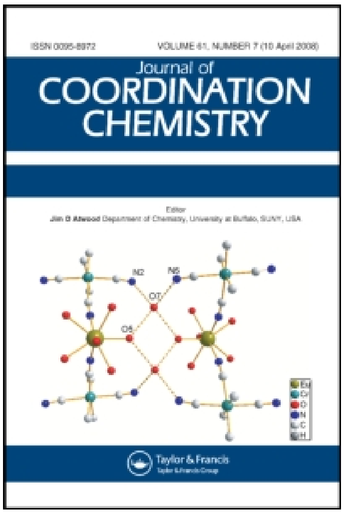

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CHARACTERIZATION OF [μ-BIS(DIPHENYLPHOSPHINO)ALKANE] BIS[*N,N*-DIALKYLDITHIOCARBAMATO)GOLD(I)] COMPLEXES: X-RAY CRYSTAL STRUCTURE OF [$(Ph_2P(CH_2)_2PPh_2)(AuS_2CNEt_2)_2$]

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CHARACTERIZATION OF [μ-BIS(DIPHENYLPHOSPHINO)ALKANE] BIS[*N,N*-DIALKYLDITHIOCARBAMATO)GOLD(I)] COMPLEXES: X-RAY CRYSTAL STRUCTURE OF $[(Ph_2P(CH_2)_2PPh_2)(AuS_2CNEt_2)_2]$

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The preparation and spectroscopic characterization of six compounds of general formula $[(Ph_2P(CH_2)_nPPh_2)(AuS_2CNR_2)_2]$, n = 1, 2 or 3 and R = Et or c-hexyl, is reported. The spectroscopic data suggests monodentate modes of coordination for the dithiocarbamate ligands and this has been confirmed by a crystal structure determination of one derivative, namely $[(Ph_2P(CH_2)_2PPh_2)(AuS_2CNEt_2)_2]$ (**1**). The phosphine ligand in **1** adopts the extended *trans*-conformation with the Au atoms existing in linear P-Au-S geometries. Crystals of **1** are triclinic, space group $P\bar{1}$ with a = 14.327(5), b = 14.411(5), c = 10.084(2)Å, α = 93.76(2), β = 104.16(2), γ = 107.53(3)° and Z = 2; the structure was refined by a full-matrix least-squares procedure to final R = 0.038 for 4898 reflections with $I \geq 3.0\sigma(I)$.

KEYWORDS: Gold(I), phosphine, dithiocarbamate, X-ray structure

INTRODUCTION

The chemistry of gold phosphine complexes is of interest owing to the medicinal applications of certain derivatives such as the monomeric gold(I) complex, (1-thio-β-*D*-gluco-pyranose 2,3,4,6-tetraacetato-*S*)(triethylphosphine)gold(I) (Auranofin), an anti-arthritic drug.[1] Auranofin also shows some anti-tumour activity [2,3] but it is the gold(I) phosphine complex $[Au(Ph_2P(CH_2)_2PPh_2)_2]^+$ which was found to be particularly active.[4,5] Continuing our interest in the field[6,7] we have prepared and characterized a series of complexes of general formula $[(Ph_2P(CH_2)_nPPh_2)(AuS_2CNR_2)_2]$, n = 1, 2 or 3 and R′ = Et or c-hexyl, and these results are reported herein.

Phosphinegold(I) dithiocarbamate complexes have been reported in the literature. Particularly relevant to the present contribution are the preparations of $[Ph_3PAu(S_2CNEt_2)]$,[8] $[Ph_3PAu(S_2CNPh_2)]$[9] and $[Et_3PAu(S_2CNEt_2)]$[10] and the crystal structure determination of the former.[11] The $[(Ph_2P(CH_2)_2PPh_2)(AuS_2CNEt_2)_2]$ complex has been examined for anti-tumour activity;[12] however, to our knowledge, no details of its characterization have been reported.

