Dimethylgold(III) Complexes.
Synthesis of Several Compounds with AuC_2S_2 Coordination.
The Crystal and Molecular Structure of $[(CH_3)_2AuSC_2H_5]_2$*

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Abstract

The synthesis and characterization of several new dimethylgold(III) complexes are reported along with the X-ray crystal structure of $[(CH_3)_2AuSC_2H_5]_2$. The latter compound crystallizes in a triclinic space group $P\bar{1}$, $a = 6.193(1)$ Å, $b = 7.852(1)$ Å, $c = 14.614(3)$ Å, $\alpha = 92.36(1)°$, $\beta = 93.99(2)°$, $\gamma = 92.19(1)°$, $Z = 2$ with $V = 707.88(23)$ Å^3. This dimer shows a *syn*-endo $Au_2(SR)_2$ rhombus with a $141.3°$ dihedral angle. Refinement gave $R = 0.078$ with a Au$\cdots$Au distance of $3.457(3)$ Å. General procedures are reported for the synthesis of dithioate complexes of $(CH_3)_2Au^{III}$.

New compounds reported are: $(CH_3)_2AuS_2$-$P(CH_3)_2$; $(CH_3)_2AuS_2P(OC_2H_5)_2$; $(CH_3)_2AuS_2P(C_6$-$H_5)(OC_2H_5)$; $(CH_3)_2Au[CH_3C(S)CH(S)OC_2H_5]$; $(CH_3)_2AuS_2COC_2H_5$; $(CH_3)_2AuS_2CC_6H_5$; $(CH_3)_2$-$Au[(CH_3)_2P(S)NP(S)(CH_3)_2]$; $[(C_2H_5)_4N][(CH_3)_2$-$AuS_2C_2(CN)_2]$.

Introduction

Interest in organogold compounds has recently [1–7] increased substantially. In addition to the recognition of their potential importance as anti-arthritis pharmaceuticals and as precursors to laser induced microcircuit formation, the stability of the gold–carbon bond allows study of these compounds as models for d^8 transition-metal catalysis. The monomeric trimethyl and dimethyl gold complexes with the formulation $(CH_3)_3AuL$, and the dimers $[(CH_3)_2AuX]_2$ (L = phosphine, X = halide) respectively, have attracted special attention [8]. Attempts in our laboratories to synthesize $(CH_3)_2AuS_2CSC_2H_5$ have resulted in the formation of the dimer $[(CH_3)_2$-$AuSC_2H_5]_2$. This result is consistent with previous work [9–11] which shows that many metal-thioxanthate complexes readily decompose in solution to metal-mercaptides (eqn. 1):
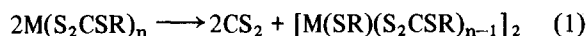
$$2M(S_2CSR)_n \longrightarrow 2CS_2 + [M(SR)(S_2CSR)_{n-1}]_2 \quad (1)$$

Variable temperature ^{1}H NMR studies [12] of

$[(CH_3)_2AuSC_2H_5]_2$ and its reaction with triphenyl-phosphine [13] reveal some unusual features. In order to understand the nature of the factors influencing M–M bonding [11] and the structural behavior in solution of $[(CH_3)_2AuSC_2H_5)]_2$, we have undertaken the X-ray crystal structure determination of this complex.

In addition, we report here the synthesis and characterization of several new dithioate complexes of the type $(CH_3)_2AuY$ (Y = dithioate).

Experimental

Chemicals were used as received, unless otherwise indicated. Metallic gold was obtained from I. Miller, Inc. (Cleveland, Ohio) and the purity was 99.999%.

Physical Measurements

Nuclear magnetic resonance measurements were obtained on Varian A60A and XL-100-V15 spectrometers. Temperature regulation was done with the aid of a Varian V-6040 Variable Temperature Controller. The probe temperature was calibrated with ethylene glycol and methanol. For ^{1}H and ^{13}C studies in CDCl$_3$, TMS was used as internal standard. All chemical shifts are reported on the δ scale.

