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Dithiocarbamate Ligands as Building-Blocks in the Coordination Chemistry of Gold

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The monodentate dithiocarbamate complexes $[Au_2(S_2CNR_2)_2\{\mu\text{-}(PPh_2)_2C{=}CH_2\}]$ (R = Me (**1**), Et (**2**), Bz (**3**)) are obtained by reaction of $[Au_2Cl_2\{\mu\text{-}(PPh_2)_2C{=}CH_2\}]$ with NaS_2CNR_2. The free sulfur atoms in complex **2** can subsequently be used to coordinate a third metal center, giving the trinuclear derivatives $[Au_2M(\mu\text{-}S_2CNEt_2)_2\text{-}\{\mu\text{-}(PPh_2)_2C{=}CH_2\}]X$ (X = ClO_4, M = Au (**5**), Ag (**6**); X = PF_6, M = Cu (**7**)). The dinuclear tricoordinate gold(I) complexes $[Au_2(\mu\text{-}S_2CNEt_2)\{\mu\text{-}(PPh_2)_2C{=}CH_2\}_2]ClO_4$ (**8**) and $[Au_2(\mu\text{-}S_2CNEt_2)\{\mu\text{-}(PPh_2)_2C{=}CH_2\}(PPh_3)_2]\text{-}ClO_4$ (**9**) are obtained by reaction of $[Au_2(\mu\text{-}S_2CNEt_2)\{\mu\text{-}(PPh_2)_2C{=}CH_2\}]ClO_4$ (**4**) with $(PPh_2)_2C{=}CH_2$ or PPh_3. The former is also obtained by reaction of $[Au_2\{\mu\text{-}(PPh_2)_2C{=}CH_2\}_2](ClO_4)_2$ with sodium *N*,*N*-diethyldithiocarbamate (1:1). The crystal structures of complexes **2** and **8** are established by X-ray crystallography.

Introduction

In the past few years there has been increasing interest in the synthesis of gold(I) derivatives containing sulfur and/or phosphorus donor ligands.[1] Among the former, dithiocarbamate complexes have extensively been studied in view of their applications as vulcanization accelerators, flotation agents, fungicides, and pesticides;[2] their antimicrobial activity has been reported,[3] and they have been used to combat metal poisoning.[4]

A large number of dithiocarbamate gold(I),[5] gold(III),[3b,5a,e,6] and gold(II)[7] complexes have been prepared, although gold(I) derivatives tend to be more interesting because their structures often involve short intra- and intermolecular gold−gold distances.

As far as we are aware, only one type of gold(I) compound containing monodentate dithiocarbamate, $[Au(S_2CNEt_2)(PR_3)]$, has been reported.[8] In the majority of dithiocarbamate gold complexes the ligand is bidentate, bridging two gold centers and forming diauracycles of the types $[Au_2(\mu\text{-}S_2CNR_2)_2]$[5g,9] and $[Au_2(\mu\text{-}S_2CNR_2)(\mu\text{-}L{-}L)]$ (L−L = diylide[5d] or diphosphine[5f]).

Dinuclear gold(I) complexes have also attracted considerable recent attention,[1b,10] and most of them display metal−metal interactions with gold−gold distances shorter than the double

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van der Waals radius of gold.[10a] These have been attributed to correlation and relativistic effects[11] that may be significant in medical applications or contribute to useful optical properties.[12]

Our current interest is focused on the synthesis of dinuclear gold complexes with monodentate $S_2CNR_2^-$ ligands; the free sulfur donor atom of these derivatives can be used to further coordinate other metallic fragments in order to prepare heteropolynuclear compounds, in which Au−M interactions could be present.

Experimental Section

Reagents. Dialkyldithiocarbamate sodium salts were purchased from Aldrich. The compounds [AuCl(tht)],[13] $[Au(tht)_2]ClO_4$,[14] $(PPh_2)_2C{=}CH_2$,[15] $[Au_2Cl_2\{\mu\text{-}(PPh_2)_2C{=}CH_2\}]$,[16] and $[Au_2\{\mu\text{-}(PPh_2)_2C{=}CH_2\}_2](ClO_4)_2$[17] were prepared by literature methods.

Caution! Perchlorate salts with organic cations may be explosive.

