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Gold Complexes with Potentially Tri- and Tetradentate Phosphinothiolate Ligands

Kirstin Ortner,[†,‡] Louise Hilditch,[§] Yifan Zheng,[§] Jonathan R. Dilworth,[§] and Ulrich Abram*,[||]

Institute of Inorganic Chemistry, University of Tübingen, Auf der Morgenstelle 18,
D-72076 Tübingen, Germany, Inorganic Chemistry Laboratories, University of Oxford, South Parks
Road, Oxford, OX1 3QR, U.K., and Institute of Chemistry/Inorganic and Analytical Chemistry, Freie
Universität Berlin, Fabeckstrasse 34-36, D-14195 Berlin, Germany

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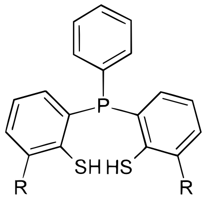
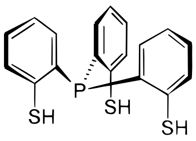
Reactions of [Au(PPh$_3$)Cl], (Bu$_4$N)[AuCl$_4$] and the organometallic gold complex [Au(damp-C^1,N)Cl$_2$] (damp$^-$ = 2-(*N*,*N*-dimethylaminomethyl)phenyl) with the potentially tri- and tetradentate proligands PhP(C$_6$H$_3$−SH-2−R-3)$_2$ (**H$_2$L^{1a}**, R = SiMe$_3$; **H$_2$L^{1b}**, R = H) and P(C$_6$H$_4$−SH-2)$_3$ (**H$_3$L^2**) result in the formation of mono- or dinuclear gold complexes depending on the precursor used. Monomeric complexes of the type [Au**L^1**Cl] are formed upon the reaction with [Au(damp-C^1,N)Cl$_2$], but small amounts of dinuclear [Au**L^1**]$_2$ complexes with gold in two different oxidation states, +1 and +3, have been isolated as side-products. The dinuclear compounds are obtained in better yields from [AuCl$_4$]$^-$. A dinuclear complex having two Au(III) centers can be isolated from the reaction of [Au(PPh$_3$)Cl] with **H$_3$L^2**, whereas from the reaction with **H$_2$L^{1b}** the mononuclear [Au(Ph$_3$P)**HL^{1b}**] is obtained, which contains a three-coordinate gold atom. Comparatively short gold−gold distances have been found in the dinuclear complexes (2.978(2) and 3.434(1) Å). They are indicative of weak gold−gold interactions, which is unusual for gold(III).

Introduction

The coordination chemistry of potentially tri- and tetradentate proligands of the types PhP(C$_6$H$_3$−SH-2−R-3)$_2$ (**H$_2$L^{1a}**, R = SiMe$_3$; **H$_2$L^{1b}**, H) and P(C$_6$H$_4$−SH-2)$_3$ (**H$_3$L^2**) has been investigated to a relatively limited extent. Mononuclear complexes have been described for the group V to group VIII transition metals[1−8] as well as for samarium,[9] tin,[9] and nickel.[4] For the last metal, however, bridging coordination of metal centers with the ligand **H$_2$L^1** or **H$_3$L^2** has also been observed. These complexes show unusual coordination polyhedra and redox behavior.[2,10] Thus, [Ni$_2${PhP(C$_6$H$_4$−S)$_3$}$_2$]$^{2+}$ can be oxidized to yield the mixed-valence [Ni(II)/Ni(III)] complex [Ni$_2${PhP(C$_6$H$_4$−S-2)$_3$}$_2$]$^+$. The oxidation is associated with considerable changes in the molecular structure and a shortening of the metal−metal distances, which is indicative of Ni−Ni interactions in the mixed-valence species.[10]



H$_2$L^{1a} (R = SiMe$_3$) **H$_2$L^{1b}** (R = H)



H$_3$L^2

The unusual abilities of phosphinothiolate ligands to stabilize complexes with metals in high formal oxidation states prompted us to investigate their chemistry with gold. The synthesis and structure of a mononuclear gold(III) cation with the bidentate {Ph$_2$P(C$_6$H$_4$−S-2)}$^-$ ligand has been reported previously, showing that reduction to gold(I) or elemental gold is not predominant when starting from gold(III) precursors, whereas polymeric products are generally formed when gold(I) precursors are used.[11]

Here, we describe reactions of **H$_2$L^1** and **H$_3$L^2** with (Bu$_4$N)-[AuCl$_4$], [Au(Ph$_3$P)Cl], and the organometallic gold(III) complex [Au(damp-C^1,N)Cl$_2$] (**1**) (damp$^-$ = 2-(*N*,*N*-dimethylaminomethyl)phenyl). The [Au(damp)] moiety has been shown to stabilize gold(III) with a wide range of coligands including thiolates and phosphines.[12−14]

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* To whom correspondence should be addressed, E-mail: abram@chemie.fu-berlin.de.

