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Di- and tetranuclear gold(II) complexes with dithiocarbamate and related ligands. X-ray structure of $[Au_2(\mu\text{-}CH_2PPh_2CH_2)_2(S_2CNMe_2)_2]$

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Abstract

The reaction of $[Au_2(\mu\text{-}CH_2PPh_2CH_2)_2(tht)_2](ClO_4)_2$ or $[Au_2(\mu\text{-}CH_2PPh_2CH_2)_2(PPh_3)(tht)](ClO_4)_2$ (tht = tetrahydrothiophene) with various dithiocarbamates gives the cationic or neutral complexes $[Au_2(\mu\text{-}CH_2PPh_2CH_2)_2\{S(MeS)CNHR\}_2](ClO_4)_2$, $[Au_2(\mu\text{-}CH_2PPh_2CH_2)_2(PPh_3)\{S(Mes)CNHR\}](ClO_4)_2$ or $[Au_2(\mu\text{-}CH_2PPh_2CH_2)_2(S_2CNR_2)_2]$. Displacement of tht from $[Au_2(\mu\text{-}CH_2PPh_2CH_2)_2(R')(tht)](ClO_4)$ ($R' = C_6F_5$ or $2,4,6\text{-}C_6F_3H_2$) gives new cationic tetranuclear complexes $[\{Au_2(\mu\text{-}CH_2PPh_2CH_2)_2(R')\}_2(\mu\text{-}S_2CNR_2)](ClO_4)$ in which the dithiocarbamate acts as a bridging ligand. The structure of $[Au_2(\mu\text{-}CH_2PPh_2CH_2)_2(S_2CNMe_2)_2]$ has been established by an X-ray diffraction study and shows that the dithiocarbamate is unidentate.

Keywords: Crystal structures; Gold complexes; Dithiocarbamato complexes; Tetranuclear complexes

1. Introduction

Binuclear gold(II) complexes containing the bis(ylide) ligand $(CH_2)_2PR_2^-$ have been extensively studied because of their high stability. They have been synthesized by oxidative addition [1–6], substitution [7–11] or electrophilic reactions [12], to give neutral or cationic compounds. Despite the work done in this area only a few gold(II) complexes with S-donor ligands have been reported [7,8,12,13] and no systematic study of dithiocarbamate and related ligands has been carried out, despite their versatile coordination modes.

In this paper we describe the following gold(II) dimers with methyl dithiocarbamate ligands: $[Au_2(\mu\text{-}CH_2PPh_2CH_2)_2\{S(MeS)CNHR\}_2](ClO_4)_2$ ($R = p\text{-}MeC_6H_4$, $o\text{-}MeC_6H_4$, $p\text{-}MeOC_6H_4$, $3,5\text{-}Me_2C_6H_3$) and $[Au_2(\mu\text{-}CH_2PPh_2CH_2)_2(PPh_3)\{S(MeS)CNHR\}](ClO_4)_2$ ($R = o\text{-}MeC_6H_4$, $p\text{-}MeOC_6H_4$, $3,5\text{-}Me_2C_6H_3$), in which the methyl group bonded to one of the sulfur atoms favours a monodentate coordination. We also describe the gold(II) dimers $[Au_2(\mu\text{-}CH_2PPh_2CH_2)_2(S_2CNR_2)_2]$ with dithiocarbamate acting as a unidentate ligand and the gold(II) tetramers $[\{Au_2(\mu\text{-}CH_2PPh_2CH_2)_2(R')\}_2(\mu\text{-}S_2CNR_2)](ClO_4)$ with bridging dithiocarbamate. The X-ray structure of $[Au_2(\mu\text{-}CH_2PPh_2CH_2)_2(S_2CNMe_2)_2]$ has been established by single-crystal X-ray analysis.

2. Experimental

IR spectra were recorded on Perkin-Elmer 599 or 883 spectrophotometers, over the range 4000–200 cm^{-1}, using Nujol mulls between polyethylene sheets; ^1H, ^{19}F and $^{31}P\{^1H\}$ NMR spectra on a Varian XL-200, as chloroform solutions; chemical shifts are quoted relative to $SiMe_4$ (^1H), $CFCl_3$ (external; ^{19}F) and 85% H_3PO_4 (external; ^{31}P). C, H and N analyses were performed with a Perkin-Elmer 240B microanalyser. Conductivities were measured in acetone solution with an apparatus Philips PW 9509. The yields, C, H and N analyses and

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some ^{1}H and ^{31}P{^{1}H} NMR data are listed in Table 1. All the reactions were carried out at room temperature.