General Procedure. 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. Conductivities were measured in ca. 5×10^{-4} M acetone solutions with a Jenway 4010 conductimeter. C, H, N 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 and ^{31}P NMR spectra were recorded on a Bruker ARX 300 in $CDCl_3$ solutions. Chemical shifts are quoted relative to $SiMe_4$ (^1H, external) and H_3PO_4 (85%) (^{31}P, external).

Synthesis of $[Au_2(S_2CNR_2)_2\{\mu\text{-}(PPh_2)_2C{=}CH_2\}]$ (R = Me (1), Et (2), Bz (3)). To a dichloromethane solution (20 mL) of $[Au_2Cl_2\{(PPh_2)_2C{=}CH_2\}]$ (0.2 mmol, 0.17 g) under N_2 was added NaS_2CNR_2 [0.4 mmol; 0.07 g (R = Me), 0.10 g (R = Et), 0.12 g (R = Bz)], and the solution immediately became yellow. The reaction mixture was stirred for 2 h, generating a white solid (NaCl), which was separated by filtration. The filtrate was evaporated to ca. 5 mL, and addition of diethyl ether (20 mL) led to precipitation of complexes **1**−**3** as yellow solids. Yield: 71 (**1**), 86 (**2**), 43% (**3**). Mass spectra: $[M]^+$ at m/z = 1030 (43, **1**), 1086 (2, **2**), 1334 (20, **3**). Anal. Calcd for $C_{32}H_{34}Au_2N_2P_2S_4$ (**1**): C, 37.29; H, 3.32; N, 2.72. Found: C, 37.79; H, 3.64; N, 2.63. $C_{36}H_{42}Au_2N_2P_2S_4$ (**2**): C, 39.8; H, 3.9: N, 2.6. Found: C, 39.78; H, 4.43; N, 2.67. $C_{56}H_{50}Au_2N_2P_2S_4$ (**3**): C, 50.37; H, 3.77; N, 2.09. Found: C, 49.74; H, 3.47; N, 1.93. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ (**1**) 36.8 (s); (**2**) 37.0 (s); (**3**) 36.4 (s). ^1H NMR ($CDCl_3$): δ (**1**) 7.74−7.33 (m, 20H, Ph), 6.22 ["t", 2H, *N*(HP) 25.3 Hz, $C{=}CH_2$], 3.47 (s, 12H, CH_3); (**2**) 7.74−7.31 (m, 20H, Ph), 6.22 ["t", 2H, *N*(HP) 25.4 Hz, $C{=}CH_2$], 3.89 (q, 8H, CH_2), 1.31 [t, 12H, ^3J(HH) 6.6 Hz, CH_3]; (**3**) 7.76−7.27 (m, 40H, Ph), 6.23 ["t", 2H, *N*(HP) 25.0 Hz, $C{=}CH_2$], 5.08 (s, 8H, CH_2).

Synthesis of $[Au_2(\mu\text{-}S_2CNEt_2)\{\mu\text{-}(PPh_2)_2C{=}CH_2\}]ClO_4$ (4). To a dichloromethane solution of $[Au_2\{(PPh_2)_2C{=}CH_2\}_2](ClO_4)_2$ (0.2 mmol, 0.28 g) was added $[Au_2(S_2CNEt_2)_2]$ (0.2 mmol, 0.14 g). The resulting mixture was stirred for 1 h to obtain a yellow solution, which was evaporated to ca. 5 mL. Diethyl ether (20 mL) was then added to precipitate a yellow solid. Yield: 66%. Mass spectra: $[M]^+$ at m/z = 938 (100). Anal. Calcd for $C_{31}H_{32}Au_2ClNO_4P_2S_2$: C, 35.87; H, 3.1; N, 1.35. Found: C, 35.46; H, 3.19; N, 1.34. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 41.0 (s). ^1H NMR ($CDCl_3$): δ 7.68−7.43 (m, 20H, Ph), 6.46 ["t", 2H, *N*(HP) 26.3 Hz, $C{=}CH_2$], 3.97 (m, 8H, CH_2), 1.39 (m, 12H, CH_3).