[†] University of Tübingen.

[‡] Present address: University of Zürich, Institute of Inorganic Chemistry, Winterthurerstrasse 190, CH-8057 Zürich, Switzerland.

[§] University of Oxford.

[||] Freie Universität Berlin.

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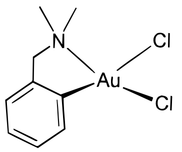

(1)

Experimental Section

Au(damp-C^1,N)Cl$_2$][14] and [Au(Ph$_3$P)Cl][15] were prepared using literature procedures. (Bu$_4$N)[AuCl$_4$] was obtained by addition of an excess of (Bu$_4$N)Cl to an aqueous solution of HAuCl$_4$ and subsequent recrystallization from CH$_2$Cl$_2$. PhP(C$_6$H$_3$−SH-2−R-3)$_2$ (R = H, SiMe$_3$) (**H$_2$L^1**) and P(C$_6$H$_4$−SH-2)$_3$ (**H$_3$L^2**) were synthesized according to ref 16. IR spectra were recorded on a Perkin-Elmer Spectrum 1000 and FAB mass spectra obtained using a TSQ 70 (FINNIGAN MAT) instrument with nitrobenzyl alcohol as the matrix (8 keV, xenon). Fast-atom bombardment (FAB) mass spectra with *m*/*z* > 1000 and field desorption (FD) spectra were recorded on a TSQ (FINNIGAN MAT 711A). Electrospray (ES) mass spectra were obtained using an API III TAGA 6000E triple−quadrupole mass spectrometer (Sciex, Canada).

Preparation of Compounds. [Au{PhP(C$_6$H$_3$−S-2−SiMe$_3$-3)$_2$}Cl] (2) and **[Au$_2${PhP(C$_6$H$_3$−S-2−SiMe$_3$-3)$_2$}$_2$] (3).** [Au(damp-C^1,N)Cl$_2$] (200 mg, 0.5 mmol) was dissolved in acetone (3 mL), and PhP(C$_6$H$_3$−SH-2−SiMe$_3$-3)$_2$ (**H$_2$L^{1a}**) (235 mg, 0.5 mmol) dissolved in CH$_2$Cl$_2$ (2 mL) was added. The clear, orange-red solution was stirred for 30 min and reduced in volume. A small amount of red blocks crystallized from this solution within 1 h. They were removed by filtration, dried in a vacuum, and analyzed to be **3**. Further concentration of the mother liquor gave red columns of **2**.

Yield of **2**: 266 mg (76%). Found: C, 41.3; H, 4.1; Cl, 4.9. Anal. Calcd for C$_{24}$H$_{29}$AuPS$_2$Si$_2$Cl: C, 41.4; H, 4.1; Cl, 5.1. IR (ν_{max}/cm^{-1}): 1560, 1540 s (C=C), 1438 s (P-phenyl), 855, 838 s (SiMe$_3$), 308 (Au−Cl). FAB$^+$ MS (*m*/*z*, %, assignment): 485 (30, [Au(PhPC$_6$H$_3$-SSiMe$_3$)]$^+$), 453 (100, [Au(PhPC$_6$H$_3$SiMe$_3$)]$^+$), 307 (38, [PhPC$_6$H$_3$-SiMe$_3$)]$^+$). FD-MS in CH$_2$Cl$_2$ (*m*/*z*, assignment): 700 (M$^+$).

Yield of **3**: <5%. Found: C, 42.8; H, 4.1. Anal. Calcd for C$_{48}$H$_{58}$-Au$_2$P$_2$S$_4$Si$_4$: C, 43.3; H, 4.4. IR (ν_{max}/cm^{-1}): 1560, 1540 s (C=C), 1438 s (P-phenyl), 855, 838 s (SiMe$_3$). FAB$^+$ MS (*m*/*z*, %, assignment): 1330 (15, [Au$_2${PhP(C$_6$H$_3$SSiMe$_3$)$_2$}]$^+$, 485 (30, [Au(PhPC$_6$H$_3$-SSiMe$_3$)]$^+$), 453 (100, [Au(PhPC$_6$H$_3$SiMe$_3$)]$^+$), 307 (38, [PhPC$_6$H$_3$-SiMe$_3$)]$^+$.