2.1. *[$Au_2(\mu$-$CH_2PPh_2CH_2)_2\{S(MeS)CNHR\}_2](ClO_4)_2$ (R = p-MeC_6H_4 (1), o-MeC_6H_4 (2), p-$MeOC_6H_4$ (3), 3,5-$Me_2C_6H_3$ (4))*

To a solution of [$Au_2(\mu$-$CH_2PPh_2CH_2)_2(tht)_2](ClO_4)_2$ [10] (0.119 g, 0.1 mmol) in dichloromethane (25 cm^3) was added 0.2 mmol of S(MeS)CNHR [14] (0.039 g (R = *p*-MeC_6H_4), 0.039 g (R = *o*-MeC_6H_4), 0.043 g (R = *p*-$MeOC_6H_4$), 0.042 g (R = 3,5-$Me_2C_6H_3$)). After stirring for 30 min, the solution was vacuum evaporated to ~5 cm^3 and diethyl ether (20 cm^3) was added. Products appeared as yellow (**1**, **3**, **4**) or orange (**2**) solids. ^{1}H NMR data (see also Table 1): **1**: δ 10.53 (s, 2H, H–N), 7.55–7.25 (m, 28H, Ph and *p*-MeC_6*H_4*), 2.74 (s, 6H, Me–S), 2.35 (s, 6H, Me); **2**: δ 10.49 (s, 2H, H–N), 7.63–7.27 (m, 28H, Ph and *o*-MeC_6*H_4*), 2.74 (s, 6H, Me–S), 2.28 (s, 6H, Me); **3**: δ 10.47 (s, 2H, H–N), 7.55–6.90 (m, 28H, Ph and *p*-$MeOC_6$*H_4*), 3.80 (s, 6H, Me–O), 2.74 (s, 6H, Me–S); **4**: δ 10.50 (s, 2H, H–N), 7.61–6.98 (m, 26H, Ph and 3,5-Me_2C_6*H_3*), 2.74 (s, 6H, Me–S), 2.30 (s, 12H, Me). Λ_M (Ω^{-1} cm^2 mol^{-1}, 5×10^{-4} M acetone solution): 211 (**1**), 218 (**2**), 214 (**3**), 211 (**4**). IR: ν(N–H), cm^{-1}: 3200 (m, br) (**1**, **3**), 3200 (w, br) (**2**, **4**).

2.2. *[$Au_2(\mu$-$CH_2PPh_2CH_2)_2(PPh_3)\{S(MeS)CNHR\}](ClO_4)_2$ (R = o-MeC_6H_4 (5), p-$MeOC_6H_4$ (6), 3,5-$Me_2C_6H_3$ (7))*

To a solution of [$Au_2(\mu$-$CH_2PPh_2CH_2)_2(PPh_3)(tht)](ClO_4)_2$ [15] (0.068 g, 0.05 mmol) in dichloromethane (20 cm^3) was added 0.05 mmol of S(MeS)CNHR (0.010 g (R = *o*-MeC_6H_4), 0.011 g (R = *p*-$MeOC_6H_4$), 0.011 g (R = 3,5-$Me_2C_6H_3$)). The solution was stirred for 90 min. The solvent was evaporated to ~5 cm^3 and addition of diethyl ether (20 cm^3) afforded orange solids which were filtered off. NMR data (see also Table 1): **5**: ^{1}H: δ 10.65 (s, 1H, H–N), 7.51–7.26 (m, 39H, Ph and *o*-MeC_6*H_4*), 2.71 (s, 3H, Me–S), 2.23 (s, 3H, Me); ^{31}P{^{1}H}: δ 19.7 (t, ^3J(PP) = 22.2 Hz, PPh$_3$); **6**: ^{1}H: δ 10.64 (s, 1H, H–N), 7.53–6.94 (m, 39H, Ph and *p*-$MeOC_6$*H_4*), 3.82 (s, 3H, Me–O), 2.73 (s, 3H, Me–S); ^{31}P{^{1}H}: δ 19.7 (t, ^3J(PP) = 23.1 Hz, PPh$_3$); **7**: ^{1}H: δ 10.69 (s, 1H, H–N), 7.50–7.26 (m, 38H, Ph and 3,5-Me_2C_6*H_3*), 2.73 (s, 3H, Me–S), 2.30 (s, 6H, Me); ^{31}P{^{1}H}: δ 19.6 (t, ^3J(PP) = 23.2 Hz, PPh$_3$). Λ_M (Ω^{-1} cm^2 mol^{-1}, 5×10^{-4} M acetone solution): 214 (**5**), 202 (**6**), 208 (**7**). IR: ν(N–H), cm^{-1}; 3200 (w, br) (**5**, **7**), 3220 (w, br) (**6**).