Table 1. Details of Data Collection and Structure Refinement for the Complexes **2** and **8**

	2	**8**·$^1/_4CH_2Cl_2$
chem formula	$C_{36}H_{42}Au_2N_2P_2S_4$	$C_{57.25}H_{54.50}Au_2Cl_{1.50}NO_4P_4S_2$
cryst habit	yellow tablet	yellow tablet
cryst size/ mm	0.50 × 0.20 × 0.02	0.4 × 0.4 × 0.1
cryst system	orthorhombic	triclinic
space group	*Pbcn*	$P\bar{1}$
a/Å	13.532(4)	14.940(2)
b/Å	12.889(4)	18.489(3)
c/Å	21.439(6)	20.504(3)
α/deg		90.271(10)
β/deg		94.119(6)
γ/deg		91.028(10)
U/Å^3	3739(2)	5648.0(14)
Z	4	4
D_c/Mg m^{-3}	1.931	1.712
M	1086.83	1455.63
F(000)	2096	2850
T/°C	−100	−100
$2\theta_{max}$/deg	50	50
μ(Mo$K\alpha$)/mm^{-1}	8.17	5.49
transmission	0.459−0.879	0.541−1.0
no. of reflns measd	3227	21 361
no. of unique reflns	3208	19 836
R_{int}	0.049	0.035
$R^a(F, F > 4\sigma(F))$	0.045	0.044
$wR^b(F^2$, all refl)	0.098	0.086
no. of params	209	1301
no. of restraints	279	1146
S^c	0.811	0.849
max. $\Delta\rho$/e Å^{-3}	1.14	2.22

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

Synthesis of $[Au_2M(\mu\text{-}S_2CNEt_2)_2\{\mu\text{-}(PPh_2)_2C{=}CH_2\}]X$ (X = ClO_4, M = Au (5), Ag (6); X = PF_6, M = Cu (7)). To a dichloromethane (**5**, **6**) or acetonitrile (**7**) solution of **2** (0.2 mmol, 0.28 g) was added $[Au(tht)_2]ClO_4$ (0.2 mmol, 0.09 g) (**5**), $AgClO_4$ (0.2 mmol, 0.04 g) (**6**), or $[Cu(NCCH_3)_4]PF_6$ (0.2 mmol, 0.07 g) (**7**). The resulting suspension was stirred for 0.5 h and then filtered. The filtrate was concentrated to ca. 5 mL, and addition of diethyl ether (20 mL) led to the precipitation of complexes **5**−**7** as yellow solids. Yield: 86 (**5**), 64 (**6**), 61% (**7**). Anal. Calcd for $C_{36}H_{42}Au_3ClN_2O_4P_2S_4$ (**5**): C, 31.25; H, 3.05; N, 2.0. Found: C, 30.95; H, 3.15; N, 2.0. $C_{36}H_{42}AgAu_2ClN_2O_4P_2S_4$ (**6**): C, 33.4; H, 3.25; N, 2.15. Found: C, 33.85; H, 3.0; N, 2.0. $C_{36}H_{42}Au_2CuF_6N_2P_3S_4$ (**7**): C, 33.35; H, 3.25; N, 2.15. Found: C, 33.35; H, 3.15; N, 1.9. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ (**5**) 41.3 (s), (**6**) 40.3 (s), (**7**) 41.0 (s). ^1H NMR ($CDCl_3$): δ (**5**) 7.65−7.45 (m, 20H, Ph), 6.48 ["t", 2H, *N*(HP) 26.5 Hz, $C{=}CH_2$], 3.98 (m, 4H, CH_2), 3.84 (m, 4H, CH_2), 1.40 (m, 6H, CH_3), 1.34 (m, 6H, CH_3); (**6**) 7.64−7.42 (m, 20H, Ph), 6.43 ["t", 2H, *N*(HP) 26.1 Hz, $C{=}CH_2$], 3.96 (m, 8H, CH_2), 1.39 (m, 12H, CH_3); (**7**) 7.64−7.43 (m, 20H, Ph), 6.43 ["t", 2H, *N*(HP) 26.3 Hz, $C{=}CH_2$], 3.98 (m, 8H, CH_2), 1.39 (m, 12H, CH_3).

Synthesis of $[Au_2(\mu\text{-}S_2CNEt_2)\{\mu\text{-}(PPh_2)_2C{=}CH_2\}_2]ClO_4$ (8). (a) To a dichloromethane (20 mL) solution of **4** (0.2 mmol, 0.21 g) was added $(PPh_2)_2C{=}CH_2$ (0.2 mmol, 0.08 g). After stirring for 2 h the initially pale yellow solution became intensely yellow. The reaction mixture was evaporated to ca. 5 mL, and addition of diethyl ether (20 mL) gave complex **8** as a yellow solid. Yield: 65%. (b) This complex can be also obtained by addition of NaS_2CNEt_2 (0.2 mmol, 0.05 g) to a dichloromethane (20 mL) suspension of $[Au_2\{(PPh_2)_2C{=}CH_2\}_2](ClO_4)_2$ (0.2 mmol, 0.14 g). After 5 min the solution became yellow.

