Syntheses and Crystal Structures of Coinage Metal Thioether-Thiolato Complexes

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Dedicated to Professor Dr. Eberhard Hoyer on the occasion of his 70th birthday

Keywords: Sulfur ligands / Copper / Silver / Gold

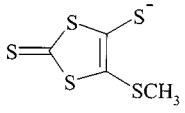
Copper(I), silver(I), and two gold(I) complexes of the type $(Ph_3P)_nM(\mathbf{L})$ [n = 1, 2, 3; **L** = 4-(methylthio)-2-thioxo-1,3-dithiole-5-thiolate ($\mathbf{L_a}$), 1,2-dicyano-1-(methylthio)ethene-2-thiolate ($\mathbf{L_b}$)] have been synthesized. The molecular structure of these complexes was determined by X-ray crystallography and shows differences in the coordinated sulfur atoms as well as in the coordination geometry of these $(Ph_3P)_nM(\mathbf{L})$ complexes. In $(Ph_3P)_2Cu(\mathbf{L})$ (**2**), the thioether thiolate ligands act as bidentate ligands, whereas in the silver and gold complexes $(Ph_3P)_3Ag(\mathbf{L})$ (**3**) and $(Ph_3P)_2Au(\mathbf{L})$ (**4**), only the thiolate sulfur is coordinated. Dissociation of one of the phosphane ligands of $(Ph_3P)_2Au(\mathbf{L_a})$ (**4a**) occurs in boiling acetone and a linear two-coordinate gold(I) center is obtained, $(Ph_3P)Au(\mathbf{L_a})$ (**5a**).

Introduction

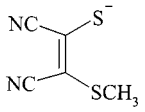
Metal complexes of 4-(methylthio)-2-thioxo-1,3-dithiole-5-thiolate ($C_3S_5^{2-}$) have been the subjects of numerous studies because some of them have been reported to exhibit conducting or superconducting properties.[1,2] The methylation of one thiolate donor atom of this delocalized dithiolate results in a thioether thiolate compound, 4-(methylthio)-2-thioxo-1,3-dithiole-5-thiolate ($\mathbf{L_a}$). The coordination ability of compounds with such sulfur donors is of interest because of the relevance to biological systems.[3] However, in marked contrast to their extensive studied transition-metal chelates,[4,5] thioether thiolato complexes with d^{10} metals are rare.

The principal difference between thiols and thioethers as ligands is that the former are more highly polarizable, but are not as effective d_π-electron acceptors as the latter.[6] Nevertheless, both kinds of sulfur atoms are soft donors and should be preferably coordinated by the soft coinage metals.[7]

We undertook the complexation of 4-(methylthio)-2-thioxo-1,3-dithiole-5-thiolate ($\mathbf{L_a}$) and 1,2-dicyano-1-(methylthio)ethene-2-thiolate ($\mathbf{L_b}$) with the d^{10} metal ions copper(I), silver(I) and gold(I) in order to examine the complexation behavior of thioether thiolate ligands. Comparison of the structures of these $(Ph_3P)_nM(\mathbf{L})$ chelates highlights differences in the coordinated donor-atom groups as well as in their coordination geometry.



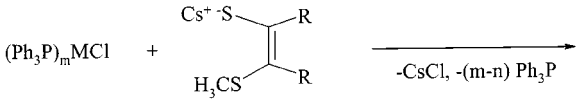
$\mathbf{L_a}$



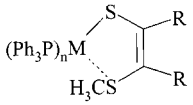
$\mathbf{L_b}$

Results and Discussion

The reaction of cesium 4-(methylthio)-2-thioxo-1,3-dithiole-5-thiolate (**1a**) and cesium 1,2-dicyano-1-(methylthio)-ethene-2-thiolate (**1b**) with the triphenylphosphane-coordinated closed-shell ions copper(I), silver(I), and gold(I) led to the coordination compounds $(Ph_3P)_2Cu(\mathbf{L})$ (**2a**, **2b**), $(Ph_3P)_3Ag(\mathbf{L})$ (**3a**, **3b**), and $(Ph_3P)_2Au(\mathbf{L})$ (**4a**, **4b**), respectively, in good yields.



1a : R-R = CS_3
1b : R = CN



	M	n
2 :	Cu	2
3 :	Ag	3
4 :	Au	2

Complexes **2**–**4** are crystalline, air- and moisture-stable solids. They are soluble in polar organic solvents, and are nonconductors in chloroform solutions, as shown by means

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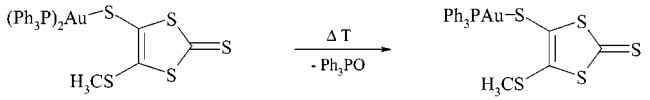
of conductivity measurements. The cumulative evidence from elemental analyses, IR, and NMR spectra establishes the composition of these compounds. Their ^{31}P NMR spectra measured in $CDCl_3$ at room temperature show only one singlet. However, from the spectrum of $(Ph_3P)_2Au(\mathbf{L_a})$ (**4a**), three nonequivalent phosphorus atoms are detectable after being allowed to stand for several weeks in chloroform. Two additional singlets are observed. These are shifted downfield relative to those of the starting complex **4a** (δ = 20.3); one was assigned to triphenylphosphane oxide (δ = 29.5) and the second at δ = 38.1 is characteristic of linearly coordinated gold(I).[8,9] Therefore it is probable that the gold complex $(Ph_3P)Au(\mathbf{L_a})$ (**5a**) is prepared from $(Ph_3P)_2Au(\mathbf{L_a})$ (**4a**). In fact, the complex **5a** can be isolated in good yields after boiling an acetone solution of the bistriphenylphosphane complex **4a** for few minutes. The trend in going from a trigonal-planar complex to a linear gold complex was not observed for the corresponding bistriphenylphosphane gold complex of 1,2-dicyano-1-(methylthio)ethene-2-thiolate (**4b**).



4a **5a**

However, from these results, the exact number of sulfur donors in the coordination sphere of the metal(I) ions remained open to investigation. Consequently, the complexes **2a**, **2b**, **3a**, **3b**, **4b**, and **5a** were further characterized by X-ray structure analysis, providing information about their sulfur-donor set. The complex $(Ph_3P)_2Cu(\mathbf{L})$ (**2**) has a distorted tetrahedral coordination geometry around the copper atom involving the two sulfur donor atoms S(1) and S(2) of $\mathbf{L_a}$ and $\mathbf{L_b}$, and two phosphorus atoms of the phosphanes. This arrangement is depicted in Figures 1 and 2, and selected interatomic distances and angles are given in Table 1.