2.3. *[$Au_2(\mu$-$CH_2PPh_2CH_2)_2(S_2CNR_2)_2$] ($R_2$ = Me_2 (8), Et_2 (9), C_4H_8 (10))*

To a solution of [$Au_2(\mu$-$CH_2PPh_2CH_2)_2(tht)_2](ClO_4)_2$ (0.239 g, 0.2 mmol) in dichloromethane (25 cm^3) was added a water solution (10 cm^3) of NaS_2CNR_2 (R_2 = Me_2 (0.0717 g, 0.4 mmol), Et_2 (0.0901 g, 0.4 mmol) or C_4H_8 (0.0677 g, 0.4 mmol)). The mixture was stirred for 20 min and the dichloromethane layer was removed using a separating funnel and dried with anhydrous magnesium sulfate (1–2 g). The filtered solution was evaporated to ~5 cm^3, whereupon addition of diethyl ether (20 cm^3) led to the precipitation of complexes as red (**8**, **9**) or orange (**10**) solids. ^{1}H NMR data (see also Table 1): **8**: δ 7.66–7.31 (m, 20H, Ph), 3.41 (s, 12H, CH$_3$); **9**: δ 7.75–7.20 (m, 20H, Ph), 3.94 (c, 8H, CH$_2$), 1.22 (t, 12H, CH$_3$); **10**: δ 7.63–7.33 (m, 20H, Ph), 3.74 (m, 8H, CH$_2$N), 1.92 (m, 8H, CH$_2$).

2.4. *[\{$Au_2(\mu$-$CH_2PPh_2CH_2)_2(C_6F_5)$\}$_2(\mu$-$S_2CNR_2)]ClO_4$ (R = Me (11), Et (12), CH_2Ph (13))*

To a solution of [$Au_2(\mu$-$CH_2PPh_2CH_2)_2(C_6F_5)(tht)]ClO_4$ [15] (0.470 g, 0.4 mmol) in dichloromethane (25 cm^3) was added a water solution (10 cm^3) of NaS_2CNR_2 (0.2 mmol) (R = Me (0.0358 g), Et (0.045 g) or CH$_2$Ph (0.0591 g)). The mixture was stirred for 30 min and the dichloromethane layer was removed using a separating funnel and dried with anhydrous magnesium sulfate (1–2 g). Concentration of the filtered solution to ~5 cm^3 and addition of n-hexane (20 cm^3) led to the precipitation of complexes as brown (**11**) or green solids (**12**, **13**). NMR data (see also Table 1): **11**: ^{1}H: δ 7.49–7.28 (m, 40H, Ph), 3.10 (s, 6H, CH$_3$); ^{19}F: δ −122.8 (m, 4F, *o*-F), −158.9 (t, 2F, *p*-F), −161.2 (m, 4F, *m*-F); **12**: ^{1}H: δ 7.50–7.36 (m, 40H, Ph), 4.54 (c, 4H, CH$_2$), 1.05 (t, 6H, CH$_3$); ^{19}F: δ −122.5 (m, 4F, *o*-F), −158.9 (t, 2F, *p*-F), −161.2 (m, 4F, *m*-F); **13**: ^{1}H: δ 7.53–7.17 (m, 50H, Ph), 5.27 (s, 4H, CH$_2$); ^{19}F: δ −122.7 (m, 4F, *o*-F), −160.9 (t, 2F, *p*-F), −161.1 (m, 4F, *m*-F). Λ_M (Ω^{-1} cm^2 mol^{-1}, 9×10^{-5} M acetone solution): 169 (**11**), 171 (**12**), 163 (**13**).

2.5. *[\{$Au_2(\mu$-$CH_2PPh_2CH_2)_2(2,4,6$-$C_6F_3H_2)$\}$_2(\mu$-$S_2CN(CH_2Ph)_2)]ClO_4$ (14)*

To a dichloromethane solution (25 cm^3) of [$Au_2(\mu$-$CH_2PPh_2CH_2)_2(2,4,6$-$C_6F_3H_2)(tht)]ClO_4$ [15] (0.4556 g, 0.4 mmol) was added a water solution (10 cm^3) of $NaS_2CN(CH_2Ph)_2$ (0.0591 g, 0.2 mmol) and the mixture was stirred for 30 min. The dichloromethane layer was removed using a separating funnel and dried with anhydrous magnesium sulfate (1–2 g). The filtered solution was evaporated to ~5 cm^3 and addition of n-hexane (20 cm^3) gave the complex **14** as red solid.