EXPERIMENTAL

Instrumentation

IR spectra were measured on a Perkin Elmer 1720X FT spectrometer in KBr discs. NMR spectra were recorded in $CDCl_3$ solutions on an ACP300 (^1H NMR at 300.13 MHz and ^{13}C NMR at 75.47 MHz) spectrometer, the internal reference was $SiMe_4$ in both cases. ^{31}P NMR spectra were recorded on a Bruker CXP-300 spectrometer. The solvent used was $CHCl_3$ and the spectra were recorded at 121.5 MHz with H_3PO_4/HCl (*ca* 0.01:0.1 *c/c*) molar solution in D_2O as external reference. FAB mass spectra were obtained, with the assistance of T. Blumenthal, on a VG ZAB 2HF instrument equipped with a FAB source. Argon was used as the exciting gas with the source pressure typically 10^{-6} mbar; the FAB voltage was 7 kV and the current 1 mA. The ion accelerating potential was 8 kV and the matrix employed was 3-nitrobenzylalcohol. The complexes were made up as *ca.* 0.5 mol dm^{-3} solutions in CH_2Cl_2; a drop was added to a drop of the matrix and the mixture was applied to the FAB probe tip.

Preparations

The $[(Ph_2P(CH_2)_nPPh_2)(AuCl)_2]$ starting materials were prepared according to the literature method.[13] The dithiocarbamate ligand $K[S_2CN(c\text{-hexyl})_2]$ was prepared by the reaction of CS_2, c-hexyl$_2$NH and KOH in tetrahydrofuran solution as per the standard procedure and $Na[S_2CNEt_2].3H_2O$ was obtained commercially (Strem). All solvents were of analytical grade and used without further purification.

The six $[(Ph_2P(CH_2)_nPPh_2)(AuS_2CNR_2)_2]$ complexes, n = 1, 2 or 3 and R′ = Et or c-hexyl, were prepared following a similar procedure described below for $[(Ph_2P(CH_2)_2PPh_2(AuS_2CNEt_2)_2]$ (**1**). $[(Ph_2P(CH_2)_2PPh_2)(AuCl)_2]$ (0.030 mmol, 0.25 g) was dissolved in CH_2Cl_2 (50 cm^3) to which was added dropwise an aqueous solution of $Na[S_2CNEt_2].3H_2O$ (0.60 mmol, 0.13g) over a 30 min. period. The transparent solution immediately turned yellow indicating the formation of the product and was stirred for 3 h, after which the aqueous phase was decanted off. The organic phase was dried over magnesium sulphate and its volume reduced *in vacuo*. The product **1** was recrystallized from a CH_2Cl_2 solution of the compound. Table 1 lists physical and analytical data for all complexes.

Crystallography

Pale yellow crystals of **1** were grown by the vapour diffusion of ethanol into a chloroform solution of the compound held under reduced pressure. The crystals were plate-like and the crystal chosen for the X-ray study was triangular with an approximate width of 0.05 mm and with each of the three edges being *ca* 0.25 mm long.

Intensity data were collected at room temperature on a Rigaku AFC6R diffractometer fitted with graphite-monochromatized MoKα radiation; λ = 0.71073 Å ($2\theta_{max}$55.0°, ω:2θ scan technique). The data set was corrected for Lorentz and polarization effects and an empirical absorption correction was applied (DIFABS[14]) such that the range of transmission coefficients was 0.929 to 1.057. A total of 4898

Table 1 Physical and microanalytical data for $[(Ph_2P(CH_2)_nPPh_2)(AuS_2CNR_2)_2]$.

Compound	Physical state	Yield (%)	M.pt. (°C)	C(%)[a]	H(%)
1$[(Ph_2P(CH_2)PPh_2)(AuS_2CNEt_2)_2]$	yellow solid	60	139–140	37.90 (38.03)	3.86 (3.76)
2$[(Ph_2P(CH_2)PPh_2)(AuS_2CNc\text{-}hexyl_2)_2]$	yellow solid	63	180–181	50.03 (49.76)	5.23 (5.21)
3$[(Ph_2P(CH_2)_2PPh_2)(AuS_2CNEt_2)_2]$	brown solid	78	215–216	36.32 (36.22)	3.73 (3.65)
4$[(Ph_2P(CH_2)_2PPh_2)(AuS_2CNc\text{-}hexyl_2)_2]$	yellow solid	63	>220 (dec.)	45.21 (44.99)	4.70 (5.19)
5$[(Ph_2P(CH_2)_3PPh_2)(AuS_2CNEt_2)_2]$	brown solid	71	84–84	40.29 (40.62)	4.20 (4.37)
6$[(Ph_2P(CH_2)_3PPh_2)(AuS_2CNc\text{-}hexyl_2)_2]$	yellow solid	60	>205 (dec.)	45.44 (46.48)	5.28 (5.17)

[a] Calculated values in parentheses.

reflections (9437 measured, 9079 unnique) satisfied the $I \geqslant 3.0\sigma(I)$ criterion of observability and were used in the subsequent analysis.