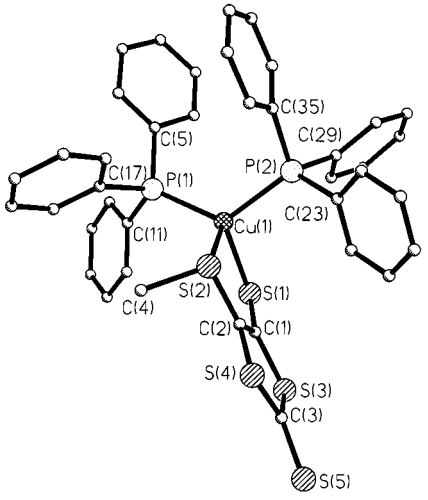


Figure 1. Molecule structure of $(Ph_3P)_2Cu(\mathbf{L_a})$ **2a**, H atoms are omitted

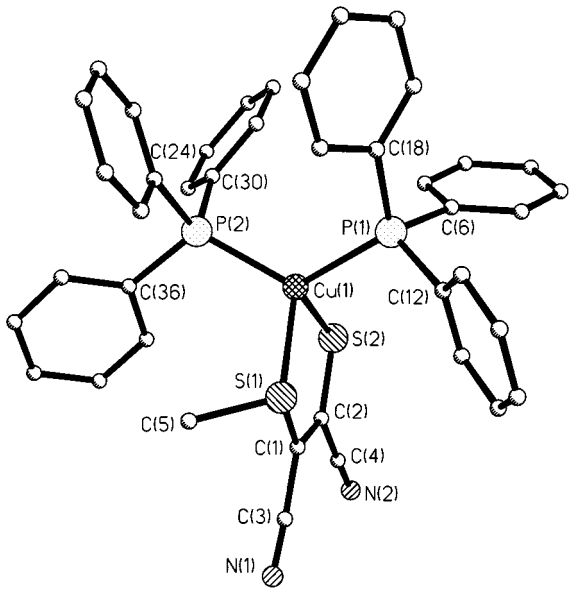


Figure 2. Molecule structure of $(Ph_3P)_2Cu(\mathbf{L_b})$ **2b**, H atoms are omitted

Table 1. Selected bond lengths [Å] and angles [deg] for $(Ph_3P)_2Cu(\mathbf{L})$ **2**

$(Ph_3P)_2Cu(\mathbf{L_a})$ **2a**		$(Ph_3P)_2Cu(\mathbf{L_b})$ **2b**	
Cu(1)−S(1)	2.3223(6)	Cu(1)−S(2)	2.3101(8)
Cu(1)−S(2)	2.4577(6)	Cu(1)−S(1)	2.3973(8)
Cu(1)−P(1)	2.2647(5)	Cu(1)−P(2)	2.2664(8)
Cu(1)−P(2)	2.2977(6)	Cu(1)−P(1)	2.2753(7)
C(1)−C(2)	1.352(3)	C(1)−C(2)	1.367(4)
C(1)−S(1)	1.722(2)	C(2)−S(2)	1.708(3)
C(2)−S(2)	1.754(2)	C(1)−S(1)	1.773(3)
C(4)−S(2)	1.807(3)	C(5)−S(1)	1.817(4)
C(1)−S(3)	1.756(2)	C(1)−C(3)	1.431(4)
C(2)−S(4)	1.807(3)	C(2)−C(4)	1.448(4)
C(3)−S(3)	1.728(2)	C(3)−N(1)	1.134(4)
C(3)−S(4)	1.718(2)	C(4)−N(2)	1.142(4)
C(3)−S(5)	1.655(2)		
P(1)−Cu(1)−P(2)	120.96(2)	P(1)−Cu(1)−P(2)	121.26(3)
S(1)−Cu(1)−S(2)	91.50(2)	S(1)−Cu(1)−S(2)	90.60(3)
P(1)−Cu(1)−S(2)	110.16(2)	P(2)−Cu(1)−S(1)	113.72(3)
P(2)−Cu(1)−S(1)	111.11(2)	P(1)−Cu(1)−S(2)	104.78(3)
P(1)−Cu(1)−S(1)	117.50(2)	P(2)−Cu(1)−S(2)	113.42(3)
P(2)−Cu(1)−S(2)	99.62(2)	P(1)−Cu(1)−S(1)	108.53(3)
Cu(1)−S(1)−C(1)	97.93(7)	Cu(1)−S(2)−C(2)	100.41(10)
Cu(1)−S(2)−C(2)	95.75(7)	Cu(1)−S(1)−C(1)	98.72(9)
Cu(1)−S(2)−C(4)	115.27(12)	Cu(1)−S(1)−C(5)	114.21(15)
C(1)−C(2)−S(2)	124.40(15)	C(2)−C(1)−S(1)	121.6(2)
C(2)−C(1)−S(1)	128.84(16)	C(1)−C(2)−S(2)	127.6(2)
C(1)−C(2)−S(4)	117.35(15)	C(2)−C(1)−C(3)	122.4(3)
C(2)−C(1)−S(3)	113.73(15)	C(1)−C(2)−C(4)	118.0(3)
S(2)−C(2)−S(4)	118.22(12)	S(1)−C(1)−C(3)	115.9(2)
S(1)−C(1)−S(3)	117.43(12)	S(2)−C(2)−C(4)	114.4(2)
C(1)−S(3)−C(3)	98.86(10)	C(2)−C(4)−N(2)	177.3(4)
C(2)−S(4)−C(3)	97.76(10)	C(1)−C(3)−N(1)	177.7(4)
S(3)−C(3)−S(4)	112.27(13)		
S(3)−C(3)−S(5)	124.20(14)		
S(4)−C(3)−S(5)	123.53(14)		

It is notable, perhaps predictably, that the copper−sulfur (thioether) bond lengths are longer [2.4577(6) Å for **2a** and