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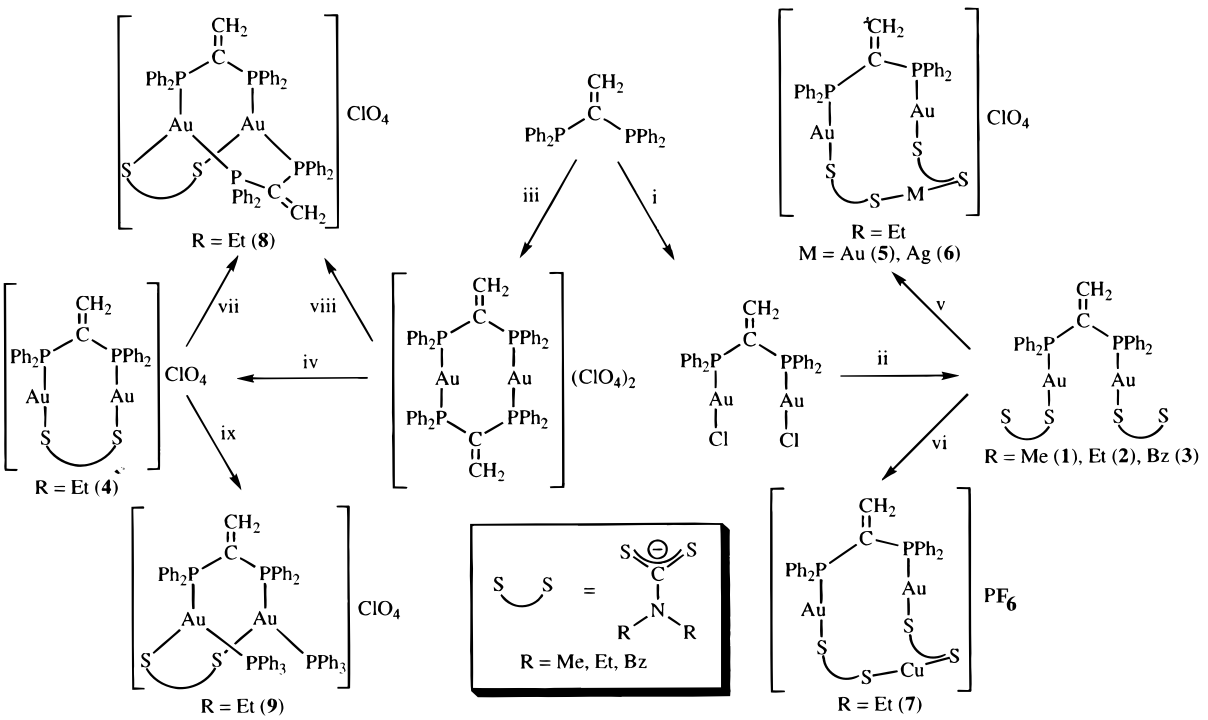
Scheme 1 (i) 2 [AuCl(tht)]; (ii) 2 NaS_2CNR_2; (iii) $[Au(tht)_2]ClO_4$; (iv) $[Au_2(\mu\text{-}S_2CNEt_2)_2]$; (v) $[Au(tht)_2]ClO_4$ or $AgClO_4$; (vi) $[Cu(MeCN)_4]PF_6$; (vii) $(PPh_2)_2C{=}CH_2$; (viii) NaS_2CNEt_2; (ix) 2 PPh_3



The reaction mixture was stirred for 2 h, generating a white solid ($NaClO_4$), which was separated by filtration. The filtrate was evaporated to ca. 5 mL, and addition of diethyl ether (20 mL) led to precipitation of complex **8**. Yield: 56%. Mass spectra: $[M]^+$ at m/z = 1334 (2). Electrospray: $[M + H]^+$ at m/z = 1335 (5). Anal. Calcd for $C_{57}H_{54}Au_2ClNO_4P_4S_2$: C, 47.75; H, 3.8; N, 0.95. Found: C, 47.2; H, 3.75; N, 0.9. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 40.1 (s). ^1H NMR ($CDCl_3$): δ 7.43−7.26 (m, 40H, Ph), 6.42 ["q", 2H, N(HP) 11.7 Hz, $C{=}CH_2$], 4.13 (m, 8H, CH_2), 1.38 (m, 12H, CH_3).