$[(Ph_2P(CH_2)_2PPh_2)(AuS_2CNEt_2)_2]$ (**1**) = $C_{36}H_{44}AuN_2P_2S_4$: M_r = 1088.9, triclinic, $P\bar{1}$, a = 14.327(5), b = 14.411(5), c = 10.084(2) Å, α = 93.76(2), β = 104.16(2), γ = 107.53(3)°, V = 1903(1) Å^3, Z = 2, D_c = 1.900 g cm^{-3}, $F(000)$ = 1052, μ = 80.59 cm^{-1}.

The structure was solved by direct-methods[15] and refined by a full-matrix least-squares procedure based on F.[16] All non-H atoms were refined with anisotropic thermal parameters and H atoms were included in the model at their calculated positions (C-H 0.97Å). The refinement was continued until convergence when R = 0.038 and R_w 0.038 for sigma weights.[16] The analysis of variance showed no special features and the maximum residual electron peak in the final difference map was 1.71 eÅ^{-3}. Scattering factors for all atoms were those incorporated in the teXsan package[16] installed on a Silicon Graphics Indigo computer system. Fractional atomic coordinates are listed in Table 2 and the numbering scheme employed is shown in Figure 1 which was drawn with ORTEP[17] at 30% probability ellipsoids. Listings of thermal parameters, H atom parameters, all bond distances and angles, and structure factor amplitudes are available on request from ERTT.

RESULTS AND DISCUSSION

A series of $[(Ph_2P(CH_2)_nPPh_2)(AuS_2CNR_2)_2]$ complexes, n = 1, 2 or 3 and R′ = Et or c-hexyl, has been prepared, characterized spectroscopically and in the case of a $[(Ph_2P(CH_2)_2PPh_2)(AuS_2CNEt_2)_2]$ (**1**), crystallographically. The complexes are air-stable solids and are soluble in common organic solvents.

Important infrared bands for the complexes are listed in Table 3, namely those assigned to ν(C–N) and ν(C–S). The ν(C–N) bonds occur in the region 1474-1483 cm^{-1} and are shifted by up to 15 cm^{-1} compared with the free ligands, thus indicating a greater bond order for the C–N bonds in the complexes. The presence of two bands in the 948–1074 cm^{-1} region suggest the presence of monodentate dithiocarbamate ligands.[-18]

The ^{1}H spectra (Table 4) are consistent with the formulation of the complexes as

Table 2 Fractional atomic coordinates for $[(Ph_2P(CH_2)_nPPh_2)(AuS_2CNEt_2)_2]$ (**1**).