2.3973(8) for **2b**] than those of the copper-sulfur(thiolate) [2.3223(6) Å and 2.3101(8) Å for **2a** and **2b**, respectively]. But the copper−sulfur (thiolate) bond length in **2a** is longer than the chelating distances [Cu−S: 2.237(2)] found for the complex of the non-methylated ligand with $Cu(Ph_3P)$.[10] An interesting pattern is also observed for the metallaheterocycle [−Cu−S(1)−C(1)−C(2)−S(2)−], which is distorted and folded along the sulfur−sulfur axis (**2a**: 12.7°, **2b**: 8.9°). The copper−phosphorus bond lengths and angles are typical.[11,12]

The silver compounds **3a** and **3b** were prepared by the chloride substitution reaction of chlorotris(triphenylphosphane)silver(I) with the corresponding thioether thiolate ligands. The yellowish orange complex $(Ph_3P)_3Ag(\mathbf{L_a})$ **3a** was found to incorporate solvent of crystallization (acetone). The molecular structures of complexes **3** are illustrated in Figure 3 and Figure 4, and selected bond lengths and angles are given in Table 2.

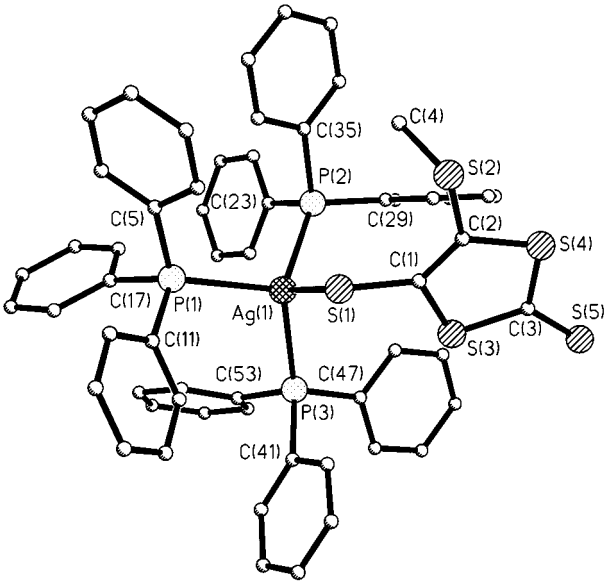


Figure 3. Molecule structure of $(Ph_3P)_3Ag(\mathbf{L_a})$ × acetone **3a**, acetone and H atoms are omitted

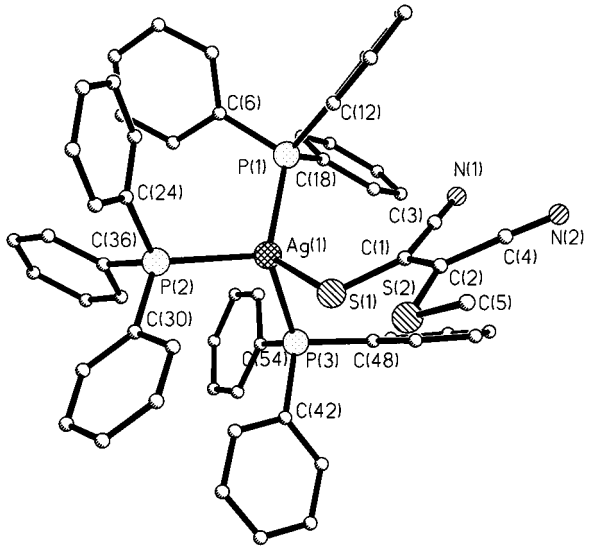


Figure 4. Molecule structure of $(Ph_3P)_3Ag(\mathbf{L_b})$ **3b**, H atoms are omitted

Table 2. Selected bond lengths [Å] and angles [deg] for $(Ph_3P)_3Ag(\mathbf{L})$ **3**

$(Ph_3P)_3Ag(\mathbf{L_a})$ × acetone **3a**		$(Ph_3P)_3Ag(\mathbf{L_b})$ **3b**	
Ag(1)−S(1)	2.5898(9)	Ag(1)−S(1)	2.6406(12)
Ag(1)−P(1)	2.6495(8)	Ag(1)−P(2)	2.6090(11)
Ag(1)−P(2)	2.5825(8)	Ag(1)−P(1)	2.5445(11)
Ag(1)−P(3)	2.5974(8)	Ag(1)−P(3)	2.5947(11)
C(1)−C(2)	1.355(4)	C(1)−C(2)	1.366(6)
C(1)−S(1)	1.719(3)	C(1)−S(1)	1.726(4)
C(2)−S(2)	1.747(4)	C(2)−S(2)	1.755(5)
C(4)−S(2)	1.794(7)	C(5)−S(2)	1.796(7)
C(1)−S(3)	1.749(3)	C(1)−C(3)	1.456(6)
C(2)−S(4)	1.758(4)	C(2)−C(4)	1.435(7)
C(3)−S(3)	1.723(3)	C(3)−N(1)	1.147(6)
C(3)−S(4)	1.710(4)	C(4)−N(2)	1.154(7)
C(3)−S(5)	1.649(4)		
P(1)−Ag(1)−P(2)	113.37(3)	P(1)−Ag(1)−P(2)	111.11(4)
P(1)−Ag(1)−P(3)	111.99(2)	P(1)−Ag(1)−P(3)	113.99(4)
P(1)−Ag(1)−S(1)	92.38(3)	P(1)−Ag(1)−S(1)	121.82(4)
P(2)−Ag(1)−P(3)	113.26(3)	P(2)−Ag(1)−P(3)	114.42(3)
P(2)−Ag(1)−S(1)	112.28(3)	P(2)−Ag(1)−S(1)	98.21(4)
P(3)−Ag(1)−S(1)	111.86(3)	P(3)−Ag(1)−S(1)	95.89(4)
Ag(1)−S(1)−C(1)	109.17(10)	Ag(1)−S(1)−C(1)	119.12(16)
C(1)−C(2)−S(2)	127.1(3)	C(1)−C(2)−S(2)	119.5(3)
C(2)−C(1)−S(1)	128.8(3)	C(2)−C(1)−S(1)	122.7(3)
C(1)−C(2)−S(4)	116.6(3)	C(2)−C(1)−C(3)	117.6(4)
C(2)−C(1)−S(3)	113.4(2)	C(1)−C(2)−C(4)	120.3(4)
S(2)−C(2)−S(4)	116.39(19)	S(1)−C(1)−C(3)	119.6(3)
S(1)−C(1)−S(3)	117.76(17)	S(2)−C(2)−C(4)	120.0(4)
C(1)−S(3)−C(3)	100.06(16)	C(2)−C(4)−N(2)	177.5(6)
C(2)−S(4)−C(3)	98.52(16)	C(1)−C(3)−N(1)	178.7(6)
S(3)−C(3)−S(4)	111.4(2)		
S(3)−C(3)−S(5)	123.8(2)		
S(4)−C(3)−S(5)	123.8(2)		