[Au$_2${PhP(C$_6$H$_4$−S-2)$_2$}$_2$] (4). (Bu$_4$N)[AuCl$_4$] (290 mg, 0.5 mmol) was dissolved in CH$_2$Cl$_2$ (2 mL), and a solution of PhP(C$_6$H$_4$−SH-2)$_2$ (**H$_2$L^{1b}**) (235 mg, 0.7 mmol) in CH$_2$Cl$_2$ (2 mL) was slowly added. The red solution was filtered after being stirred for 30 min, and it was then kept for crystallization. Tiny red plates were obtained. Yield: 93 mg, 36%. Found: C, 42.6; H, 2.5. Anal. Calcd for C$_{36}$H$_{26}$Au$_2$P$_2$S$_4$: C, 41.5; H, 2.3. IR (ν_{max}/cm^{-1}): 1569, 1550 s (C=C), 1445, 1434, 1419 s (P-phenyl). FAB$^+$ MS (*m*/*z*, %, assignment): 1044 (15, [Au$_2${PhP-(C$_6$H$_4$S)$_2$}$_2$]$^+$), 845 (8, [Au{PhP(C$_6$H$_4$S)$_2$}$_2$]$^+$).

[(PPh$_3$)Au{P(C$_6$H$_4$−S-2)$_2$(C$_6$H$_4$−SH-2)}] (5). A solution of P(C$_6$H$_4$−SH-2)$_3$ (**H$_3$L^2**) (163 mg, 0.5 mmol) in CH$_2$Cl$_2$ was added to a solution of [Au(Ph$_3$P)Cl] (247 mg, 0.5 mmol). The reaction mixture changed from colorless to yellow. After the solution was stirred for 1 h the solvent was allowed to evaporate slowly, leaving a mixture of red (compound **4**) and yellow crystals (compound **5**). This mixture was extracted with *n*-hexane in which the yellow compound was soluble. Slow evaporation of the *n*-hexane extracts results in yellow, light-sensitive, luminous crystals. When the reaction is performed with strict exclusion of air, the formation of **4** can be suppressed. Yield: 170 mg (43%). Found: C, 54.8; H, 4.1. Anal. Calcd for C$_{36}$H$_{29}$AuP$_2$S$_2$: C, 55.0; H, 3.7. IR (ν_{max}/cm^{-1}) 1572,1542 s (C=C), 1436, s (P-phenyl). FAB$^+$ MS (*m*/*z*, %, assignment): 785 (36, [Au(Ph$_3$P){PhP(C$_6$H$_4$S)(C$_6$H$_4$-SH)}]$^+$).

[Au{P(C$_6$H$_4$−S-2)$_3$}]$_2$ (6). [(Ph$_3$P)AuCl] (104 mg, 0.21 mmol) and P(C$_6$H$_4$−SH-2)$_3$ (**H$_3$L^2**) (25 mg, 0.07 mmol) were dissolved in CH$_2$Cl$_2$ (5 mL) and stirred in air for 1 h. The volume was reduced to about 1 mL, and the yellow solution was stoppered and kept for crystallization. Insoluble red crystals of **6** appeared on the glass walls over a period of several days. They were filtered off and washed with CH$_2$Cl$_2$. Yield: 33 mg, 28%. Found: C, 40.2; H, 2.4. Anal. Calcd for C$_{36}$H$_{24}$Au$_2$P$_2$S$_6$: C, 39.1; H, 2.2. IR (ν_{max}/cm^{-1}): 1568 s (C=C), 747 (phenyl).

X-ray Structure Determinations. Single crystals suitable for X-ray crystallography were taken directly from the reaction mixture (**5** and **6**) or were obtained by slow diffusion of *n*-hexane into a CH$_2$Cl$_2$ solution of complex **4.**

Intensities for the X-ray structure determinations were collected on an automated single-crystal diffractometer of type CAD4 or DIP2000 (both Enraf-Nonius, Delft) with Mo Kα (λ = 0.710 73 Å) or Cu Kα (λ = 1.541 84 Å) radiations at a temperature of −65 °C. HELENA[17] and DENZO[18] were used for data reduction. An empirical absorption correction (ψ scans) was applied to the CAD4 data set. The structures were solved by direct methods using SHELXS97.[19] Subsequent Fourier-difference map analyses yielded the positions of the non-hydrogen atoms. Refinement was performed using SHELXL97.[20] Hydrogen atoms have been included at calculated positions and treated using the "riding model" option of SHELXL97. Crystal data and more details of the data collections and refinements are contained in Table 1. Additional information on the structure determinations of compounds **2** and **3** is contained in ref 21 and has been deposited with the Fachinformationszentrum Karlsruhe as CSD 410274 (**2**) and CSD 410275 (**3**).