Synthesis of $[Au_2(\mu\text{-}S_2CNEt_2)\{\mu\text{-}(PPh_2)_2C{=}CH_2\}(PPh_3)_2]ClO_4$ (9). To a dichloromethane solution of **4** (0.2 mmol, 0.21 g) was added PPh_3 (0.4 mmol, 0.11 g). After stirring for 2 h the initial pale yellow solution turned to bright yellow. The reaction mixture was evaporated to ca. 5 mL, and addition of diethyl ether (20 mL) gave complex **9** as a yellow solid. Yield: 56%. Mass spectra, m/z: 1200 (7), $[M - PPh_3]^+$; 938 (100), $[M - 2PPh_3]^+$; 1067 (50), $[M - \text{vdpp}]^+$. Anal. Calcd for $C_{67}H_{62}Au_2ClNO_4P_4S_2$: C, 51.50; H, 3.99; N, 0.89. Found: C, 50.98; H, 3.58; N, 0.89. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 39.8 (s), 36.5 (m, PPh_3). ^1H NMR ($CDCl_3$): δ 7.95−7.38 (m, 50H, Ph), 6.46 (m, 2H, $C{=}CH_2$), 3.79 (m, 4H, CH_2), 1.19 (m, 6H, CH_3).

Crystal Structure Determinations. Crystals were mounted in inert oil on glass fibers. Data were collected using monochromated Mo Kα radiation (λ = 0.710 73 Å). A Siemens P4 difractometer with an LT-2 low-temperature attachment was used (scan type ω). Cell constants were refined from setting angles of ca. 60 reflections in the 2θ range 7−23°. Absorption corrections were applied on the basis of Ψ-scans. Structures were solved by the heavy atom method and refined anisotropically on F^2 (program SHELXL-93).[18] 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. Special refinement details for complex **8**: the dichloromethane molecule is disordered over a center of symmetry, and its carbon atom was not located. The composition is thus one molecule of complex to 1/4 molecule of dichloromethane. Further details are given in Table 1.

Results and Discussion

Our first objective was the synthesis of gold(I) complexes with monodentate dithiocarbamate. Thus, the treatment of the dinuclear complex $[Au_2Cl_2\{\mu\text{-}(PPh_2)_2C{=}CH_2\}]$ with 2 equiv of N,N-dialkyldithiocarbamate (alkyl = methyl, ethyl, benzyl), as illustrated in Scheme 1, results in the formation of three new derivatives $[Au_2(S_2CNR_2)_2\{\mu\text{-}(PPh_2)_2C{=}CH_2\}]$ (R = Me (**1**), Et (**2**), Bz (**3**)) that should contain monodentate dithiocarbamate.

Their elemental analyses and physical and spectroscopic properties are in accordance with the proposed stoichiometry. The molar conductivities of these products in acetone solution (Λ_M = 2 (**1**), 4 (**2**), 3 (**3**) Ω^{-1} cm^2 mol^{-1}) rule out an ionic formulation. Usually, the IR spectra of complexes with a bidentate dithiocarbamate ligand show the ν(C═N) stretching absorption above 1485 cm^{-1}, whereas in compounds with the ligand possessing a monodentate coordination it appears below 1485 cm^{-1}. In complexes **1**−**3** it is found at 1463 (**1**), 1472 (**2**), and 1469 (**3**) cm^{-1}, also indicating a monodentate coordination by the sulfur donor ligand.[19]

The molecular structure of complex **2** has been confirmed by X-ray structure analysis (Figure 1). Selected bond lengths and angles are presented in Table 2. The molecule displays crystallographic 2-fold symmetry, the 2-fold axis passing along the double bond C(1)−C(2). The coordination of the gold atoms is almost linear, with a P−Au−S(2) angle of 174.43(12)°. The very dissimilar Au−S distances, Au−S(2) 2.319(4) and Au−S(1) 2.969(4) Å, show that the dithiocarbamate ligands are essentially monodentate. However, the longer distance may represent a weak contact between the gold and the second sulfur atom; cf. complexes such as $[Au^{II}_2(\mu\text{-}CH_2PPh_2CH_2)_2(S_2CNR_2)_2]$,[7b] in which the bonded distances are 2.439, 2.431(2) Å and the nonbonded Au−S distances 3.313, 3.306 Å in two independent molecules, and $[Au(S_2CNEt_2)(PPh_3)]$[8] with 2.338