Infrared spectra were recorded on a Beckman IR-3 spectrometer having a range of 625–4000 cm^{-1}. The spectra were obtained from KBr pellets (if solids) or from neat liquids sandwiched between NaCl plates. Calibration was checked with a polystyrene film. Solution molecular weights were determined using a Mechrolab Vapor Phase Osmometer calibrated with benzil.

X-ray photoelectron spectra were obtained using a Varian IEE spectrometer equipped with a high intensity anode and with a 620/L computer. Spectrometer base pressures were $\sim 5 \times 10^{-7}$ torr, rising to $\sim 10^{-6}$ torr with the X-ray source on. Samples were studied as finely ground powders dusted on the cellulose tape which was wrapped around gold cylinders. Melting points were determined on a laboratory device Mel-Temp melting point block and are recorded uncorrected. Spectral resolution was done by a duPont 310 curve resolver.

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The X-ray data, 3450 reflections, $2\theta \leqslant 55°$, were obtained using a Syntex P2$_1$ diffractometer, at room temperature. Centering 15 well-defined reflections gave cell constants: $a = 6.193(1)$ Å, $b = 7.852(1)$ Å and $c = 14.614(3)$ Å, $\alpha = 92.36(1)°$, $\beta = 93.99(2)°$, $\gamma = 92.19(1)°$. Refinement established the triclinic space group $P\bar{1}$, $Z = 2$ with $V = 707.88(23)$ Å^3. Although $\mu = 215.65$ cm^{-1} for monochromatized MoKα radiation, no absorption corrections were made for the crystal having dimensions 0.10 × 0.10 × 0.15 mm. With 1752 reflections having $I/\sigma(I) > 3.0$, anisotropic refinement for Au and S with isotropic refinement for C gave a $R = 0.105$. Excluding h = 0, 6 and 7 layers due to excessive absorption and secondary extinctions (Table VI), $R = 0.078$, $R_w = 0.085$ with no changes in the positional parameters.

Preparation of Compounds and Complexes

Dimethylgold Iodide

Metallic gold (10 g) was dissolved in *aqua regia*. Evaporation of the volatile acids took place by heating in a mineral oil bath at 120 °C. Heating was continued for 3 hours and the H$_2$O and HCl were evaporated leaving the gold trichloride as a brown material. The gold trichloride was dissolved in water and pyridine was added with stirring. Pyridine-gold(III) trichloride was obtained as a yellow precipitate [13] which was dried under vacuum (m.p. 226–227 °C), yield 82%. This was dissolved by heating in anhydrous pyridine and cooled in a freezing mixture (ice + NaCl). To the cold suspension of dipyridine-dichlorogold(III) chloride thus obtained, methyl magnesium iodide prepared from magnesium (3.4 g), methyl iodide (20 g) and ether (100 ml) was slowly added. Throughout these operations and for 10 minutes thereafter, vigorous stirring was maintained. Water was added, followed by heptane and concentrated HCl. The heptane layer was separated and treated with ethylenediamine until no further precipitate [dimethylgold(III) ethylenediamine iodide] was produced. This was extracted with water. The aqueous solution was acidified with dilute hydrochloric acid and the white precipitate separated and dried under vacuum over phosphoric oxide (yield 5.3 g, 26%). Dimethylgold iodide is a light-sensitive material. This material is stored in the refrigerator in the dark, and recrystallized prior to use from petroleum ether.

Dimethyl(N,N-dimethyldithiocarbamato)gold(III)

To a suspension of sodium N,N-dimethyldithiocarbamate (0.12 g in 20 ml of THF), dimethylgold-(III) iodide (0.3 g in 5 ml THF) was added with stirring. After filtration a yellow solution was obtained. The yellow residue remaining upon vacuum evaporation was extracted with CH$_2$Cl$_2$. Upon cooling at −20 °C yellow crystals were obtained. M.p. 161–163 °C, yield 86%.

The ^{1}H and ^{13}C NMR spectra data are given in Tables I and II, respectively.