Results and Discussion

The potentially tri- and tetradentate phosphinothiolates **H$_2$L^1** and **H$_3$L^2** proved to be powerful chelating ligands that are able to stabilize gold(III) despite the reducing capacity of both aromatic thiols and phosphines. This may be explained by the rapid chelation of P and thiolate S donor atoms, which stabilizes a square-planar d^8 complex. Reduction would then be inhibited, since this would require a considerable rearrangement to give the linear coordination favored by the d^{10} configuration of gold(I). The nature of the products is primarily controlled by the gold starting materials used, and the temperature and reaction time do not play a dominant role.

Monomeric gold(III) compounds of the composition [AuCl-(**L^1**)] are obtained when [Au(damp-C^1,N)Cl$_2$] (**1**) is used as precursor. The complete substitution of the organometallic damp$^-$ ligand is unusual and has only been observed during the complex reaction of **1** with 4-methyl-3-mercapto-1,2,4-triazole (HSmetriaz), where [Au^I(HSmetriaz)$_2$]Cl was one of the isolated products,[22] whereas the Au−C σ bond remains when the chloro ligands are replaced by thiolates or phosphines.[12−14,23] This can also be assumed for the first step of the reaction of [Au(damp-C^1,N)Cl$_2$] with ligands of the type **H$_2$L^1**.

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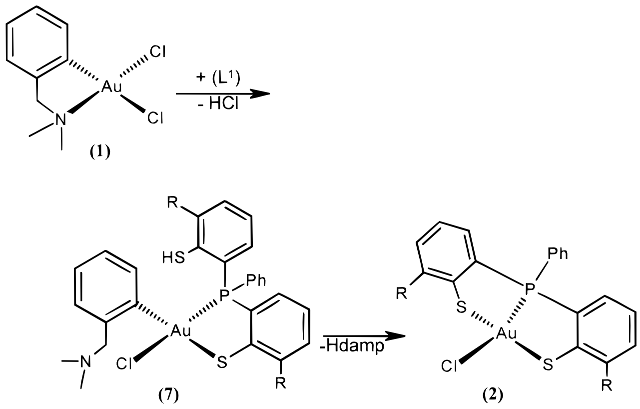
Table 1. X-ray Structure Data Collection and Refinement Parameters

	$[Au_2\{PhP(C_6H_4{-}S\text{-}2)_2\}_2]CH_2Cl_2$ (**4**)	$[(PPh_3)Au\{P(C_6H_4{-}S\text{-}2)_2(C_6H_4{-}SH\text{-}2)\}]$ (**5**)	$[Au\{P(C_6H_4{-}S\text{-}2)_3\}]_2$ (**6**)
cryst size [mm^3]	0.3 × 0.2 × 0.15	0.8 × 0.4 × 0.3	0.15 × 0.05 × 0.05
formula	$C_{37}H_{28}Cl_2P_2S_4Au_2$	$C_{36}H_{29}P_2S_2Au$	$C_{36}H_{24}P_2S_6Au_2$
fw [g mol^{-1}]	1127.61	784.62	1104.79
cryst syst	cubic	monoclinic	monoclinic
space group	*Fd*3*c*	*P*2$_1$/*c*	*P*2$_1$/*n*
temp [°C]	−60	−120	−60
radiation λ [Å]	Mo Kα, 0.710 73	Mo Kα, 0.710 73	Cu Kα, 1.541 84
a [Å]	49.678(8)	11.833(1)	10.422(2)
b [Å]	49.678(8)	18.158(1)	14.163(2)
c [Å]	49.678(8)	14.909(1)	11.364(2)
α (deg)	90	90	90
β (deg)	90	102.58(1)	94.48(1)
γ (deg)	90	90	90
V [Å^3]	122600(34)	3126.4(4)	1672.2(6)
Z	96	4	2
D_{calc} [g cm^{-3}]	1.466	1.667	2.194
μ [mm^{-1}]	6.09 (Mo Kα)	4.966 (Mo Kα)	20.88 (Cu Kα)
measd reflns	14 084	11 383	3638
independent reflns	3236	6010	2833
obsd reflns	1830	5311	1688
no. parameters	236	370	208
R1(*F*)/wR2(*F*^{2})^a	0.0582/0.1390	0.0627/0.1532	0.0552/0.0866
GOF	0.913	1.124	0.978

[a] $R1 = |F_o - F_c|/|F_o|$; $wR2 = [w(F_o^2 - F_c^2)^2/(wF_o^2)]^{-1/2}$.