Three triphenylphosphane groups and a thioether thiolate ligand **L**, which is bonded only through the thiolate sulfur atom to silver, surround the silver ion in **3a** and **3b**. In compounds **3**, the configuration about the silver ion can be described as a distorted tetrahedron. The angles at the metal site range from 92.38(3) to 113.37(3)° and from 95.89(4) to 121.82(4)° for **3a** and **3b**, respectively. The Ag−P distances average 2.6 Å and are longer than the sum of the single-bond covalent radii (2.44 Å),[13] but are comparable with those determined for other triphenylphosphane silver(I) compounds [2.503(5) Å,[14] 2.557(6) Å,[15] and 2.616(3) Å[16]]. The observed silver−sulfur (thiolate) bond lengths of 2.5898(9) Å (**3a**) and 2.6406(12) Å (**3b**) are longer than single covalent bonds, but are appreciably shorter than the van der Waals contact (3.52 Å).[13] Chlorobis(triphenylphosphane) gold(I) reacts with the cesium thiolate salts **1** to $(Ph_3P)_2Au(\mathbf{L})$ (**4**). Figure 5 represents a view of the molecular structure of $(Ph_3P)_2Au(\mathbf{L_b})$ **4b**. Although the angles deviate somewhat from the idealized geometry of 120°, the coordination about the gold ion is essentially trigonal planar. Relevant bond lengths and angles are given in Table 3. The Au−P(2) distance of 2.3806(13) Å is considerably longer than the Au−P(1) distance of 2.3101(13) Å, and

is also longer than the Au−P distances of 2.323(4) Å and 2.339(4) Å in $(Ph_3P)_2AuCl$.[17] It is also interesting to observe that complex **4b** shows longer Au−P and Au−S distances than in the corresponding complexes with the non-methylated dithiolate ligands $[(Ph_3PAu)_2S_2C_2(CN)_2]$[18] and $(Bu_4N)[Ph_3PAu(S_2C_2(CN)_2]$.[19] In boiling acetone, one of the phosphane ligands dissociates from $(Ph_3P)_2Au(\mathbf{L_a})$ (**4a**), whereas $(Ph_3P)_2Au(\mathbf{L_b})$ (**4b**) remains unchanged. The structure of the resulting complex $(Ph_3P)Au(\mathbf{L_a})$ (**5a**) is shown in Figure 6, and selected bond lengths and angles are given in Table 3.

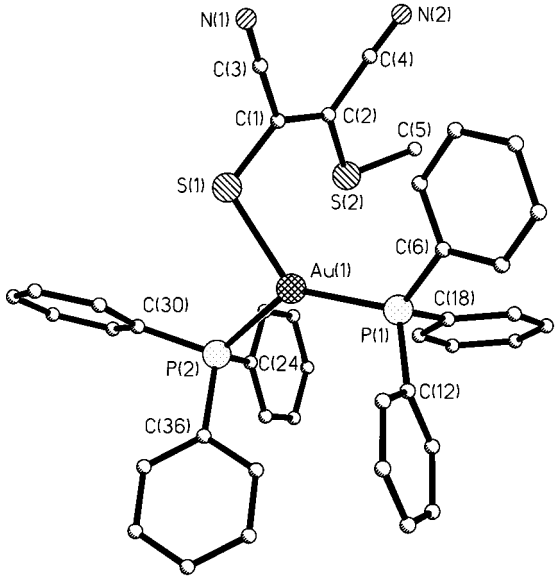


Figure 5. Molecule structure of $(Ph_3P)_2Au(\mathbf{L_b})$ **4b**, H atoms are omitted

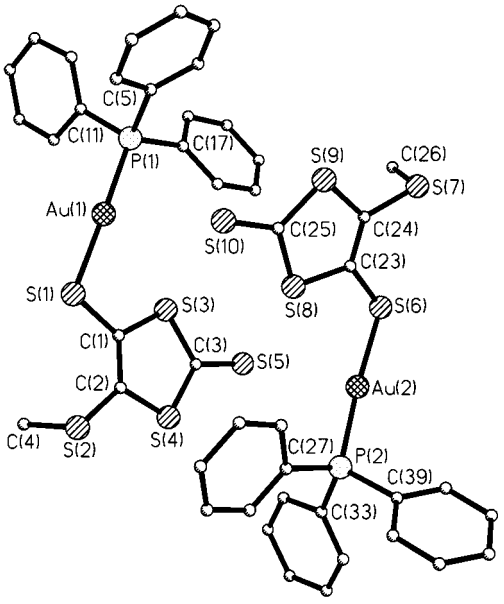


Figure 6. Molecule structure of $(Ph_3P)Au(\mathbf{L_a})$ **5a**, H atoms are omitted

Two crystallographically independent molecules of $(Ph_3P)Au(\mathbf{L_a})$ (**5a**) are present in the asymmetric unit. Each gold atom is bis-coordinated in a linear fashion to the thiolate sulfur of $\mathbf{L_a}$, and the phosphorus atom of the triphenylphosphane. The Au−S distances [2.3078(13) and 2.3144(14) Å] are slightly shorter than those found for triphenylphosphane gold (I) complexes with the non-methylated C_3S_5 ligand, such as $(Ph_3PAu)_2C_3S_5$ [2.3474(11), 2.3435(12) Å] and $(Bu_4N)[Ph_3PAu(C_3S_5)]$ [2.476(3), 2.405(3) and 2.413(3),

Table 3. Selected bond lengths [Å] and angles [deg] for $(Ph_3P)_2Au(\mathbf{L_b})$ (**4b**) and $(Ph_3P)Au(\mathbf{L_a})$ (**5a**)