Sodium dimethyldithiophosphinate [14]

Tetramethyldithiodiphosphite [(CH$_3$)$_2$P̈–P̈-(CH$_3$)$_2$], 5 g, was mixed with 7 g of sodium sulfide and 6.3 g of sulfur in a three-necked flask equipped with an N$_2$ inlet, a stirrer and a reflux condenser. Dioxane was added (plus a ml of water per 100 ml of dioxane) and the mixture was refluxed for 22 hours. The hot solution was filtered. After cooling the solution, precipitation took place. Recrystallization from wet hot dioxane gave white crystals, m.p. 153–156 °C.

Dimethyl(dimethyldithiophosphinato)gold(III)

To a suspension of sodium dimethyldithiophosphinate (0.2 g in 30 ml THF), dimethylgold(III) iodide (0.45 g in 10 ml THF) was added with stirring. After filtration, vacuum evaporation produced a white residue which was purified chromatographically (ethanol on silica gel). M.p. 48–50 °C. ^{1}H and ^{13}C NMR spectral data are given in Tables I and II, respectively. The product is a white crystalline material with a characteristic pungent odor. It is air stable. The IR bands are shown in Table III. It is soluble in most organic solvents. Yield 80%. *Anal.* Calcd. for C$_4$H$_{12}$PS$_2$Au: C, 13.44; H, 3.36; S, 17.93. Found: C, 13.40; H, 3.37; S, 18.10.

Potassium ethyldithiophosphate [15]

To 4 g of powdered phosphorus pentasulfide suspended in 20 cc of benzene and heated to 65–80 °C, ethanol (3.2 g) was added over a period of 1½ hours with enough heating to hold the reaction mixture at reflux. Refluxing was continued for two hours, during which time the reaction temperature rose to 90–100 °C. After cooling to 0°, an alcoholic solution of potassium hydroxide was added until the solution was alkaline. The product was then precipitated by adding ether. After recrystallization from warm dioxane, white crystals were obtained, yield 82%.

Dimethyl(ethyldithiophosphate)gold(III)

To a suspension of potassium ethyldithiophosphate (0.316 g in 30 ml THF), dimethylgold(III) iodide (0.5 g in 10 ml THF) was added with stirring. After filtration and removal of the excess solvent under vacuum, a yellow oily material was obtained. ^{1}H and ^{13}C NMR are given in Tables I and II, respectively. The material is air stable but produces a pungent odor. The IR absorption frequencies of the spectrum given are in Table IV. It is soluble in most organic solvents. Yield 78%. *Anal.* Calcd. for C$_6$H$_{16}$O$_2$PS$_2$Au: C, 17.52; H, 3.89. Found: C, 17.49; H, 3.92.

TABLE I. ^{1}H NMR Spectra of Organogold Dithiolate Complexes.

	CH_3-Au^b	$O-CH_2-$	$N-CH_3$	$N-CH_2-$	$C-CH_3$	$S-CH_2-$	$P-CH_3$	C_6H_5	$-CH-$
1. $(CH_3)_2AuS_2CN(CH_3)_2$	1.00		3.19						
2. $(CH_3)_2AuS_2COC_2H_5$	1.18	4.67			1.52				
3. $(CH_3)_2AuS_2CC_6H_5$	1.22								
4. $[(CH_3)_2AuS_2C_2(CN)_2]N(C_2H_5)_4$	0.88			3.28	1.32				
5. $(CH_3)_2AuS_2P(CH_3)_2$	1.04						2.01 $^2J = 13$ Hz		
6. $(CH_3)_2AuS_2P(C_6H_5)(OC_2H_5)$	1.16	4.32 $^3J = 3.1$ Hz			1.44			7.51	
7. $(CH_3)_2AuS_2P(OC_2H_5)_2$	1.18	4.23 $^3J = 2.9$ Hz			1.42				
8. $[(CH_3)_2AuSC_2H_5]_2$	0.94				1.43	3.07			
9. $(CH_3)_2AuS_2P_2(CH_3)_4N^c$	1.08						1.85 $^2J = 12$ Hz		
10. $(CH_3)_2Au(C_2H_5-O-SacSac)^d$	0.97 1.14	4.49			2.47			7.54 8.09	6.88

^{a}Using $CDCl_3$ as a solvent and solutions of 0.5 *M*. ^{b}Chemical shifts in δ units. $^c-S_2P_2(CH_3)_4N$ = tetramethyldithioimidodiphosphinate. $^d-C_2H_5O-SacSac$ = o-ethylthio-acetothioacetate.