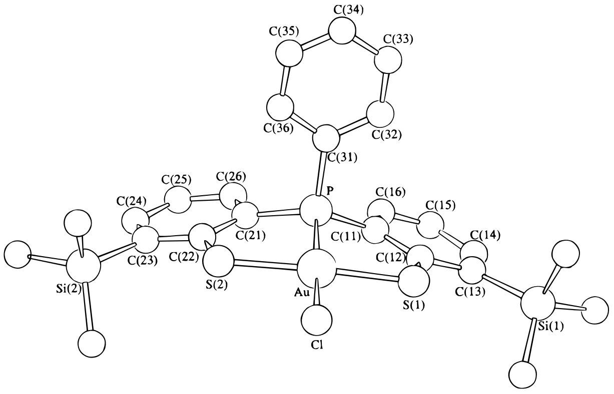


Figure 1. Structure[24] of complex **2** along with the atomic numbering scheme. H atoms have been omitted for clarity.

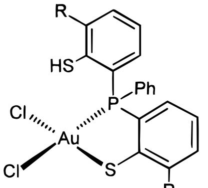
Table 2. Selected Bond Lengths (Å) and Angles (deg) for Complex **2**

Au−P	2.227(2)	Au−Cl	2.352(2)
Au−S(1)	2.325(2)	S(1)−C(12)	1.781(6)
Au−S(2)	2.310(2)	S(2)−C(22)	1.779(7)
P−Au−S(1)	86.38(6)	S(1)−Au−Cl	95.70(6)
P−Au−S(2)	86.82(7)	S(2)−Au−Cl	92.14(6)
P−Au−Cl	172.89(6)	C(11)−P−C(21)	117.6(3)
S(1)−Au−S(2)	168.72(6)		

The formation of intermediates such as **7** is supported by the mass spectrometric evidence of gold species in the reaction mixtures having both phosphinothiolate and damp$^-$ coordinated to gold (e.g., $[Au(damp)\{PhP(C_6H_3{-}S\text{-}2{-}SiMe_3\text{-}3)_2\}]^+$ at *m*/*z* = 800 with 95% abundance). In the second step the organometallic ligand is displaced by the chelating tridentate ligand and complexes of the composition of **2** are formed. The presence of the organometallic ligand, however, seems to be mandatory for the formation of mononuclear gold(III) complexes. Reduction of the gold is obviously inhibited, and the compounds [AuCl(**L^1**)] are formed in reasonable yields. Partial reduction of gold and the formation of the mixed-valent complex **3** is only observed as a side reaction.[21] $[AuCl\{PhP(C_6H_3{-}S\text{-}2{-}SiMe_3\text{-}3)_2\}]$ (**2**) could be isolated in crystalline form, whereas with $\{PhP(C_6H_4{-}S\text{-}2)_2\}$ only a red oil was obtained and all our attempts to crystallize this compound failed. The spectroscopic data of the oil (IR, MS), however, strongly suggest a composition of $[AuCl\{PhP(C_6H_4{-}S\text{-}2)_2\}]$.

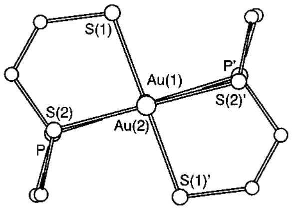
The structure of $[AuCl\{PhP(C_6H_3{-}S\text{-}2{-}SiMe_3\text{-}3)_2\}]$ (**2**) (Figure 1) shows a distorted square coordination environment for the gold atom. The primary source of the distortion is the presence of the pyramidal phosphorus atom and constraints due to the aromatic backbones in the tridentate ligand, which almost invariably occupies facial sites in octahedral complexes. The C(11)−P−C(21) angle of 117.6° at the sp^3-hybridized P atom reflects considerable strains inside the five-membered chelate rings, which lead to deviations of 0.17 Å from a least-squares plane formed by the donor atoms. The bonding situation is comparable with that in the $[Ni\{PhP(C_6H_4{-}S\text{-}2)_2\}(SC_6H_4{-}Ph\text{-}2)]^-$ anion, another example where a ligand of type **H$_2$L^1** is constrained to an almost planar coordination mode by a d^8 metal center.[10] Selected bond lengths and angles of $[AuCl\{PhP(C_6H_3{-}S\text{-}2{-}SiMe_3\text{-}3)_2\}]$ are summarized in Table 2.

