</i> > 4 σ (<i>F</i>)) ^a	0.0391	0.0233
<i>wR</i> (<i>F</i> ² , all reflns) ^b	0.0959	0.0534
no. of reflns used	6876	3832
no. of params	487	271
no. of restraints	0	204
<i>S</i> ^c	1.054	0.991
max. $\Delta\rho$ e Å ⁻³	1.781	0.792

^a $R(F) = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^b $wR(F^2) = [\sum \{w(F_o^2 - F_c^2)^2\} / \sum \{w(F_o^2)^2\}]^{0.5}$; $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, where $P = [F_o^2 + 2F_c^2] / 3$ and *a* and *b* are constants adjusted by the program. ^c $S = [\sum \{w(F_o^2 - F_c^2)^2\} / (n - p)]^{0.5}$, where *n* is the number of data and *p* the number of parameters.

for C₃₈H₃₄Ag₂Cl₂O₈P₂S₂, **2a**: C, 44.2; H, 3.3; S, 6.2. Found: C, 43.9; H, 3.3; S, 5.9. Calcd for C₄₀H₃₄Ag₂F₆O₃P₂S₄, **2b**: C, 42.5; H, 3.0; S, 11.3. Found: C, 42.1; H, 3.1; S, 11.6. ³¹P{¹H} NMR {(CD₃)₂CO, -80 °C}, δ : 9.4 [d, br, *J*_{av}(AgP) = 637 Hz] (**2a**); 9.2 [d, br, *J*_{av}(AgP) = 625 Hz] (**2b**). ¹⁹F NMR (CDCl₃), δ : -77.58 (**2b**). ¹H NMR (CDCl₃), δ : 7.70–7.25 (m, 30H, Ph), 4.34 (d, 4H, CH₂) (**2a**); 7.71–7.00 (m, 30H, Ph), 4.16 (d, 4H, CH₂) (**2b**).

Preparation of [AuCl(PPh₂CH₂SPh)] (3). PPh₂CH₂SPh (0.100 g, 0.32 mmol) was added to a solution of [AuCl(tht)] (0.104 g, 0.32 mmol)

in 20 mL of CH₂Cl₂ and the reaction mixture was stirred for 1 h. The solvent was evaporated to ca. 5 mL, and addition of 20 mL of hexane gave **3** as a white solid. Yield: 70%. Mass spectra: [M - Cl]⁺ at *m/z* 505 (100%). Anal. Calcd for C₁₉H₁₇AuClPS, **3**: C, 42.2; H, 3.2; S, 5.9. Found: C, 41.9; H, 2.7; S, 5.9. ³¹P{¹H} NMR (CDCl₃), δ : 27.1 (s). ¹H NMR (CDCl₃), δ : 7.72–7.03 (m, 15H, Ph), 3.83 (d, 2H, CH₂).

Preparation of [Au₂(PPh₂CH₂SPh)₂](CF₃SO₃)₂ (4). To a solution of **3** (0.175 g, 0.32 mmol) in CH₂Cl₂ (20 mL) was added AgCF₃SO₃ (0.083 g, 0.32 mmol), and the mixture was stirred for 1 h. The AgCl was filtered off, and the solution was layered with hexane. Crystals of **4** were obtained within 3 days. Yield: 50%. Mass spectra: [AuPPh₂CH₂SPh]⁺ at *m/z* 505 (100%); [M + CF₃SO₃]⁺ at *m/z* 1159 (5%). Anal. Calcd for C₄₀H₃₄Au₂F₆O₆P₂S₄, **4**: C, 36.7; H, 2.6; S, 9.8. Found: C, 36.6; H, 2.4; S, 9.8. ³¹P{¹H} NMR ((CD₃)₂CO), δ : 34.5 (s). ¹⁹F NMR ((CD₃)₂CO), δ : -77.98. ¹H NMR ((CD₃)₂CO), δ : 8.10–7.52 (m, 30H, Ph), 5.58 (m, 4H, CH₂).

Crystal Structure Determinations. Crystals were mounted in inert oil on glass fibers. Data were collected using monochromated Mo K α radiation ($\lambda = 0.71073$ Å) on a Siemens P4 diffractometer (**4**) or a Stoe STADI-4 (**2a**), both with Siemens LT-2 low-temperature attachment (scan type ω or ω/θ). Cell constants were refined from setting angles of ca. 60 reflections in the 2 θ range 7–25° (**4**) or $\pm\omega$ angles of 56 reflections in the 2 θ range 20–23° (**2a**). Absorption corrections were applied on the basis of ψ scans. Structures were solved by the heavy atom method (**4**) or direct methods (**2a**) and refined anisotropically on *F*² (program SHELXL-93).³¹ Hydrogen atoms were included using a riding model. To improve refinement stability, a range of restraints to local ring symmetry and light atom displacement parameters were employed for complex **4**. Complex **2a** showed a marked tendency to crystallize as interpenetrating twins; despite careful selection of the crystal using polarized light, the residual electron density is higher than expected for a silver compound and may be attributed to a small twin component. Further details are given in Table 3.

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Supporting Information Available: X-ray crystallographic information about **2a** and **b** in CIF format, is available (9 pages). Ordering information is given on any current masthead page.

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