$(Ph_3P)_2Au(\mathbf{L_b})$ **4b**		$(Ph_3P)Au(\mathbf{L_a})$ **5a**			
Au(1)−S(1)	2.4884(16)	Au(1)−S(1)	2.3078(13)	Au(2)−S(6)	2.3144(14)
Au(1)−P(1)	2.3101(13)	Au(1)−P(1)	2.2592(13)	Au(2)−P(2)	2.2685(13)
Au(1)−P(2)	2.3806(13)	C(1)−C(2)	1.352(7)	C(23)−C(24)	1.347(7)
C(1)−C(2)	1.341(11)	C(1)−S(1)	1.744(5)	C(23)−S(6)	1.739(5)
C(1)−S(1)	1.724(7)	C(2)−S(2)	1.751(5)	C(24)−S(7)	1.758(5)
C(2)−S(2)	1.762(9)	C(4)−S(2)	1.750(7)	C(26)−S(7)	1.766(7)
C(5)−S(2)	1.803(16)	C(1)−S(3)	1.741(5)	C(23)−S(8)	1.752(5)
C(1)−C(3)	1.432(12)	C(2)−S(4)	1.752(5)	C(24)−S(9)	1.754(6)
C(2)−C(4)	1.483(10)	C(3)−S(3)	1.729(5)	C(25)−S(8)	1.743(6)
C(3)−N(1)	1.147(11)	C(3)−S(4)	1.714(5)	C(25)−S(9)	1.715(5)
C(4)−N(2)	1.1081(10)	C(3)−S(5)	1.652(5)	C(25)−S(10)	1.648(6)
P(1)−Au(1)−P(2)	130.71(4)	P(1)−Au(1)−S(1)	177.76(5)	P(2)−Au(2)−S(6)	174.54(57)
P(1)−Au(1)−S(1)	132.40(3)	Au(1)−S(1)−C(1)	101.83(16)	Au(2)−S(6)−C(23)	103.66(17)
P(2)−Au(1)−S(1)	96.63(6)	C(1)−C(2)−S(2)	125.2(4)	C(23)−C(24)−S(7)	126.0(4)
Au(1)−S(1)−C(1)	110.0(2)	C(2)−C(1)−S(1)	126.2(4)	C(24)−C(23)−S(6)	126.0(4)
C(1)−C(2)−S(2)	120.2(5)	C(1)−C(2)−S(4)	116.5(4)	C(23)−C(24)−S(9)	116.7(4)
C(2)−C(1)−S(1)	125.0(6)	C(2)−C(1)−S(3)	114.3(4)	C(24)−C(23)−S(8)	114.6(4)
C(2)−C(1)−C(3)	119.4(7)	S(2)−C(2)−S(4)	118.3(3)	S(7)−C(24)−S(9)	117.2(3)
C(1)−C(2)−C(4)	120.5(8)	S(1)−C(1)−S(3)	119.5(3)	S(6)−C(23)−S(8)	119.4(3)
S(1)−C(1)−C(3)	115.5(6)	C(1)−S(3)−C(3)	99.3(2)	C(23)−S(8)−C(25)	98.6(3)
S(2)−C(2)−C(4)	119.3(7)	C(2)−S(4)−C(3)	98.2(3)	C(24)−S(9)−C(25)	98.2(3)
C(2)−C(4)−N(2)	177.1(9)	S(3)−C(3)−S(4)	111.8(3)	S(8)−C(25)−S(9)	111.9(3)
C(1)−C(3)−N(1)	178.6(10)	S(3)−C(3)−S(5)	122.7(3)	S(8)−C(25)−S(10)	122.6(3)
		S(4)−C(3)−S(5)	125.6(3)	S(9)−C(25)−S(10)	125.5(4)

2.483(3) Å].[20] However, the gold−sulfur (thiolate) bond length in **5a** is very similar to those found for the bis-chelate of the non-methylated C_3S_5 with gold(III) (Bu_4N)-$[Au(C_3S_5)_2]$ [2.311 to 2.327 Å].[21,22]

The Au−P distances [2.2592(13) and 2.2685(13) Å] in **5a** are typical of two-coordinate gold(I) compounds, as are the P−Au−S angles of 177.76(5)° and 174.54(5)°.[8,9,23] This slight deviation from the linearity is common for gold(I) structures.[24]

The present work has shown that the thioether thiolate compounds 4-(methylthio)-2-thioxo-1,3-dithiole-5-thiolate (**L_a**) and 1,2-dicyano-1-(methylthio)ethene-2-thiolate (**L_b**) form stable complexes with closed-shell d^{10} ions. However, the molecular structure of these complexes is not predictable. We believe that the restricted bite angle of the sulfur donor atoms within **L** and their different donor abilities play an important role in determining the final structures of the metal(I) complexes. Additionally, the strong phosphane donors and their size are of relevance in the complexation of coinage metals.[8,12]

Experimental Section

General Remarks: All chemicals and solvents used in the synthesis were of reagent grade and were used without further purification. The metal salts $(Ph_3P)_3CuCl$, $(Ph_3P)_3AgCl$, and $(Ph_3P)_2AuCl$ were prepared by published methods.[17,25,26] − IR: Perkin−Elmer 2000 FT. − UV/Vis: Shimadzu 160A. − NMR: Varian Gemini 300 (300.075 MHz, 75.462 MHz and 121.470 MHz, for ^1H, ^{13}C and ^{31}P, respectively). For ^1H and ^{13}C NMR spectra, $CDCl_3$ was used as solvent with TMS as internal standard. For ^{31}P NMR spectra, $CDCl_3$ was used as solvent with H_3PO_4 (85%) as external standard, δ_P= 82.43. − Melting points: Boetius point apparatus, uncorrected. − Elemental analyses: Heraeus CHN rapid analyzer.

Cesium 4-(Methylthio)-2-thioxo-1,3-dithiole-5-thiolate (1a) and Cesium 1,2-Dicyano-1-(methylthio)ethene-2-thiolate (1b): To a stirred chloroform solution (50 mL) of 4-(benzoylthio)-5-(methylthio)-2-thioxo-1,3-dithiole[27] (10 mmol, 3.16 g) (for **1a**) or 1-(benzoylthio)-1,2-dicyano-2-(methylthio)ethene[28] (2.60 g) (for **1b**) was added cesium hydroxide hydrate (10 mmol, 1.70 g) in methanol (10 mL). After about 1 min, the cesium thiolates started to separate. Diethyl ether (100 mL) was added to precipitate the product completely. This cesium salt was recovered by filtration, washed with diethyl ether and air dried.