Table 1
Analytical and spectroscopical data of compounds **1–14**

Complex no.	Complex	Yield (%)	Analysis (%)			$\delta(PPh_2)$ ($^{31}P\{^1H\}$) [$^3J(P–P)$] (Hz)	$\delta(CH_2)$ (^1H) [N]	$\nu(Au–C_{ylide})$ (cm^{-1})
			C	H	N			
1	$[Au_2(\mu\text{-}CH_2PPh_2CH_2)_2\{S(MeS)CNHR\}_2](ClO_4)_2$ R = *p*-MeC_6H_4	85	39.0 (39.05)	3.7 (3.55)	1.8 (2.0)	42.63(s)	2.05('d') [10.8]	565
2	$[Au_2(\mu\text{-}CH_2PPh_2CH_2)_2\{S(MeS)CNHR\}_2](ClO_4)_2$ R = *o*-MeC_6H_4	78	39.05 (39.05)	3.85 (3.55)	1.5 (2.0)	42.68(s)	2.06('d') [11.0]	570
3	$[Au_2(\mu\text{-}CH_2PPh_2CH_2)_2\{S(MeS)CNHR\}_2](ClO_4)_2$ R = *p*-$MeOC_6H_4$	90	38.1 (38.2)	3.25 (3.5)	1.90 (1.95)	42.66(s)	2.02('d') [10.5]	565
4	$[Au_2(\mu\text{-}CH_2PPh_2CH_2)_2\{S(MeS)CNHR\}_2](ClO_4)_2$ R = 3,5-$Me_2C_6H_3$	71	39.15 (40.0)	3.95 (3.75)	1.5 (1.95)	42.66(s)	2.03('d') [10.6]	567
5	$[Au_2(\mu\text{-}CH_2PPh_2CH_2)_2(PPh_3)\{S(MeS)(CNHR\}](ClO_4)_2$ R = *o*-MeC_6H_4	71	43.95 (44.65)	3.75 (3.7)	0.7 (0.95)	44.09(d) [22.7]	1.99('d') [9.9] 1.60('t') [9.6]	568
6	$[Au_2(\mu\text{-}CH_2PPh_2CH_2)_2(PPh_3)\{S(MeS)CNHR\}](ClO_4)_2$ R = *p*-$MeOC_6H_4$	74	43.85 (44.2)	3.85 (3.65)	0.9 (0.95)	44.05(d) [23.1]	1.98('d') [10.6] 1.53('t') [9.1]	567
7	$[Au_2(\mu\text{-}CH_2PPh_2CH_2)_2(PPh_3)\{S(MeS)CNHR\}](ClO_4)_2$ R = 3,5-$Me_2C_6H_3$	74	45.45 (45.05)	4.0 (3.8)	0.5 (0.95)	44.05(d) [23.2]	1.98('d') [10.5] 1.53('t') [9.7]	567
8	$[Au_2(\mu\text{-}CH_2PPh_2CH_2)_2(S_2CNMe_2)_2]$	75	38.65 (38.5)	3.8 (3.8)	2.7 (2.65)	41.5(s)	2.01('d') [9.9]	569
9	$[Au_2(\mu\text{-}CH_2PPh_2CH_2)_2(S_2CNEt_2)_2]$	72	40.55 (40.8)	4.4 (4.5)	2.5 (2.5)	41.5(s)	2.02('d') [9.5]	571
10	$[Au_2(\mu\text{-}CH_2PPh_2CH_2)_2(S_2CNC_4H_8)_2]$	65	40.9 (40.95)	4.0 (3.95)	2.45 (2.5)	41.3(s)	2.00('d') [9.5]	573
11	$[\{Au_2(\mu\text{-}CH_2PPh_2CH_2)_2(C_6F_5)\}_2(\mu\text{-}S_2CNMe_2)]ClO_4$	42	39.35 (38.85)	2.5 (2.85)	0.5 (0.65)	40.5(s)	1.88('d') [8.4] 1.46('d') [10]	567
12	$[\{Au_2(\mu\text{-}CH_2PPh_2CH_2)_2(C_6F_5)\}_2(\mu\text{-}S_2CNEt_2)]ClO_4$	55	39.1 (39.45)	3.0 (3.2)	0.45 (0.65)	40.9(s)	1.90('d') [8.1] 1.49('d') [9.1]	568
13	$[\{Au_2(\mu\text{-}CH_2PPh_2CH_2)_2(C_6F_5)\}_2(\mu\text{-}S_2CNBz_2)]ClO_4$	57	42.0 (42.5)	2.7 (3.0)	0.65 (0.60)	40.9(s)	2.01('d') [8.3] 1.52('d') [9.5]	566
14	$[\{Au_2(\mu\text{-}CH_2PPh_2CH_2)_2(C_6F_3H_2)\}_2(\mu\text{-}S_2CNBz_2)]ClO_4$	74	45.5 (45.85)	3.1 (3.45)	0.4 (0.65)	36.7(s)	1.78('d') [9.6] 1.37('d') [9.6]	565

NMR data (see also Table 1): ^{1}H: δ 7.61–7.32 (m, 50H, Ph), 6.53 (m, 4H, $C_6F_3H_2$), 5.09 (s, 4H, CH_2); ^{19}F: δ -113.9 (m, 4F, *o*-F), -173.3 (m, 2F, *p*-F). Λ_M (Ω^{-1} cm^2 mol^{-1}, 9×10^{-5} M acetone solution: 178 (**14**).