The reduction of gold and the formation of mixed-valent gold(I)/gold(III) complexes is negligible when (**1**) is used as precursor but becomes dominating when $[AuCl_4]^-$ is used. Obviously, intermediates of the composition **8** can act as “monodentate thiol” and reduce gold(III) partially to gold(I) species, which can bind to gold(III) building blocks to give dimeric and oligomeric species. Mass spectrometric studies of reaction mixtures containing $[AuCl_4]^-$ and $PhP(C_6H_4{-}SH\text{-}2)_2$



(8)

(**H_2L^{1b}**) give evidence for the formation of $[Au_3L^{1b}{}_4]$ (*m/z* = 1887), $[Au_3L^{1b}{}_3]$ (*m/z* = 1563), $[Au_2L^{1b}{}_3]$ (*m/z* = 1367), $[Au_3L^{1b}{}_2]$ (*m/z* = 1239), and $[Au_2L^{1b}{}_2]$ (*m/z* = 1043) units. A compound of the composition $[Au_2L^{1b}{}_2]$ (**4**) has been isolated in crystalline form. Its structure (Figure 2) corresponds to that of the mixed-valence side-product of the reaction of [Au(damp-C^1,N)Cl_2] with **L^{1a}**.[21] Selected bond lengths and angles of the binuclear complex are given in Table 3. The square-planar gold(III) coordination site shows a maximum deviation of 0.031(6) Å from a least-squares plane formed by the donor atoms. The gold atom is displaced from this plane by 0.080(3) Å toward Au(2), which has a linear coordination environment comprising two thiolate groups as expected for a gold(I) center. The Au(1)−S(1) bond is slightly longer than the Au(2)−S(2) bond, which can be attributed to a higher extent of strain in the square environment of Au(1) compared with the linear coordination of Au(2). The Au−Au distance of 2.978(2) Å is comparable with values found in other bi- or multinuclear gold compounds[25,26] and is consistent with a bonding "aurophilic" interaction. This is remarkable because Au(1) doubtlessly represents a gold(III) site and both gold atoms are elongated from their ideal coordination environments toward each other. The linear S(2)−Au(2)−S(2)′ unit is in an eclipsed arrangement relative to the P−Au−P′ vector with a deviation of only 2.5°, as is illustrated in **9**. Examples for the stabilization of gold(III) and gold (I) in the same molecule are rare. To our knowledge there is only one structural report of a comparable compound, Au_4Cl_8 (**10**).[27] Four chloro ligands act as bridges between two gold(I) and two gold(III) centers in this compound. The Au(I)−Au(I) distance is 3.02 Å. Au_4Cl_8 is described as extremely air-sensitive, whereas the mixed-valence phosphinothiolato complexes do not undergo any reactions in air.



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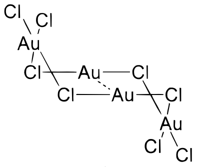

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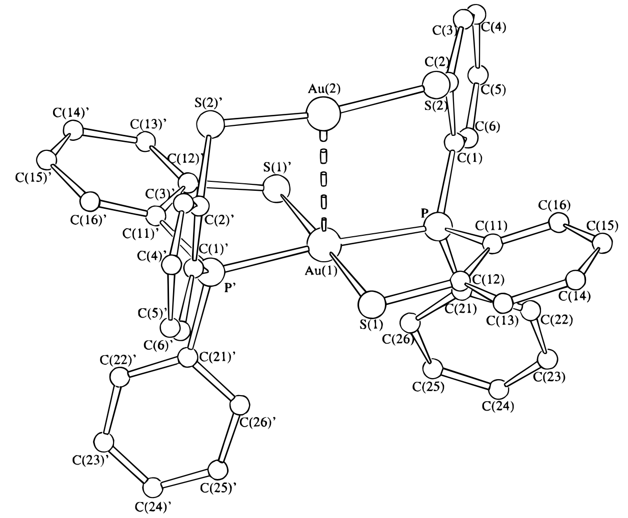


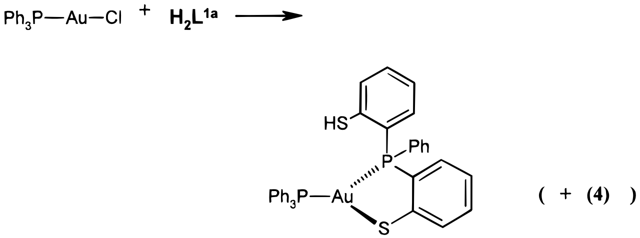
Figure 2. Structure[24] of complex **4** along with the atomic numbering scheme. H atoms have been omitted for clarity.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for Complex **4**[a]

Au(1)−P	2.342(4)	S(1)−C(12)	1.76(2)
Au(1)−S(1)	2.345(4)	S(2)−C(2)	1.81(2)
Au(2)−S(2)	2.295(5)	Au(1)−Au(2)	2.978(2)
P−Au(1)−P′	174.6(2)	S(1)−Au(1)−S(1)′	177.6(2)
P−Au(1)−S(1)	87.1(2)	S(2)−Au(2)−S(2)′	169.9(3)
P−Au(1)−S(1)′	92.8(2)		

[a] Symmetry code: (′) 1.5 − *x*, 1 − *z*, 1 − *y*.