Atom	*x*	*y*	*z*
Au(1)	0.63440(3)	0.07630(3)	0.26930(4)
Au(2)	0.37593(3)	0.49678(3)	0.25014(4)
S(11)	0.7957(2)	0.1247(2)	0.2391(3)
S(12)	0.8111(2)	0.1512(2)	0.5375(3)
S(21)	0.2229(2)	0.4440(3)	0.3037(3)
S(22)	0.1933(3)	0.4021(3)	0.0052(3)
P(11)	0.4740(2)	0.0115(2)	0.2771(2)
P(21)	0.5315(2)	0.5507(2)	0.2216(2)
N(11)	0.9662(7)	0.1638(6)	0.4354(8)
N(21)	0.0453(7)	0.3765(7)	0.1239(11)
C(11)	0.8683(8)	0.1485(7)	0.4131(10)
C(12)	1.0152(8)	0.1540(9)	0.3278(11)
C(13)	1.0175(12)	0.0520(11)	0.2997(15)
C(14)	1.0337(9)	0.1888(10)	0.5768(12)
C(15)	1.0817(11)	0.2932(12)	0.6157(13)
C(21)	0.1440(8)	0.4053(7)	0.1391(11)
C(22)	-0.0274(11)	0.3418(15)	-0.0105(16)
C(23)	-0.0582(12)	0.2341(16)	-0.0476(14)
C(24)	0.0054(10	0.3834(10	0.2417(16)
C(25)	0.0015(15)	0.4851(14)	0.2800(24)
C(111)	0.4640(8)	0.0210(7)	0.4522(9)
C(121)	0.3854(7)	0.0681(7)	0.1900(8)
C(122)	0.4173(8)	0.1691(8)	0.1938(10)
C(123)	0.3483(11)	0.2145(9)	0.1341(12)
C(124)	0.2507(12)	0.1612(11)	0.0732(13)
C(125)	0.2183(10)	0.0639(11)	0.0666(14)
C(126)	0.2855(9)	0.0182(8)	0.1256(12)
C(131)	0.4194(7)	-0.1161(7)	0.2049(8)
C(132)	0.4354(9)	-0.1456(7)	0.0818(10)
C(133)	0.3894(9)	-0.2399(8)	0.0175(10)
C(134)	0.3288(9)	-0.3077(7)	0.0749(11)
C(135)	0.3134(8)	-0.2799(8)	0.1979(11)
C(136)	0.3565(8)	-0.1853(7)	0.2621(9)
C(211)	0.5281(7)	0.5503(6)	0.0414(8)
C(221)	0.6087(7)	0.6739(7)	0.3047(9)
C(222)	0.6395(9)	0.6933(8)	0.4450(10)
C(223)	0.6947(9)	0.7883(10)	0.5121(12)
C(224)	0.7154(9)	0.8619(9)	0.4397(15)
C(225)	0.6873(11)	0.8444(9)	0.2990(16)
C(226)	0.6328(10)	0.7493(9)	0.2312(11)
C(231)	0.6050(7)	0.4745(7)	0.2876(8)
C(232)	0.5736(9)	0.4128(8)	0.3800(10)
C(233)	0.6290(11)	0.3550(9)	0.4318(12)
C(234)	0.7110(12)	0.3540(10)	0.3926(14)
C(235)	0.7417(10)	0.4140(12)	0.3039(14)
C(236)	0.6898(9)	0.4740(9)	0.2489(11)

$[(Ph_2P(CH_2)_nPPh_2)(AuS_2CNR_2)_2]$ and the simplicity of the spectra indicates fluxional behaviour under the conditions of the nmr experiment. The ^{13}C nmr data (Table 5) are also remarkable for their simplicity with only one resonance being observed for each chemically equivalent C atom. Notable in the spectra are the resonances due to the quarternary C atoms which have been shifted upfield relative to the free ligands, thus suggesting a decrease in the delocalization of π-electron