2.6. Crystal structure analysis of compound 8

Crystal data. $C_{34}H_{40}Au_2N_2P_2S_4$, $M_r=1060.79$, triclinic, $P\bar{1}$, $a=9.814(3)$, $b=11.982(4)$, $c=16.702(5)$ Å, $\alpha=95.52(3)$, $\beta=94.26(2)$, $\gamma=110.52(3)$°, $V=1818.5$ Å^3, $Z=2$, $D_x=1.937$ Mg m^{-3}, λ(Mo Kα) = 0.71073 Å, $\mu=8.4$ mm^{-1}, $F(000)=1020$, $T=-95$ °C.

Data collection and reduction. A red–brown tablet $\sim 0.45\times0.4\times0.2$ mm was mounted in inert oil (type RS3000, donated by Riedel de Haën) and transferred to the cold gas stream of the diffractometer (Siemens R3 system with LT-2 low temperature attachment). A total of 8086 intensities (6413 unique, R_{int} 0.019) was measured to 2θ 50°. Cell constants were refined from diffractometer angles of 50 reflections in the 2θ range 20–23°. Absorption corrections were based on ψ-scans, with transmission factors 0.44–0.87.

Structure solution and refinement. The structure was solved by the heavy-atom method and refined on F^2 using the program SHELXL-93 [16]. H atoms were included using a riding model. The weighting scheme was $w^{-1}=[\sigma^2(F_o^2)+(0.056P)^2]$, with $P=(F_o^2+2F_c^2)/3$. The final $R_w(F^2)$ for all reflections was 0.080, with a conventional $R(F)$ of 0.031, for 402 parameters and 284 restraints; $S=0.99$, max. $\Delta/\sigma=0.33$, max. $\Delta\rho=1.66$ e Å^{-3}. Final atomic coordinates are given in Table 2, with selected bond lengths and angles in Table 3. See also Section 4.

3. Results and discussion

The neutral tetrahydrothiophene (tht) in $[Au_2(\mu\text{-}CH_2PPh_2CH_2)_2(tht)_2](ClO_4)_2$ or $[Au_2(\mu\text{-}CH_2PPh_2CH_2)_2(PPh_3)(tht)](ClO_4)_2$ can be readily displaced by addition of methyl dithiocarbamate in a 1:2 or 1:1 molar ratio, respectively (Eqs. (1) and (2)). The tht is also displaced by dithiocarbamate in a 1:2 molar ratio in a dichloromethane/water mixture (Eq. (3)).

Complexes **1–10** were isolated as orange (**2**, **5–7**, **10**), yellow (**1**, **3**, **4**) or red (**8**, **9**) solids, air- and moisture-stable at room temperature. They are soluble in dichloromethane, chloroform and acetone, except for **8–10**, which are slightly soluble in acetone. All the complexes are insoluble in diethyl ether. Complexes **1–7** behave as 2:1 electrolytes in acetone solution (complexes **8–10** are not soluble enough). Complex **9** has previously been mentioned by Fackler and co-workers, but no spectroscopic data were reported [12].

The IR spectra show a weak band at ~ 567 cm^{-1} assignable to ν(Au–C$_{ylide}$) [17], and a ν(N–H) absorption at 3200 cm^{-1} in complexes **1–4**, **8–10** (see Section 2).

Table 2
Atomic coordinates ($\times10^4$) for **8**

	x	y	z
Au(1)	6208.8(2)	665.4(2)	484.0(1)
P(1)	3190.6(14)	450.7(12)	1212.2(8)
S(1)	8392.3(15)	1776.6(13)	1428.8(9)
S(2)	7834(2)	3596.6(13)	467.7(9)
N(1)	10002(5)	4095(4)	1635(3)
C(1)	7552(6)	797(5)	−462(3)
C(2)	5010(5)	603(5)	1485(3)
C(3)	8832(6)	3251(5)	1200(3)
C(4)	10488(7)	5348(6)	1470(5)
C(5)	10932(7)	3822(7)	2253(4)
C(11)	3069(5)	1781(5)	842(3)
C(12)	1738(6)	1755(5)	483(3)
C(13)	1616(7)	2785(6)	229(4)
C(14)	2814(6)	3839(6)	331(4)
C(15)	4139(7)	3861(5)	697(4)
C(16)	4271(6)	2836(5)	947(3)
C(21)	2213(6)	298(5)	2102(3)
C(22)	1688(7)	−792(6)	2378(4)
C(23)	1059(8)	−907(7)	3104(4)
C(24)	952(7)	73(7)	3535(4)
C(25)	1480(8)	1172(7)	3266(4)
C(26)	2132(8)	1291(6)	2555(4)
Au(1′)	5563.8(2)	9508.1(2)	4433.4(1)
P(1′)	4027(2)	7771.2(13)	5685.9(9)
S(1′)	6973(2)	8823.2(14)	3496.1(9)
S(2′)	3848(2)	7528(2)	2832.1(11)
N(1′)	6067(6)	8003(5)	1954(3)
C(1′)	5620(6)	10852(5)	3707(3)
C(2′)	5388(6)	8014(5)	5037(3)
C(3′)	5635(6)	8112(5)	2690(3)
C(4′)	5078(9)	7371(6)	1233(4)
C(5′)	7620(8)	8536(7)	1814(5)
C(11′)	3996(6)	6571(5)	6285(3)
C(12′)	4844(7)	5884(5)	6131(4)
C(13′)	4840(7)	4989(6)	6611(4)
C(14′)	3999(7)	4799(6)	7233(4)
C(15′)	3154(7)	5490(5)	7405(4)
C(16′)	3146(6)	6371(5)	6922(3)
C(21′)	2214(6)	7268(5)	5133(3)
C(22′)	1229(6)	7849(6)	5317(4)
C(23′)	−160(7)	7431(6)	4906(4)
C(24′)	−603(7)	6444(6)	4315(4)
C(25′)	359(7)	5870(7)	4139(4)
C(26′)	1766(7)	6296(6)	4548(4)