Dimethylgold(III) Complexes

TABLE II. ^{13}C NMR Spectra of Organogold Dithiolate Complexes.

	CH_3-Au^b	$O-CH_2-$	$N-CH_3$	$N-CH_2-$	$S-CH_2-$	$P-CH_3$	$C-CH_3$	C_6H_5
1. $(CH_3)_2AuS_2CN(CH_3)_2$	5.50		40.28					
2. $(CH_3)_2AuS_2COC_2H_5$	5.87	69.52					13.69	
3. $(CH_3)_2AuS_2CC_6H_5$	7.87							125.0 127.77 128.17 138.41
4. $(C_2H_5)_4N[(CH_3)_2AuS_2C_2(CN)_2]$	4.54			60.01			7.94	
5. $(CH_3)_2AuS_2P(CH_3)_2$	12.14					31.51 $^2J = 4.7$ Hz		
6. $(CH_3)_2AuS_2P(C_6H_5)(OC_2H_5)$	9.76	62.64 $^3J = 0.7$ Hz					16.11 $^4J = 1$ Hz	128.01 128.73 129.04 131.94
7. $(CH_3)_2AuS_2P(OC_2H_5)_2$	8.33	64.28 $^3J = 0.4$ Hz					15.79 $^4J = 0.8$ Hz	
8. $[(CH_3)_2AuSC_2H_5]_2$	12.02				23.13	20.19		
9. $(CH_3)_2AuS_2P_2(CH_3)_4N$	14.07				25.60 $^2J = 7.8$ Hz			
10. $(CH_3)_2Au[CH_3C(S)CHC(S)OC_2H_5]$	10.07 10.49	67.99					39.48	

^{a}Using CDCl$_3$ as a solvent and solutions of 1 M. ^{b}Chemical shifts in ppm from TMS.

TABLE III. Binding Energies of Some Organogold Dithiolate Complexes.

Compound	Au$_{4f_{7/2}}$	S$_{2p_{3/2}}$	Reference
	85.5	162.8	This work
	85.9	162.9	This work
KAuCl$_4$	87.59		41
Au°	83		This work
		164.5	28
		166.5	28

Sodium phenyl-O-ethyl-dithiophosphonate [16]

This salt was prepared by reaction of phenyl-phosphonothionic dichloride and sodium sulfhydrate in absolute ethanol. White crystals were obtained.

Dimethyl(phenyl-O-ethyl-dithiophosphonato)gold (III)

To a suspension of sodium phenyl-O-ethyl-dithiophosphonate (0.24 g in 20 ml THF), dimethylgold-(III) iodide (0.32 g in 10 ml THF) was added with stirring. After filtration and removal of the excess solvent under vacuum, a yellow oil was obtained. The ^{1}H and ^{13}C NMR spectral data are given in Tables I and II, respectively. Yield 70%. The material is an air-stable complex with a characteristic pungent odor. The IR bands are shown in Table III. It is soluble in most organic solvents. *Anal.* Calcd. for C$_{10}$H$_{16}$OPS$_2$Au: C, 27.09; H, 3.61; S, 14.45. Found: C, 27.27; H, 3.64; S, 14.63.

O-ethylthioacetothioacetate

O-ethyl iminoacetate [17] hydrochloride (5 g) was suspended in 50 ml pyridine. H$_2$S was passed through the mixture for 24 hours while stirring and cooling in an ice bath. The solution turned yellow. To this solution 50 g of ice was added, followed by 30 ml dilute hydrochloric acid. The mixture was extracted with ether (2 X 5 ml). The ether solution was dried over CaCl$_2$ for 2 hours. Evaporation of the ether left a pale yellow air-sensitive residue which was distilled at 110–110.5 °C. Yield 77%. The O-ethylthioacetate obtained (3 g) was added to a suspension of sodium hydride (0.35 g) in ether and the mixture was stirred for 48 hours at room temperature. The reaction mixture then was added to 20 ml of water and extracted with ethyl ether. The ether extracts were dried over anhydrous sodium sulfate for 4 hours. Evaporation of the ether took place and the pure O-ethylthioacetothioacetate was obtained after distillation as an orange material. Yield 57%.