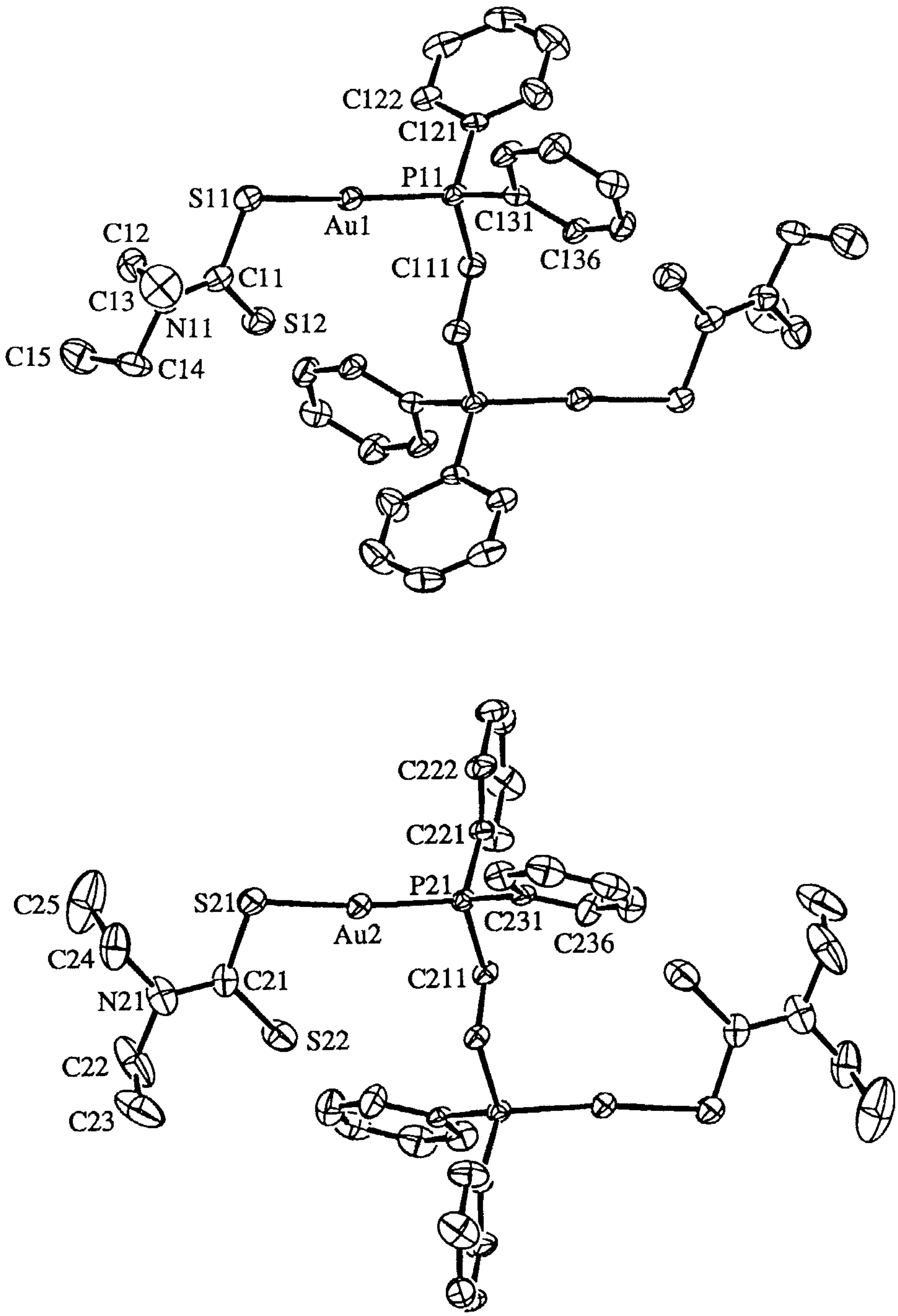

Figure 1 The molecular structure of $[(Ph_2P(CH_2)_2PPh_2)(AuS_2CNEt_2)_2]$ (**1**) showing the crystallographic numbering scheme employed.

Table 3 Infrared data (cm^{-1}) for $[(Ph_2P(CH_2)_nPPh_2)(AuS_2CNR_2)_{22}]$.

Complex	υ(C-N)	υ(C = S)	υ(C-S)
1	1482m	1074 m	984 m
2	1483 sh	1056 m	951 w
3	1484 s	1074 m	987 m
4	1474 s	1058 w	948 w
5	1481 s	1072 m	985 w
6	1481 s	1057 w	965 m

s = strong, sh = shoulder, m = medium, w = weak.

Table 4 ^{1}H nmr data (δ, p.p.m.) for $[(Ph_2P(CH_2)_nPPh_2)(AuS_2CNR_2)_2]$.[a]

Compound	Ha	Hb	H1	H2	H3	H4	phenyl-H
1	212 br		3.95 br,m	1.37 t (6.88)^{b}			7.86–7.19 m
2	2.13 br		n.o.	3.02 br	1.84 br	1.27 br,m	8.05–7.29 m
3	2.87 br		3.95q (7.03)^{b}	1.37 t (7.05)^{b}			7.86–7.44 m
4	2.87 br		n.o.	n.o.	1.80 br	1.24 br	7.75–7.47 m
5	2.92 d (6.50)^{b}	2.02 br	3.92q (6.96)^{b}	1.33 t (7.01)^{b}			7.84–7.40 m
6	2.92 m	2.00 br	4.32 br	2.17 br	1.84 br	1.25 br	7.77–7.43 m

[a] Spectra run in $CDCl_3$ solution relative to TMS as an internal reference. The Ha and Hb atoms refer to the methylene H atoms of the alkyl chain with the Ha atom being closest to the P atom. The H1-H4 atoms are those of the dithiocarbamate ligand with H1 being closest to the N atom; n.o. = not observed; br = broad, s = singlet, d = doublet, t = triplet, q = quartet and m = multiplet. Numbers in parentheses are coupling constants given in Hz. [b] $^2J_{HH}$.