Gold(I) species containing phosphinothiolates can be obtained when [Au(Ph_3P)Cl] is used as a precursor. The reaction of **H_2L^{1b}** with [Au(Ph_3P)Cl] initially gives a small amount of red crystalline **4**, and over the course of a few hours yellow luminescent crystals of the three-coordinate gold(I) species [Au(Ph_3P)(**HL^{1b}**)] (**5**) form as the major product.



(5)

The gold atom in [Au(Ph_3P)(**HL^{1b}**)] is coordinated by the two P atoms and one of the thiolato groups of the phosphinothiol in a distorted trigonal arrangement (Figure 3). The second thiol group remains protonated and does not contribute to the coordination sphere of the metal (distance H(2)−Au: ~3.2 Å). Compound **5** is the first three-coordinate gold(I) complex having a P,S,P coordination sphere. Selected bond lengths and angles are summarized in Table 4. The deviations of the coordination sphere of gold from a regular trigonal planar geometry are mainly due to the restricted bite angle of the chelating PS ligand (86.0(1)°), which results in P(2)−Au−P(1)/S(1) angles of 129.9(1) and 143.5(1)°, respectively. This is comparable with the situation in $[Au(Ph_3P)(bipy)]^+$,[28] $[Au(PhMe_2P)(MSe_4)]^-$ (M = Mo, W) complexes,[29] or $[Au(Ph_3P)(dmit)]^-$ ($dmit^{2-}$ = 4,5-

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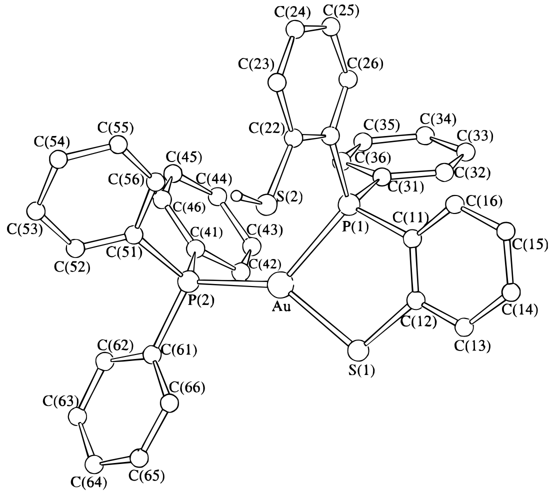


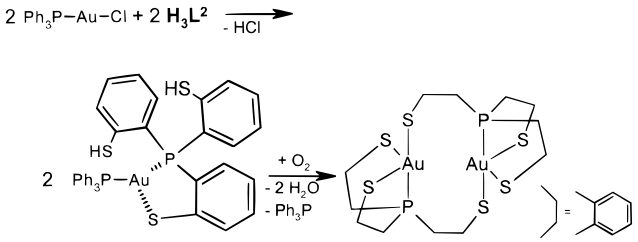
Figure 3. Structure[24] of complex **5** along with the atomic numbering scheme. Carbon H atoms have been omitted for clarity.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for Complex **5**

Au−P(1)	2.399(2)	S(1)−C(12)	1.81(1)
Au−P(2)	2.284(2)	S(2)−C(22)	1.71(1)
Au−S(1)	2.358(3)		
P(1)−Au−P(2)	129.9(1)	P(2)−Au−S(1)	143.5(1)
P(1)−Au−S(1)	86.0(1)		

dimercaptoisotrithione).[30] The metal atom is situated 0.097 Å outside the plane that is formed by P(1), P(2), and S(1). The Au−P(2) bond length is in the range that has been observed for other three-coordinate [Au(Ph$_3$P)(L−L)] complexes of gold(I).[31] No binding Au···Au interactions can be detected in the solid-state structure of **5**. The shortest intermolecular Au···Au distance is 7.5 Å.

The formation of a complex with a noncoordinated thiol group from **H$_2$L^{1b}** and [Au(Ph$_3$P)Cl] and the unexpected oxidation of gold(I) to gold(III), which yields **4** where presumably air is the oxidant, prompted us to attempt similar reactions with **H$_3$L^2**. From reactions of the potentially tetradentate proligand with [Au(damp-C^1,N)Cl$_2$] or [AuCl$_4$]$^-$ we only isolated insoluble polymeric compounds. With [Au(Ph$_3$P)Cl], however, a yellow compound was obtained that is readily soluble in dichloromethane when anaerobic conditions are used. Upon concentration of the solution a yellow oil remains, which we assign to [Au(Ph$_3$P)(**H$_2$L^2**)] (**11**) on the basis of its mass spectrum.