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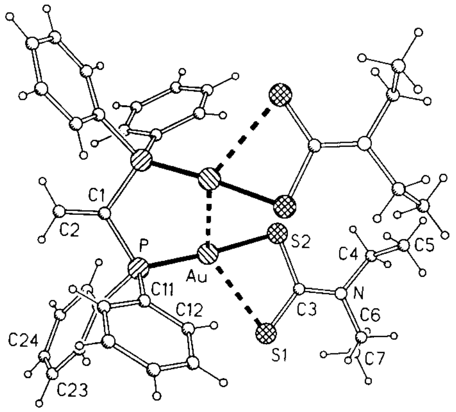

Figure 1. Molecular structure of complex **2**. Radii are arbitrary. Only the asymmetric unit is numbered.

Table 2. Selected Bond Lengths [Å] and Angles [deg] for **2**[a]

Au−P	2.234(3)	Au−S(2)	2.319(4)
Au−S(1)	2.969(4)	Au−Au#1	3.3429(12)
P−C(1)	1.815(11)	P−C(21)	1.816(14)
P−C(11)	1.826(13)	S(1)−C(3)	1.658(13)
S(2)−C(3)	1.765(13)	C(1)−C(2)	1.26(2)
C(3)−N	1.33(2)	C(4)−C(5)	1.47(2)
C(4)−N	1.485(14)	C(6)−N	1.45(2)
C(6)−C(7)	1.50(2)		

P−Au−S(2)	174.43(12)	P−Au−S(1)	117.79(12)
S(2)−Au−S(1)	66.42(11)	P−Au−Au#1	76.52(9)
S(2)−Au−Au#1	97.97(8)	S(1)−Au−Au#1	130.89(9)
C(1)−P−C(21)	104.3(6)	C(1)−P−C(11)	108.0(4)
C(21)−P−C(11)	103.1(6)	C(1)−P−Au	111.4(5)
C(21)−P−Au	118.0(5)	C(11)−P−Au	111.4(4)
C(3)−S(1)−Au	77.6(5)	C(3)−S(2)−Au	96.7(4)
C(2)−C(1)−P	122.7(6)	P#1−C(1)−P	114.6(11)
N−C(3)−S(1)	123.3(10)	N−C(3)−S(2)	117.9(9)
S(1)−C(3)−S(2)	118.8(8)	C(5)−C(4)−N	111.1(10)
N−C(6)−C(7)	114.3(11)		

[a] Symmetry transformations used to generate equivalent atoms: #1, -*x*+1, *y*, -*z*+1/2.

and 3.015 Å. The Au−Au distance is 3.3429(12) Å and is longer than those found in other dinuclear gold(I) systems such as $[Au_2\{\mu\text{-}(PPh_2)_2C{=}CH_2\}]Cl_2$ (2.977(1) Å),[16] which has the same phosphine ligand; the two P−Au−S moieties are twisted with respect to each other by 59° (torsion angle Au−P···P′−Au′). As expected, the longer C−S bond involves the coordinated S atom (C(3)−S(2) 1.765(13), C(3)−S(1) 1.658(13) Å).

The above-mentioned ionic species $[Au_2(\mu\text{-}S_2CNEt_2)\{\mu\text{-}(PPh_2)_2C{=}CH_2\}]ClO_4$ (**4**) can also be prepared through a metathesis reaction of $[Au_2\{\mu\text{-}(PPh_2)_2C{=}CH_2\}_2](ClO_4)_2$ and $[Au_2(\mu\text{-}S_2CNEt_2)_2]$ (see Scheme 1). Its physical and spectroscopic properties are clearly different from those of **2**: it is a uni-univalent electrolyte in acetone solution (Λ_M = 142 Ω^{-1} cm^2 mol^{-1}) and its ν(C=N) band appears at 1501 cm^{-1}.[19]