Table 5 ^{13}C nmr data (δ, p.p.m.) for $[(Ph_2P(CH_2)_nPPh_2)(AuS_2CNR_2)_2]$.[a]

Compound	Cq	Ca	Cb	C1	C2	C3	C4	Cα	Cβ	Cγ	Cδ
1	204.4	28.2 d (23.5)^{b}		49.8	12.3			128.9	133.8 d (15.0)^{c}	129.7	131.7
2	n.o.	29.2 d (24.7)^{b}		53.5	31.2	27.7	23.9	128.6 d (8.5)^{b}	135.5 d (10.4)^{c}	129.5	131.0
3	205.7	24.0 t (20.1)^{b,c}		49.3	12.2			129.2 t (11.4)^{b}	133.4 t (7.1)^{c}	129.8	131.6
4	202.8	23.1 t (19.8)^{b,c}		53.3	29.6	26.5	24.8	129.5 t (11.4)^{b}	133.6 t (6.9)^{c}	130.8	132.1
5	205.8	28.3 dd (11.6)^{b} (34.7)^{d}	20.0 s	49.3	12.2			130.5 d (12.0)^{b}	134.2 d (6.2)^{c}	131.9	133.5
6	206.0	28.7 br	20.0 s	53.2	30.2	26.5	24.7	129.0 d (10.8)^{b}	134.0 d (7.0)^{c}	131.3	133.3

[a] Spectra run in $CDCl_3$ solution relative to TMS as internal reference. The numbering scheme is as for Table 4. Numbers in parentheses are coupling constants given in Hz; n.o. = not observed; br = broad, s = singlet, d = doublet, dd = doublet of doublets, t = triplet. [b] $^1J_{PC}$ [c] $^2J_{PC}$ [d] $^3J_{PC}$.

density in the S_2CN chromophore. The ^{31}P spectra for each compound featured one resonance, consistent with molecular symmetry; there were no obvious trends in the ^{31}P chemical shifts with values of δ being 34.9, 28.6, 35.5, 34.7, 29.6 and 31.1 for compounds **1** to **6**, respectively.

The FAB MS results showed ions in both the low and, to a lesser extent, in the high molecular weight regions. In no case was the molecular ion, $[M]^+$, observed. The most abundant fragment in all spectra except for 4, was that corresponding to the $[(Ph_2P(CH_2)_nPPh_2)(Au_2S_2CNR_2)]^+$ ion; in the spectrum of **4** this species had a relative abundance of 75% and the predominant ion was $[(Ph_2P(CH_2)_nPPh_2)(Au_2S)]^+$, *i.e.*, with n = 2. All spectra featured the following ions in addition to the two mentioned above: $[(Ph_2P(CH_2)_nPPh_2)(Au)]^+$ and $[(Ph_2PCH_2)Au)]^+$ and in the high molecular weight region: $[(Ph_2P(CH_2)_nPPh_2)_2(Au_3S)]^+$.

The combined spectroscopic results confirm the stoichiometry of the complexes, suggest a high degree of symmetry, at least in solution, and suggest monodentate coordination for the dithiocarbamate ligand. Unambiguous structure assignment has been afforded by a single-crystal structure analysis of a representative complex, namely $[(Ph_2P(CH_2)_2PPh_2)(AuS_2CNEt_2)_2]$ (**1**).

The molecular structure of $[(Ph_2P(CH_2)_2PPh_2)(AuS_2CNEt_2)_2]$ (**1**) is shown in Figure 1 and selected interatomic parameters are listed in Table 6. There are two molecules in the crystallographic asymmetric unit, each of which is situated about a centre of inversion which bisects the C(111)-C(111)' (or C(211)-C(211)' for molecule 2) bond. This has the consequence that each $[(Ph_2P(CH_2)_nPPh_2)(AuS_2CNEt_2)_2]$ molecule exists in the extended *trans*-conformation. The Au atoms

Table 6 Selected interatomic distances (Å) and bond angles (°) for $[(Ph_2P(CH_2)_2PPh_2)(AuS_2CNEt_2)_2]$ (**1**).