1a: Orange crystals (1.85 g, 54%), m.p. > 250 °C. − IR (KBr): $\tilde{\nu}$ = 2978 and 2911 cm^{-1} (CH), 1416 (CH, C=C) 1310 (CH), 1060 and 1030 (C=S). − ^1H NMR (CD_3OD): δ = 2.36 (s, 3 H, $-CH_3$). − ^{13}C NMR (CD_3OD): δ = 18.6 (-CH_3), 121.0 (C-4), 163.6 (C-5), 214.9 (C=S). − $C_4H_3CsS_5 \cdot 0.5\ H_2O$ (353.30): calcd. C 13.60, H 1.14, S 45.38; found C 13.99, H 1.20, S 45.67.

1b: Yellow crystals (2.70 g, 90%), m.p. > 250 °C. − IR (KBr): $\tilde{\nu}$ = 2181 (CN) cm^{-1}, 1457, 1421 (CH, C=C), 1159, 1117, 1050, 969, 858, 520, and 503 (CH). − ^1H NMR (CD_3OD): δ = 2.43 (s, 3 H, $-CH_3$). − ^{13}C NMR (CD_3OD): δ = 16.0 ($-CH_3$), 113.7 (C-1), 117.8 (CN), 119.5 (CN), 138.5 (C-2). − $C_5H_3N_2CsS_2 \cdot 0.5\ H_2O$ (297.14): calcd. C 20.21, H 1.36, N 9.43, S 21.58; found C 20.03, H 1.03, N 9.06, S 21.58.

Complexes $(Ph_3P)_2Cu(L)$, $(Ph_3P)_3Ag(L)$, and $(Ph_3P)_2Au(L)$ (2) − (4): Solid $(Ph_3P)_nMCl$ (0.5 mmol, M = Cu, *n* = 3: 440 mg; M = Ag, *n* = 3: 465 mg; M = Au, *n* = 2: 380 mg) was added to a solution of CsL (0.5 mmol, **1a**: 176 mg; **1b**: 148 mg) in acetone (50 mL). After being stirred for 20 min., the yellow−orange reaction mixture was filtered. The volume of this acetone solution was reduced to 20 mL, and cooled to −5 °C overnight, yielding a crystalline solid, which was filtered off, washed with 2-propanol and air dried.

Cu Complex $(Ph_3P)_2Cu(L_a)$ (2a): Tawny crystals (285 mg, 71%), m.p. 182−184 °C dec. − IR (KBr): $\tilde{\nu}$ = 3050, 3002, 2917, 1184, 1158, 1095, 1005, 961, 881, 741, and 694 cm^{-1} (CH), 1480, 1434, and 1424 (CH, C=C), 1307 (CH), 1054 and 1034 (C=S). − UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 432 nm (3.72), 355 (3.91), 264 (4.43), 232 (4.47). − ^1H NMR ($CDCl_3$): δ = 1.80 (s, 3 H, $-CH_3$), 7.23−7.39 (m, 30 H, -P−C_6H_5). − ^{13}C NMR ($CDCl_3$): δ = 23.8 (-CH_3), 118.6 (C-4), 165.1 (C-5), 214.1 (C=S), 129.4 ($^3J_{C,P}$ = 8.7 Hz), 130.4, 134.0 ($^1J_{C,P}$ = 24.6 Hz), 134.2 ($^2J_{C,P}$ = 15.0 Hz). − ^{31}P NMR ($CDCl_3$): δ = 1.3. − $C_{40}H_{33}CuP_2S_5$ (799.44): calcd. C 60.10, H 4.16, S 20.05; found C 60.21, H 4.05, S 20.98.

Cu Complex $(Ph_3P)_2Cu(L_b)$ (2b): Orange crystals (220 mg, 60%), m.p. 202−205 °C dec. − IR (KBr): $\tilde{\nu}$ = 3470, 3054, 2917, 1183, 1156, 1125, 1095, 1027, 999, 751, 743, 707, 695, 527, 518, 503, and 492 cm^{-1} (CH), 2190 (CN), 1479, 1456, and 1434 (CH, C=C). − UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 397 nm (3.52), 238 (4.32). − ^1H NMR ($CDCl_3$): δ = 1.87 (s, 3 H, $-CH_3$), 7.25−7.41 (m, 30 H, -P−C_6H_5). − ^{13}C NMR ($CDCl_3$): δ = 20.7 (-CH_3), 105.7 (C-1), 116.5 and 116.8 (CN), 147.9 (C-2), 128.8 ($^3J_{C,P}$ = 8.3 Hz), 130.1, 132.6 ($^1J_{C,P}$ = 28.4 Hz), 133.5 ($^2J_{C,P}$ = 13.7 Hz). − ^{31}P NMR ($CDCl_3$): δ = 0.4. − $C_{41}H_{33}CuN_2P_2S_2$ (743.35): calcd. C 66.25, H 4.47, N 3.77, S 8.63; found C 65.86, H 4.48, N 3.65, S 8.24.

Ag Complex $(Ph_3P)_3Ag(L_a)$ × Acetone (3a): Yellowish orange crystals (443 mg, 77%), m.p. 149−151 °C dec. − IR (KBr): $\tilde{\nu}$ = 3052, 3002, 2913, 1184, 1157, 1093, 997, 866, 743, and 694 cm^{-1} (CH), 1478, 1434, and 1414 (CH, C=C), 1307 (CH), 1056 and 1038 (C=S). − UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 416 nm (3.78), 306 (3.92), 257 (4.38), 232 (4.44). − ^1H NMR ($CDCl_3$): δ = 1.91 (s, 3 H, $-CH_3$), 2.18 (s, 6 H, -$(CH_3)_2CO$), 7.30−7.41 (m, 45 H, -P−C_6H_5). − ^{13}C NMR ($CDCl_3$): δ = 21.1 (-CH_3), 31.6 ($CH_3)_2CO$), 118.6 (C-4), 164.3 (C-5), 207.6 ($(CH_3)_2CO$), 212.6 (C=S), 128.8 ($^3J_{C,P}$ = 8.4 Hz), 129.7, 133.7 ($^2J_{C,P}$ = 17.3 Hz), 134.2 ($^1J_{C,P}$ = 11.6 Hz). − ^{31}P NMR ($CDCl_3$): δ = 3.7. − $C_{61}H_{54}AgOP_3S_5$ (1164.12): calcd. C 62.93, H 4.67, S 13.77; found C 63.04, H 4.39, S 14.38.