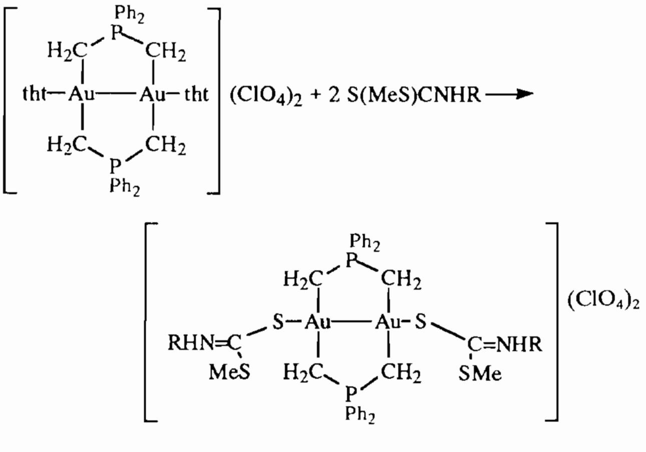
The ^{31}P{^{1}H} NMR spectra show a singlet (**1–4**, **8–10**) or a doublet (**5–7**) for the PPh_2 group. A triplet corresponding to PPh_3 (**5–7**) is also observed because of the coupling to two equivalent PPh_2 groups (see Table 1 and Section 2).

The ^{1}H NMR spectra show the ylide methylene proton resonances as pseudodoublets at ~ 2 ppm for complexes **1–4**, **8–10** and as a pseudodoublet and pseudotriplet for complexes **5–7**. The latter resonate at higher field and are more complicated than the former because of the coupling to PPh_3 ligands. Signals from the dithiocarbamate ligands are also observed (Table 1 and