Parameter	molecule n = 1	molecule n = 2
Au-S(n1)	2.307(3)	2.304(3)
Au-P(n1)	2.228(3)	2.226(3)
S(n1)-C(n1)	1.76(1)	1.71(1)
S(n2)-C(n1)	1.66(1)	1.68(1)
P(n1)-C(n11)	1.806(9)	1.806(8)
P(n1)-C(n21)	1.794(9)	1.80(1)
P(n1)-C(n31)	1.790(9)	1.791(9)
N(n1)-C(n1)	1.31(1)	1.31(1)
C(n11)-C(n11)′	1.52(2)	1.50(2)
S(n1)-Au-P(n1)	172.1(1)	174.13(9)
Au-S(n1)-C(n1)	99.4(4)	98.5(4)
Au-P(n1)-C(n11)	111.9(3)	112.0(3)
Au-P(n1)-C(n21)	116.2(3)	116.1(3)
Au-P(n1)-C(n31)	112.6(3)	111.3(3)
C(n11)-P(n1)-C(n21)	103.4(4)	105.1(4)
C(n11)-P(n1)-C(n31)	106.7(4)	106.6(4)
C(n21)-P(n1)-C(n31)	105.1(4)	105.1(4)
S(n1)-C(n1)-S(n2)	119.4(6)	119.8(6)
S(n1)-C(n1)-N(n1)	116.4(7)	117.6(8)
S(n2)-C(n1)-N(n1)	124.2(8)	122.6(9)
C(n1)-N(n1)-C(n2)	124.4(9)	122(1)
C(n1)-N(n1)-C(n4)	120.4(9)	121(1)
C(n2)-N(n1)-C(n4)	115.2(9)	117(1)

exist in essentially the same environments in both molecules and in the following discussion, parameters for the Au(2) atom are given in parentheses.

The Au(1) atom exists in a linear geometry defined by a phosphorus atom of the ($Ph_2P(CH_2)_nPPh_2$) ligand, Au(1)-P(11) 2.228(3)Å (2.226(3) Å) and a sulfur atom derived from a monodentate diethyldithiocarbamate ligand, Au(1)-S(11) 2.307(3) Å (2.304(3) Å). The deviations from ideal linear geometry about the Au(1) atom, *i.e.*, P(11)-Au-S(11) 172.1(1)° (174.13(9)°) may be related to the close approach of the S(12) atom to the Au(1) atom, *i.e.*, 3.083(3) Å (Au(2)...S(22) 3.009(3) Å). The secondary Au...S interactions are significantly less than the sum of the van der Waals radii for these atoms of 3.5 Å;[19] however, then are too long to be considered as bonding interactions. Similar intramolecular contacts have been observed in related complexes. Thus, a weak Au...S interaction of 3.167(6) Å has been found in the structure of [c-$hexyl_3PAuS_2CO$-c-hexyl].[20] Similarly, a weak Au...O contact of 3.066(6) Å has been observed in the structure of [c-$hexyl_3PAuS_2COEt$][21] (compared with the sum of the van der Waals radii for these atoms of 3.20 Å).[19] In addition, a weak Au...N intramolecular contact of 2.951(8) Å has been noted in the structure of [Ph_3PAu(2-pymS)], where 2-pymS is pyrimidine-2-thionate,[7] and which again is shorter than the sum of the van der Waals radii for these atoms (3.25 Å)[19]

Despite the close approach of the S(12) atom to the Au(1) atom, the diethyldithiocarbamate ligand must be considered as coordinating essentially in the monodentate mode. Hence, the S(11)-C(11) distance of 1.76(1) Å is significantly longer than the S(12)-C(11) distance of 1.66(1) Å; the differences between the comparable parameters in the S(21)-C(21)-S(22) moiety, while following the expected trend, are not experimentally distinguishable. The differences between the two independent molecules relate to the relative dispositions of the thiolate ligand to the rest of the molecule, primarily as seen in the P(11)-Au(1)-S(11)-C(11) and P(21)-Au(2)-S(21)-C(21) torsion angles of −129.5(7) and −175(1)°, respectively indicating a significant twist about the Au(1)-S(11) bond. The remaining parameters describing the diethyldithiocarbamate ligand are unexceptionable and are not discussed further. Similarly, the parameters associated with the $Ph_2P(CH_2)_2PPh_2$ ligand are unremarkable.

The structure of **1** may be compared with that of [$Ph_3PAuS_2CNEt_2$][11] which, to a first approximation, adopts essentially the same structure about the Au atom; the Au-P, Au-S and P-Au-S parameters are 2.251(3) Å, 2.338(3) Å and 175.7(1)°, respectively. The Au-P and Au-S bond distances in **1** are significantly shorter than those reported for the [$Ph_3PAuS_2CNEt_2$] complex,[11] a fact which may reflect the reduced steric hindrance in the former complex where a methylene substituent has replaced a phenyl group on the tertiary phosphine ligand.