(11) **(6)**

All our attempts to crystallize the complex failed. Solutions of **11**, however, slowly separate red crystals of **6** when exposed to air. The yield of the binuclear gold(III) complex is increased when air is bubbled through the solution at room-temperature.

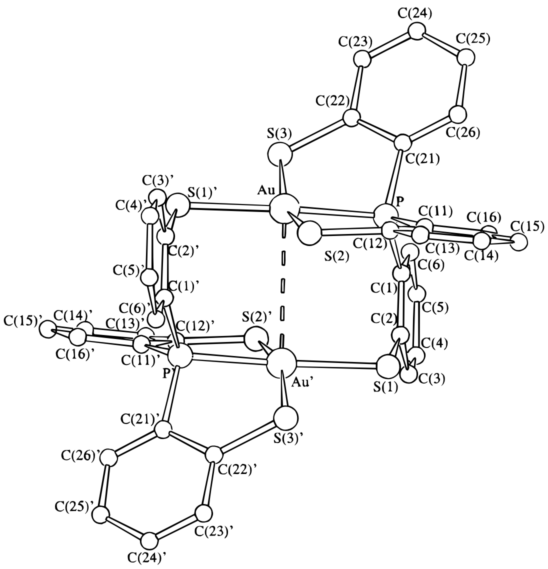
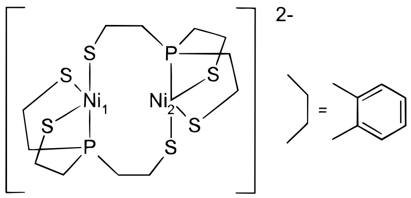


Figure 4. Structure[24] of complex **6** along with the atomic numbering scheme. H atoms have been omitted for clarity.

Compound **6** is practically insoluble in all organic solvents. Figure 4 shows the molecular structure of the complex. Selected bond lengths and angles are given in Table 5. Two thiolato functions and the phosphorus atom of (**L^2**)$^{3-}$ bind to one gold(III) center, whereas the third thiolate site forms a bridge to the second gold atom. The two square-planar coordination spheres are in an eclipsed arrangement with S−Au−Au−S and S−Au−Au−P dihedral angles of 11.15° and 5.67°, respectively. The gold atoms are elongated from the least-squares planes formed by their donor atoms by 0.138 Å toward each other, resulting in an Au−Au distance of 3.43 Å, which is in the range of the sum of their van der Waals radii.[32] This is remarkable for two gold(III) units and indicates weak interactions between the metal atoms. The structure of **6** can be compared with the binuclear nickel(II) complex [Ni$_2$(L^2)$_2$]$^{2-}$ (**12**), which can be oxidized to the mixed-valent Ni(II)/Ni(III) chelate [Ni$_2$(L^2)$_2$]$^-$ and serves as model for a strongly chelating, sulfur-containing coordination environment, as is contained in enzymes such as hydrogenase



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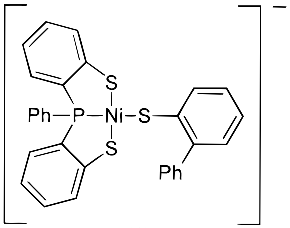

(13)

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Table 5. Selected Bond Lengths (Å) and Angles (deg) for Complex **6**[a]

Au−P	2.282(4)	S(1)−C(2)	1.76(1)
Au−S(2)	2.327(4)	S(2)−C(12)	1.76(2)
Au−S(3)	2.357(4)	S(3)−S(22)	1.76(2)
Au−S(1)′	2.358(4)	Au−Au′	3.434(1)
P−Au−S(2)	88.0(1)	P−Au−S(1)′	174.1(1)
P−Au−S(3)	83.4(1)	S(2)−Au−S(3)	159.8(1)

[a] Symmetry code: (′) 2−*x*, −*y*, 2−*z*.

or carbon monoxide dehydrogenase.[10] It is interesting to note that the comparable complex [Ni(**L**$^{\mathbf{1a}}$)(SC$_6$H$_4$−Ph-2)] (**13**) cannot be oxidized to a Ni(III) species.[10] This suggests a strong influence of the chelating capacity of the ligands on their ability to stabilize high formal oxidation states of metals, and this is dramatically illustrated by the gold compounds described in the present paper.

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Supporting Information Available: Three X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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