Table 3
Selected bond lengths (Å) and angles (°) for **8**

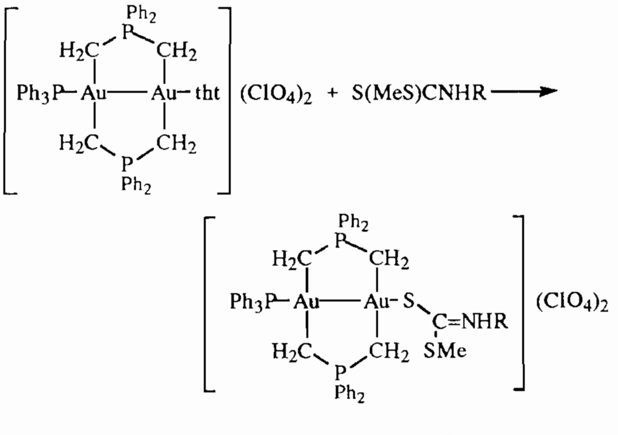
Au(1)–C(2)	2.107(5)	Au(1)–C(1)	2.115(5)
Au(1)–S(1)	2.439(2)	Au(1)–Au(1)#1	2.6585(12)
P(1)–C(2)	1.750(5)	P(1)–C(1)#1	1.754(5)
P(1)–C(11)	1.803(5)	P(1)–C(21)	1.817(6)
S(1)–C(3)	1.753(6)	S(2)–C(3)	1.682(6)
N(1)–C(3)	1.338(7)	N(1)–C(5)	1.463(8)
N(1)–C(4)	1.468(8)	Au(1′)–C(1′)	2.096(6)
Au(1′)–C(2′)	2.099(6)	Au(1′)–S(1′)	2.431(2)
Au(1′)–Au(1′)#2	2.6444(8)	P(1′)–C(2′)	1.747(6)
P(1′)–C(1′)#2	1.758(6)	P(1′)–C(21′)	1.810(6)
P(1′)–C(11′)	1.822(6)	S(1′)–C(3′)	1.731(6)
S(2′)–C(3′)	1.690(6)	N(1′)–C(3′)	1.339(8)
N(1′)–C(4′)	1.449(8)	N(1′)–C(5′)	1.478(9)
C(2)–Au(1)–C(1)	175.8(2)	C(2)–Au(1)–S(1)	86.8(2)
C(1)–Au(1)–S(1)	89.1(2)	C(2)–Au(1)–Au(1)#1	91.15(14)
C(1)–Au(1)–Au(1)#1	93.0(2)	S(1)–Au(1)–Au(1)#1	176.13(4)
C(2)–P(1)–C(1)#1	106.7(3)	C(2)–P(1)–C(11)	111.7(2)
C(1)#1–P(1)–C(11)	110.7(3)	C(2)–P(1)–C(21)	109.8(2)
C(1)#1–P(1)–C(21)	113.2(3)	C(11)–P(1)–C(21)	104.8(2)
C(3)–S(1)–Au(1)	102.6(2)	C(3)–N(1)–C(5)	122.8(5)
C(3)–N(1)–C(4)	121.0(5)	C(5)–N(1)–C(4)	116.0(5)
P(1)#1–C(1)–Au(1)	111.2(3)	P(1)–C(2)–Au(1)	113.0(3)
N(1)–C(3)–S(2)	121.2(4)	N(1)–C(3)–S(1)	117.0(4)
S(2)–C(3)–S(1)	121.8(3)	C(1′)–Au(1′)–C(2′)	173.2(2)
C(1′)–Au(1′)–S(1′)	88.1(2)	C(2′)–Au(1′)–S(1′)	88.2(2)
C(1′)–Au(1′)–Au(1′)#2	91.2(2)	C(2′)–Au(1′)–Au(1′)#2	93.3(2)
S(1′)–Au(1′)–Au(1′)#2	170.93(4)	C(2′)–P(1′)–C(1′)#2	106.9(3)
C(2′)–P(1′)–C(21′)	111.9(3)	C(1′)#2–P(1′)–C(21′)	109.9(3)
C(2′)–P(1′)–C(11′)	111.1(3)	C(1′)#2–P(1′)–C(11′)	112.3(3)
C(21′)–P(1′)–C(11′)	104.9(3)	C(3′)–S(1′)–Au(1′)	100.7(2)
C(3′)–N(1′)–C(4′)	123.8(6)	C(3′)–N(1′)–C(5′)	121.8(6)
C(4′)–N(1′)–C(5′)	114.4(6)	P(1′)#2–C(1′)–Au(1′)	110.3(3)
P(1′)–C(2′)–Au(1′)	111.0(3)	N(1′)–C(3′)–S(2′)	121.1(5)
N(1′)–C(3′)–S(1′)	117.8(5)	S(2′)–C(3′)–S(1′)	121.1(3)

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



R= *p*-MeC$_6$H$_4$ (**1**), *o*-MeC$_6$H$_4$ (**2**), *p*-MeOC$_6$H$_4$ (**3**), 3,5-Me$_2$C$_6$H$_3$ (**4**).

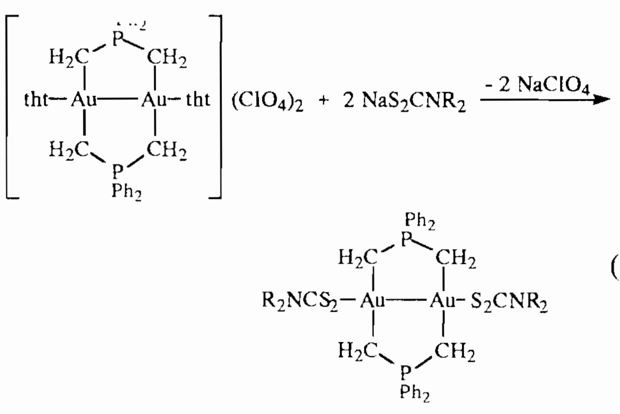
(1)



R= *o*-MeC$_6$H$_4$ (**5**), *p*-MeOC$_6$H$_4$ (**6**), 3,5-Me$_2$C$_6$H$_3$ (**7**).

(2)

Section 2); it is noteworthy that complexes **8**–**10** show a single signal for the alkyl groups of the dithiocarbamate ligand in the ^{1}H NMR spectra even at −90 °C in deuterodichloromethane. In the similar compound [(μ-CH$_2$){Au(μ-CH$_2$PPh$_2$CH$_2$)}$_2$(S$_2$CNMe$_2$)$_2$] the signal of the dithiocarbamate methyl group splits at −55 °C [18]. Therefore, pentacoordination around the gold atoms



(3)

R2= Me2 (**8**), Et2 (**9**), C4H8 (**10**).