Ag Complex $(Ph_3P)_3Ag(L_b)$ (3b): Yellow crystals (210 mg, 40%), m.p. 146−149 °C dec. − IR (KBr): $\tilde{\nu}$ = 3469, 3052, 3004, 2922, 1184, 1156, 1115, 1092, 1069, 1047, 1026, 997, 744, 694, 515, 503, and 492 cm^{-1} (CH), 2180 (CN), 1479, 1456, and 1434 (CH, C=C). − UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 367 nm (3.79), 253 (4.50). − ^1H NMR ($CDCl_3$): δ = 1.98 (s, 3 H, $-CH_3$), 7.29−7.34 (m, 45 H, -P−C_6H_5). − ^{13}C NMR ($CDCl_3$): δ = 17.4 (-CH_3), 111.9 (C-1), 115.8 (CN), 117.4 (CN), 139.8 (C-2), 128.9 ($^3J_{C,P}$ = 8.9 Hz), 129.9, 133.6 ($^2J_{C,P}$ = 17.2 Hz), 133.7 ($^2J_{C,P}$ = 17.2 Hz). − ^{31}P NMR ($CDCl_3$): δ = 4.50. − $C_{29}H_{48}AgN_2P_3S_2$ (1049.96): calcd. C 67.49, H 4.61, N 2.67, S 6.11; found C 66.82, H 4.87, N 1.87, S 5.36.

Au Complex $(Ph_3P)_2Au(L_a)$ (4a): Yellowish orange crystals (320 mg, 69%), m.p. 112−113 °C dec. − IR (KBr): $\tilde{\nu}$ = 3050, 2913, 1182, 1158, 1097, 996, 863, 744, and 693 cm^{-1} (CH), 1479, 1434, and 1395 (CH, C=C), 1308 (CH), 1056 and 1037 (C=S). − UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 409 nm (4.02), 300 (4.15), 235 (4.58). − ^1H NMR ($CDCl_3$): δ = 2.28 (s, 3 H, $-CH_3$), 7.38−7.47 (m, 30 H, -P−C_6H_5). − ^{13}C NMR ($CDCl_3$): δ = 19.9 (-CH_3), 125.0 (C-4), 151.0 (C-5), 211.8 (C=S), 129.1 ($^3J_{C,P}$ = 9.9 Hz), 130.6, 133.2 ($^1J_{C,P}$ = 26.7 Hz), 134.1 ($^2J_{C,P}$ = 16.5 Hz). − ^{31}P NMR ($CDCl_3$):

Table 4. Crystallographic Data for $(Ph_3P)_2Cu(\mathbf{L})$ (**2a**, **2b**), $(Ph_3P)_3Ag(\mathbf{L})$ (**3a**, **3b**), $(Ph_3P)_2Au(\mathbf{L_b})$ (**4b**), and $(Ph_3P)Au(\mathbf{L_a})$ (**5a**)

formula	$C_{40}H_{33}P_2S_5Cu$ (**2a**)	$C_{41}H_{33}N_2P_2S_2Cu$ (**2b**)	$C_{61}H_{54}OP_3S_5Ag$ (**3a**)	$C_{59}H_{48}N_2P_3S_2Ag$ (**3b**)	$C_{41}H_{33}N_2P_2S_2Au$ (**4b**)	$C_{22}H_{18}S_5PAu$ (**5a**)
M	799.44	743.29	1164.12	1049.89	876.72	670.60
T [K]	293(2)	293(2)	293(2)	293(2)	293(2)	213(2)
space group	$P2_1/c$	$P2_1/n$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$P2_1/c$
a [Å]	10.9131(7)	14.6398(4)	13.950(1)	12.3830(1)	10.066(3)	9.6818(6)
b [Å]	19.955(2)	13.3941(4)	14.226(1)	25.3111(3)	12.968(3)	17.6618(10)
c [Å]	18.1957(12)	19.7794(6)	14.332(1)	16.9067(2)	15.755(6)	27.8585(16)
α [deg]			86.22(1)		98.96(1)	
β [deg]	106.101(5)	104.285(1)	87.02(1)	92.367(1)	105.43(1)	98.8700(10)
γ [deg]			82.22(1)		104.79(1)	
V [Å^3]	3807.0(5)	3758.56(19)	2809.2(3)	5294.5(1)	1860.8(10)	4706.8(5)
Z	4	4	2	4	2	8
d_{calc} [g cm^{-3}]	1.395	1.314	1.376	1.317	1.565	1.893
μ [mm^{-1}]	0.960	0.808	0.670	0.589	4.183	6.771
$F(000)$	1648	1536	1200	2160	868	2592
crystal size [mm^{-3}]	0.5 × 0.4 × 0.3	0.30 × 0.25 × 0.20	0.25 × 0.22 × 0.20	0.25 × 0.25 × 0.20	0.30 × 0.25 × 0.10	0.30 × 0.20 × 0.15
θ range	1.55 to 26.01°	1.56 to 27.95°	1.92 to 26.03°	1.45 to 27.88°	1.67 to 27.03°	1.37 to 27.04°
Index range	$-13 \le h \le 13$	$-19 \le h \le 18$	$-17 \le h \le 17$	$-14 \le h \le 15$	$-12 \le h \le 12$	$-12 \le h \le 12$
	$-18 \le k \le 24$	$-17 \le k \le 15$	$-17 \le k \le 17$	$-32 \le k \le 33$	$-16 \le k \le 16$	$-19 \le k \le 22$
	$-22 \le l \le 22$	$-23 \le l \le 24$	$-10 \le l \le 17$	$-21 \le l \le 19$	$-20 \le l \le 20$	$-33 \le l \le 35$
R (all data)	$R_1 = 0.0497$	$R_1 = 0.0728$	$R_1 = 0.0654$	$R_1 = 0.1006$	$R_1 = 0.0703$	$R_1 = 0.0581$
	$wR_2 = 0.0867$	$wR_2 = 0.1191$	$wR_2 = 0.0963$	$wR_2 = 0.1579$	$wR_2 = 0.0873$	$wR_2 = 0.0917$
R [$I > 2\sigma(I)$]	$R_1 = 0.0305$	$R_1 = 0.0474$	$R_1 = 0.0318$	$R_1 = 0.0526$	$R_1 = 0.0344$	$R_1 = 0.0339$
	$wR_2 = 0.0796$	$wR_2 = 0.1040$	$wR_2 = 0.0852$	$wR_2 = 0.1253$	$wR_2 = 0.0775$	$wR_2 = 0.0829$