The free sulfur atoms of complex **2** can coordinate a metal center by reaction with $[Au(tht)_2]ClO_4$, $AgClO_4$, or $[Cu(MeCN)_4]PF_6$, affording trinuclear complexes **5**−**7**, in which the dithiocarbamate ligands bridge two different metal centers, a situation that, as far as we are aware, is unprecedented (see Scheme 1). Their elemental analyses and spectroscopic and physical properties are in accordance with the proposed formulation, and they are uni-univalent electrolytes in acetone (Λ_M = 149 (**5**), 154 (**6**), 166 Ω^{-1} cm^2 mol^{-1}). In their IR spectra, the ν(C=N) stretching band appears at 1494 (**5**), 1499 (**6**), and 1495 (**7**) cm^{-1}, as expected for bidentate dithiocarbamate ligands. Their mass spectra (LSIMS$^+$) display the peak corresponding to the molecular ion at *m*/*z* = 1283 (23, **5**), 1195 (3, **6**), and 1148 (13, **7**).

Table 3. Selected Bond Lengths [Å] and Angles [deg] for **8**

Au(1)−P(3)	2.306(2)	Au(1)−P(1)	2.351(2)
Au(1)−S(1)	2.554(2)	Au(1)−Au(2)	2.9019(6)
Au(2)−P(2)	2.309(2)	Au(2)−P(4)	2.339(2)
Au(2)−S(2)	2.664(2)	P(3)−C(51)	1.818(8)
S(1)−C(5)	1.727(8)	S(2)−C(5)	1.746(8)
Au(1′)−P(3′)	2.309(2)	Au(1′)−P(1′)	2.339(2)
Au(1′)−S(1′)	2.662(3)	Au(1′)−Au(2′)	2.9002(6)
Au(2′)−P(2′)	2.313(2)	Au(2′)−P(4′)	2.365(2)
Au(2′)−S(2′)	2.608(2)		

P(3)−Au(1)−P(1)	143.19(8)	P(3)−Au(1)−S(1)	117.56(8)
P(1)−Au(1)−S(1)	98.99(8)	P(3)−Au(1)−Au(2)	93.99(5)
P(1)−Au(1)−Au(2)	85.89(5)	S(1)−Au(1)−Au(2)	96.14(6)
P(2)−Au(2)−P(4)	149.09(8)	P(2)−Au(2)−S(2)	114.41(8)
P(4)−Au(2)−S(2)	96.49(8)	P(2)−Au(2)−Au(1)	96.28(6)
P(4)−Au(2)−Au(1)	90.28(6)	S(2)−Au(2)−Au(1)	77.14(5)
C(5)−S(1)−Au(1)	106.1(3)	C(5)−S(2)−Au(2)	113.1(3)
P(3′)−Au(1′)−P(1′)	147.08(8)	P(3′)−Au(1′)−S(1′)	119.71(8)
P(1′)−Au(1′)−S(1′)	92.97(8)	P(3′)−Au(1′)−Au(2′)	93.96(6)
P(1′)−Au(1′)−Au(2′)	88.83(6)	S(1′)−Au(1′)−Au(2′)	91.33(6)
P(2′)−Au(2′)−P(4′)	147.12(8)	P(2′)−Au(2′)−S(2′)	119.38(8)
P(4′)−Au(2′)−S(2′)	93.40(8)	P(2′)−Au(2′)−Au(1′)	95.02(6)
P(4′)−Au(2′)−Au(1′)	89.71(6)	S(2′)−Au(2′)−Au(1′)	76.98(6)
C(5′)−S(1′)−Au(1′)	103.3(3)	C(5′)−S(2′)−Au(2′)	107.5(3)

The structural arrangement of the dithiocarbamate ligands could produce intermetallic contacts in the Au_2M. Unfortunately, no suitable crystals for X-ray diffraction studies have been obtained.