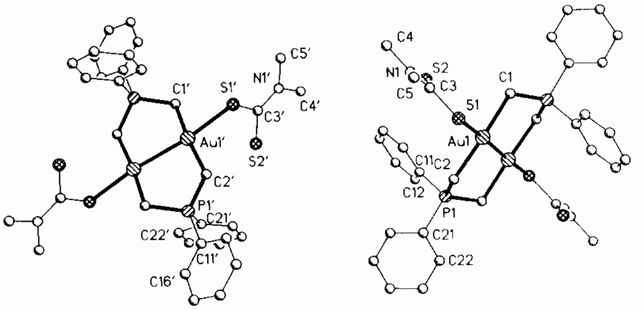


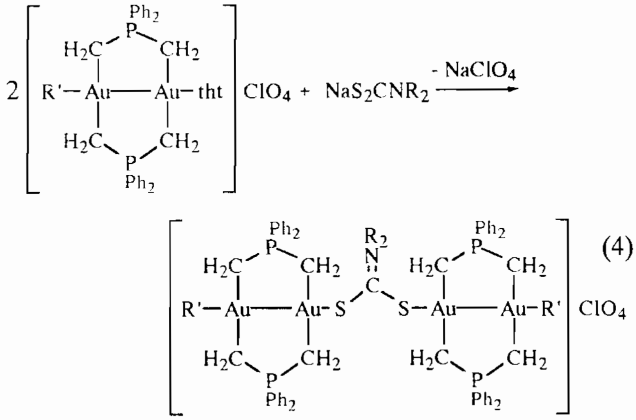
Fig. 1. The two independent molecules of complex **8** in the crystal, showing the numbering scheme of the asymmetric unit. H atoms are omitted.

cannot be rejected; it is known that dithiocarbamates are usually bidentate and only a few gold compounds containing monodentate dithiocarbamates have been reported [18–23]. In order to solve this problem, the structure of $[Au_2(\mu\text{-}CH_2PPh_2CH_2)_2(S_2CNMe_2)_2]$ (**8**) was determined by single-crystal X-ray diffraction study.

The X-ray structure determination of **8** (Fig. 1) shows that the dithiocarbamate ligands are monodentate in the solid state, with non-bonding Au...S2 distances > 3.3 Å; as expected the C–S bond lengths are shorter for the non-coordinated than for the coordinated S atoms (~1.69 and 1.74 Å respectively). There are two independent molecules, each of which lies across a crystallographic inversion centre, thus imparting a chair geometry to the eight-membered rings with the phosphorus atoms 0.8 Å out of the Au_2C_4 plane. The main significant difference between the two molecules is that the gold environment in molecule 2 (primed atoms) is markedly less planar; the mean deviation from the best plane of Au1 and its four neighbours is 0.03 and 0.13 Å for molecules 1 and 2, respectively. If S1' is omitted, the latter deviation decreases to 0.03 Å, since S1' lies 0.55 Å from the Au_2C_4 plane (only 0.13 Å in molecule 1).

The Au–Au bond lengths (2.6585(12), 2.6444(8) Å) are similar to those of other S-bonded Au(II) systems (2.649(9), 2.662(1) [7], 2.651(1) [8] Å); the Au–S bond lengths (2.439, 2.431(1) Å) correspond to the longest Au(II)–S bonds previously observed (2.35–2.43 Å [7,8], but these were all polysulfide species).

In a similar way, by using suitable stoichiometry and starting from dinuclear gold derivatives with only one facile leaving group such as $[Au_2(\mu\text{-}CH_2PPh_2CH_2)_2(R')(tht)](ClO_4)$ ($R' = C_6F_5$ or 2,4,6-$C_6F_3H_2$), tetranuclear complexes with bridging dithiocarbamate can be obtained (Eq. (4)).



(4)

R'= C6F5, R= Me (**11**), Et (**12**), CH2Ph (**13**);
R'= 2,4,6-C6F3H2, R= CH2Ph (**14**).

Complexes **11–14** are brown (**11**), green (**12**, **13**) or red (**14**) solids, air- and moisture-stable at room temperature. They are soluble in dichloromethane, chloroform, slightly soluble in acetone and insoluble in diethyl ether. They behave as 1:1 electrolytes in acetone solution.

The IR spectra show $\nu(Au\text{–}C_{ylide})$ at ~567 cm^{-1}, as in the previous complexes. The ^1H NMR spectra show two doublets for the CH_2–P groups at ~1.90 and 1.40 ppm and a single signal for the dithiocarbamate. Because of the position of the CH_2–P signal in the previous complexes (**8**, **9**), we can assign the signal at 1.90 ppm to the methylene *cis* to the dithiocarbamate. A singlet is observed in the $^{31}P\{^1H\}$ NMR spectra. ^{19}F NMR shows three signals for the C_6F_5 complexes and two for the $C_6F_3H_2$ derivatives, which confirms that the fluorophenyl groups are equivalent (see Table 1 and Section 2).

4. Supplementary material

Full details of the structure determination have been deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany, from where this material can be obtained on quoting the full literature citation and the reference number CSD-400673.

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