The crystal structure of **1** is molecular, there being no significant intermolecular contacts in the lattice. The closest intermolecular interaction in the lattice occurs between the C(12) and C(24)^a atoms (symmetry operation a: $1+x$, y, z) at 3.51(2) Å. It is noteworthy that there are no significant Au...Au interactions in the lattice, with the shortest contact of this type occuring between the Au(2) and Au(2)^b atoms (symmetry operation b: $1-x$, $1-y$, $1-z$) at 5.387(1) Å and the shortest contact involving the Au(1) atom is 5.680(1) Å between the Au(1) and Au(1)^c atoms (symmetry operation c: $1-x$, $-y$, $-z$).

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References

1. D.R. Haynes and M.W. Whitehouse, in K.D. Rainsford and G.P. Velo (eds.), *New Developments in Antirheumatic Therapy*, (Kluwer, Dordrecht, 1989, Ch. 8).
2. C.K. Mirabelli, R.K. Johnson, C.M. Sung, K. Muirhead and S.T. Crooke, *Cancer Res.*, **45**, 32 (1985).
3. C.K. Mirabelli, R.K. Johnson, D.T. Hill, L.F. Faucette, G.R. Girard, G.Y. Kuo, C.M. Sung and S.T. Crooke, *J. Med. Chem.*, **29**, 218 (1986).
4. S.J. Berners-Price, C.K. Mirabelli, R.K. Johnson, M.R. Mattern, F.L. McCabe, L.F. Faucette, C.-M. Sung, S.-M. Mong, P.J. Sadler and S.T. Crooke, *Cancer Res.*, **46**, 5486 (1986).
5. S.J. Berners-Price, G.R. Girard, D.T. Hill, B.M. Sutton, P.S. Jarrett, L.F. Faucette, R.K. Johnson, C.K. Mirabelli and P.J. Sadler, *J.Med. Chem.*, **33**, 1386 (1990).
6. P.D. Cookson and E.R.T. Tiekink, *J. Coord. Chem.*, **26**, 313 (1992).
7. P.D. Cookson and E.R.T. Tiekink, *J. Chem. Soc., Dalton Trans.*, 259 (1993).
8. H.C. Brinkhoff, A.G. Matthijssen and C.G. Oomes, *Inorg. Nucl. Chem. Lett.*, **7**, 87 (1971).
9. G.E. Coates, C. Kowala and J.M. Swan. *Aust. J. Chem.*, **19**, 539 (1966).
10. G.L.M. van Gaal, J.W. Diesveld, F.W. Pijpers and J.G.M van der Linden, *Inorg. Chem.*, **18**, 3251 (1979).
11. J.G. Wijnhoven, W.P.J.H. Bosman and P.T. Beurskens, *J. Cryst. Molec. Struct.*, **2**, 7 (1972).
12. C.K. Mirabelli, D.T.Hill, L.F. Faucette, F.L. McCabe, G.R. Girard, D.B. Bryan, B.M. Sutton, J. O'Leary Bartus, S.T. Crooke and R.K. Johnson, *J. Med. Chem.*, **30**, 2181 (1987).
13. A.K. Al-Saády, C.A. McAuliffe, R.V. Parish and J.A. Sandbank, *Inorg. Synth.*, **23**, 191 (1985).
14. N. Walker and D. Stuart, *Acta Cryst.*, **A39**, 158 (1983).
15. G.M. Sheldrick, "SHELXS86. Program for the automatic solution of crystal structure", (Göttingen University, Germany, 1986).
16. TeXsan, Structure Analysis Package, (Molecular Structure Corporation, Texas, 1992).
17. C.K. Johnson, ORTEPII, *Report 5138, Oak-Ridge National Laboratory*, Tennessee (1976).
18 F. Bonati and R. Ugo, *J. Organomet. Chem.*, **10**, 257 (1967).
19. A. Bondi, *J. Phys. Chem.*, **68**, 441 (1964).
20. G. Siasios and E.R.T., Tiekink, *Z. Kristallogr.* **204**, 95 (1993).
21. G. Siasios and E.R.T. Tiekink, *Z. Kristallogr.* **205**, 261 (1993).