TABLE IV. Infrared Spectra of Organogold Dithiolate Complexes.

Compound	Absorption Frequencies (cm^{-1})
(CH$_3$)$_2$AuS$_2$CC$_6$H$_5$[a]	2920(w), 1592(m), 1452(m), 1342(w), 1319(w), 1272(vs), 1243(w), 1220(m), 1192(m), 1145(m), 1012(m), 1003(vs), 954(s), 945(w), 778(vs), 770(m), 684(vs), 678(m)
[N(C$_2$H$_5$)$_4$][a][(CH$_3$)$_2$AuS$_2$C$_2$(CN)$_2$]	2990(m), 2915(m), 2212(s), 1485(m), 1470(s), 1440(m), 1415(w), 1395(w), 1220(m), 1195(m), 1178(m), 1155(m), 1120(w), 1050(vw), 1005(s), 870(w), 810(m), 790(m)
[(CH$_3$)$_2$AuSC$_2$H$_5$]$_2$[a]	2980(w), 2905(w), 1450(m), 1440(m), 1379(m), 1260(s), 1220(s), 1195(s), 1062(m), 1035(m), 980(m), 830(w), 805(m), 775(m), 670(m)
(CH$_3$)$_2$AuS$_2$P(CH$_3$)$_2$[a]	2995(w), 2905(w), 1400(mb), 1300(m), 1290(s), 1220(s), 1195(s), 955(vs), 910(s), 860(m), 750(m), 740(vs)
(CH$_3$)$_2$AuS$_2$P(OC$_2$H$_5$)$_2$[b]	2996(m), 2910(m), 1475(vb), 1445(wb), 1395(w), 1226(m), 1196(m), 1165(w), 1045(sh), 1020(vs), 970(s), 825(m), 800(mb)
(CH$_3$)$_2$AuS$_2$P(OC$_2$H$_5$)(C$_6$H$_5$)[b]	2995(w), 2907(w), 1440(w), 1227(w), 1193(w), 1120(m), 1027(sb), 947(sb), 790(wb), 750(m), 730(m), 695(w), 675(w)
(CH$_3$)$_2$Au[CH$_3$C(S)CHC(S)OC$_2$H$_5$]	2995(s), 2912(s), 1510(sh), 1503(s), 1475(w), 1440(w), 1392(m), 1367(w), 1330(sh), 1310(s), 1197(sb), 1155(m), 1090(w), 1030(wb), 1010(m), 900(m), 830(m), 805(wb), 695(s)
(CH$_3$)$_2$AuS$_2$P$_2$(CH$_3$)$_4$N[a]	2995(w), 2910(w), 1410(wb), 1302(m), 1290(m), 1200(s), 1185(s), 980(w), 947(s), 910(w), 878(w), 850(vw), 760(w), 723(m), 695(s)

[a]KBr discs. [b]Net liquids in NaCl plates. vw = very weak, w = weak, wb = weak broad, m = medium, mb = medium broad, s = strong, sb = strong broad, vs = very strong, sh = shoulder.

Dimethyl(O-ethylthioacetothioacetate)gold(III)

Sodium hydride (0.08 g) was suspended in DMSO (5 ml) and the mixture was cooled until some small amount of DMSO (m.p. 16 °C) solidified. O-ethylthioacetothioacetate (0.362 g) was added to the suspension slowly with stirring. After 10 minutes dimethylgold(III) iodide (0.7 g in 10 ml THF) was added with continuation of stirring. The solution obtained was evaporated in vacuum and a brown-black residue was extracted with pentane. Evaporation of the pentane took place and the residue was purified chromatographically (ethanol on silica gel). The product was a brown material, m.p. 35–37 °C. ^{1}H and ^{13}C NMR spectral data are given in Tables I and II, respectively. The material is an air-stable reddish solid. The IR absorption frequencies of the IR spectral are given in Table IV. It is soluble in most organic solvents. Yield 70%. *Anal.* Calcd. for $C_8H_{15}OS_2Au$: C, 24.8; H, 3.87. Found: C, 24.66; H, 4.00.