As is well-known, the structural chemistry of gold(I) is characterized by its linear coordination. However, some examples of tricoordinate gold(I) complexes have been described,[20] although there is only one dithiocarbamate derivative reported to date.[5b] To increase the number of this type of compound, we reacted $[Au_2\{\mu\text{-}(PPh_2)_2C{=}CH_2\}_2](ClO_4)_2$ with NaS_2CNEt_2 (1:2) or $[Au_2(\mu\text{-}S_2CNEt_2)\{\mu\text{-}(PPh_2)_2C{=}CH_2\}]ClO_4$ (**4**) with $(PPh_2)_2C{=}CH_2$ (1:1). The resulting complex (**8**) displays two gold centers in a tricoordinate environment, coordinated by one sulfur of the dithiocarbamate and two phosphorus atoms, one from each diphosphine (see Scheme 1; X-ray structure, see below). In a similar way, the reaction of **4** with PPh_3 in a 1:2 molar ratio affords the new tricoordinate species $[Au_2(\mu\text{-}S_2CNEt_2)\{\mu\text{-}(PPh_2)_2C{=}CH_2\}(PPh_3)_2]ClO_4$ (**9**).

In the IR spectra of complexes **8** and **9** the ν(C=N) stretching band appears at 1480 (**8**) and 1481 (**9**) cm^{-1}, lower than previously reported values for this system,[5b] probably associated with the tricoordination. Their molar conductivities in acetone (Λ_M = 132 (**8**), 156 (**9**) Ω^{-1} cm^2 mol^{-1}) prove that the dithiocarbamate ligands are coordinated to the gold centers rather than being counterions. Moreover, the $^{31}P\{^1H\}$ spectrum of **9** shows two singlets at 39.8 and 36.5 ppm. No P−P coupling is observed, whereas gold(I) linear compounds containing the unit P−Au−PPh_3 usually display AB systems.[21]

The crystal structure of complex **8** (Table 3) has been established by X-ray diffraction; the asymmetric unit of complex **8** has two independent but closely similar molecules (A and B), one of which is shown in Figure 2. Both molecules consist of two gold atoms bridged by two diphosphines and one dithiocarbamate ligand and presenting short intramolecular gold−gold contacts of 2.9019(6) and 2.9002(6) Å. These distances are longer than those found in dinuclear dithiocarbamate complexes such as $[Au_2(\mu\text{-}S_2CNR_2)_2]$ (2.76−2.8 Å),[5c,9b,22]

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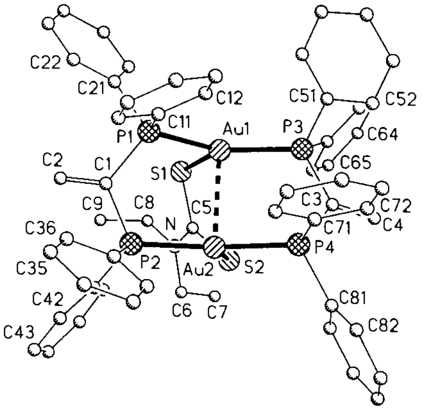

Figure 2. Structure of one of the two independent cations of complex **8**. H atoms are omitted for clarity.

slightly longer than those in [$Au_2\{\mu\text{-}(CH_2)_2PPh_2\}(\mu\text{-}S_2CNEt_2)$] (2.868(1) and 2.867(1) Å), but similar to those in the related compound [$Au_2(S_2CNEt_2)(dppm)_2$][BH_3CN] (2.949(1) Å).[5b] The Au−S bond distances, 2.554(2) and 2.664(2) (molecule A) and 2.662(3) and 2.608(2) (molecule B) Å, are shorter than those in [$Au_2(S_2CNEt_2)(dppm)_2$][BH_3CN] (2.648(3) and 2.703(3) Å), but longer than those in other three-coordinate complexes such as [$Au(SCN)(PPh_3)_2$] (2.468(4) Å).[23] The Au−P bond distances lie in the range 2.306(2)−2.365(2) Å and are also typical of three-coordinate complexes.

The gold atoms display a distorted trigonal planar geometry with angles close to 143° (P−Au−P), 117°, and 100° (P−Au−S); the distortion is less marked than in [$Au_2(S_2CNEt_2)$-$(dppm)_2$][BH_3CN], where the P−Au−P angle is 160°. The Au atoms lie maximally 0.07 Å out of the respective PS_2 planes, and the interplanar angles are 6° and 11° in the two molecules. The mutual rotations of the coordination planes are expressed by the torsion angles P(1)−Au(1)−Au(2)−P(2) 14°, 15°; P(3)−Au(1)−Au(2)−P(4) 21°, 15°; and S(1)−Au(1)−Au(2)−S(2) 36°, 41°.

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Supporting Information Available: Two X-ray crystallographic files, in CIF format, are available on the Internet only. Access and ordering information is given on any current masthead page.

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