δ = 19.9. − $C_{40}H_{33}AuP_2S_5$ (932.94): calcd. C 51.50, H 3.57, S 17.19; found C 51.89, H 3.59, S 17.69.

Au Complex $(Ph_3P)_2Au(L_b)$ (4b): Yellow crystals (500 mg, 63%), m.p. 118−120 °C dec. − IR (KBr): $\tilde{\nu}$ = 3436, 3051, 2918, 1183, 1156, 1096, 998, 747, 694, 533, 520, 508, and 498 cm^{-1} (CH), 2195 (CN), 1468 and 1435 (CH, C=C). − UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 360 nm (4.15), 239 (4.42). − ^{1}H NMR ($CDCl_3$): δ = 2.40 (s, 3 H, −CH_3), 7.39−7.48 (m, 30 H, -P−C$_6H_5$). − ^{13}C NMR ($CDCl_3$): δ = 17.2 (-CH$_3$), 114.2 (C-1), 118.3 (CN), 119.1 (CN), 129.9 (C-2), 128.9 ($^3J_{C,P}$ = 10.0 Hz), 130.6, 132.2 ($^1J_{C,P}$ = 33.1 Hz), 133.9 ($^2J_{C,P}$ = 15.6 Hz). − ^{31}P NMR ($CDCl_3$): δ = 27.8. − $C_{41}H_{33}AuN_2P_2S_2$ (876.77): calcd. C 56.17, H 3.79, N 3.20, S 7.31; found C 56.14, H 3.34, N 3.02, S 8.44.

Au Complex $(Ph_3P)Au(L_a)$ (5a): A mixture of $(Ph_3P)_2Au(L_a)$ **4a** (280 mg, 0.3 mmol) in acetone (20 mL) was heated at reflux for a few minutes and then filtered. 2-Propanol (ca. 5 mL) was added dropwise to the filtrate. The solution was allowed to stand at room temperature. The yellow crystals formed were filtered and air dried to afford yellowish orange crystals (320 mg, 69%), m.p. 153−155 °C dec. − IR (KBr): $\tilde{\nu}$ = 3050, 2913, 1181, 1101, 998, 887, 747, 711, and 692 cm^{-1} (CH), 1479, 1448, 1436, and 1309 (CH, C=C), 1308 (CH), 1060 and 1034 (C=S). − UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 409 nm (4.00), 304 (4.08), 235 (4.46). − ^{1}H NMR ($CDCl_3$): δ = 2.31 (s, 3 H, −CH_3), 7.50−7.58 (m, 15 H, -P−C$_6H_5$). − ^{13}C NMR ($CDCl_3$): δ = 20.0 (−CH$_3$), 125.3 (C-4), 149.3 (C-5), 217.7 (C=S), 128.9, 129.6 ($^3J_{C,P}$ = 11.6 Hz), 132.2 ($^4J_{C,P}$ = 2.9 Hz), 134.3 ($^2J_{C,P}$ = 13.9 Hz). − ^{31}P NMR ($CDCl_3$): δ = 38.1. − $C_{22}H_{18}AuPS_5$ (670.60): calcd. C 39.40, H 2.71, S 23.90; found C 39.67, H 2.98, S 24.17.

X-ray Crystallographic Study: Crystals of $(Ph_3P)_2Cu(\mathbf{L})$ (**2a**, **2b**), $(Ph_3P)_3Ag(\mathbf{L})$ (**3a**, **3b**), $(Ph_3P)_2Au(\mathbf{L_b})$ (**4b**), and $(Ph_3P)Au(\mathbf{L_a})$ (**5a**) were formed by the slow evaporation of their solutions in acetone. Crystal data and crystallographic experimental data for the complexes **2a**, **2b**, **3a**, **3b**, **4b**, and **5a** are listed in Table 4. Data were collected on a Stoe STADI4 diffractometer (**2a**, **3a**, **4b**) and on a Bruker AXS SMART-CCD (**2b**, **3b**, **5a**), using Mo-K_α radiation.

The structures were solved by direct methods and the heavy-atom procedures were used (SHELXS-86[29]). An empirical absorption correction for **2a**, **3a**, **4b** (ψ-scan, 10 reflections) and **2b**, **3b**, and **5a** (SADABS[30]) was applied. Anisotropic displacement parameters for all non-hydrogen atoms were used. For **2a**, **2b**, **3a**, **3b**, and **4b** all hydrogen atoms could be localized unambiguously with a difference Fourier map. These hydrogen atoms were refined isotropically. The hydrogen atoms of the phenyl group of **5a** could not be localized completely, therefore these hydrogen atoms were refined with the "-1.2-option" of the riding modus. Molecular-numbering schemes are shown in Figure 1 [$(Ph_3P)_2Cu(L_a)$ **2a**], Figure 2 [$(Ph_3P)_2Cu(L_b)$ **2b**], Figure 3 [$(Ph_3P)_3Ag(L_a)$ × acetone, **3a**], Figure 4 [$(Ph_3P)_3Ag(L_b)$ **3b**], Figure 5 [$(Ph_3P)_2Au(L_b)$ **4b**], and Figure 6 [$(Ph_3P)Au(L_a)$ **5a**]. Selected bond length and angles are located in Tables 1, 2, and 3.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-147226 (**2a**), CCDC-147222 (**2b**), CCDC-147225 (**3a**), CCDC-147223 (**3b**), CCDC-147227 (**4b**), CCDC-147224 (**5a**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44(1223)336−033; E-mail: deposit@ccdc.cam.ac.uk].

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