Sodium tetramethyldithioimidodiphosphinate [18]

An ether solution of $(CH_3)_2P(S)NH_2$ (1 g) was cooled to 0 °C and dropped into an ether suspension of $(CH_3)_2P(S)(Br)$ (0.63 g) and NaOBut (1.34 g). The mixture was stirred for 30 minutes, then 1 ml concentrated HCl was added. Vacuum evaporation produced a residue which was recrystallized from hot water. The tetramethyldithioimidodiphosphinate obtained was treated with an equimolar amount of CH_3ONa in methanol and this formed sodium tetramethyldithioimidodiphosphinate which was crystallized upon the addition of ether.

Dimethyl(tetramethyldithioimidodiphosphinate)-gold(III)

To a suspension of sodium tetramethyldithio-imidodiphosphinate (0.42 g in 30 ml THF), dimethyl-gold iodide was added with stirring. After filtration, evaporation under vacuum produced a white residue which was purified chromatographically (ethanol on silica gel). Yield 82%, a white solid with a m.p. 88–90 °C. The ^{1}H and ^{13}C NMR spectral data are given in Tables I and II, respectively. It is an air-stable complex. The IR absorption frequencies of the spectrum are given in Table IV. It is soluble in most organic solvents. *Anal.* Calcd. for $C_6H_{18}NP_2S_2Au$: C, 16.9; H, 4.22; S, 15.01. Found: C, 17.0; H, 4.40; S, 15.11.

Tetraethylammonium cyanodithioformate [19]

To 49 g of sodium cyanide, 30 ml of dimethyl-formamide were added with stirring. After 10 minutes of stirring, carbon disulfide (7.6 g) was added. The sodium cyanodithioformate dimethyl-formamide complex obtained was recrystallized from ether. To a solution of the sodium cyanodithio-formate DMF complex (3.86 g) in boiling ethanol,

tetraethylammonium bromide (2.31 g) in boiling ethanol was added with stirring. The dark solid which recrystallized on cooling the mixture to 0 °C was removed by filtration and recrystallized from ethanol.

Tetraethylammonium dimethyl(1,2-dicyanoethyl-ene-1,2-dithiolate)gold(III)

To a solution of tetramethylammonium cyano-dithioformate (0.4 g in 30 ml of THF), dimethyl-gold(III) iodide (0.3 g in 10 ml THF) was added with stirring. A yellow precipitate was obtained which was identified as sulfur. After evaporation of the solvent in vacuum, the remaining yellow-orange material was recrystallized from chloroform/ether. Conductivity measurements showed that the complex is a 1:1 electrolyte. The ^{1}H and ^{13}C NMR spectral data are given in Tables I and II, respectively. It is a yellow, air-stable solid, m.p. 94–97 °C, soluble in polar solvents. The absorption frequencies of the IR spectrum are given in Table IV. Molecular weight determination showed that the complex is monomeric. *Anal.* Calcd. for $C_{10}H_{16}N_3S_2Au$: C, 33.87; H, 5.24; Found: C, 33.96, H, 5.28.

Tetramethyl(di-μ-ethylmercapto)digold(III)

Ethanethiol (1 ml excess) was added to a suspension of sodium hydride (0.08 g in THF) at 0 °C under nitrogen. A white suspension of the mercaptide salt was formed. To this suspension, dimethyl-gold(III) iodide (0.4 g in 10 ml THF) was added with stirring. After filtration and evaporation of the solvent under vacuum, a white residue remained which was purified chromatographically (ethanol on silica gel). A molecular weight determination suggested the dimer formation. The ^{1}H and ^{13}C NMR spectral data are given in Tables I and II, respectively. The compound is a white, air-stable solid [29], m.p. 48–50 °C, soluble in most organic solvents. The IR absorption frequencies of the spectrum are given in Table IV. *Anal.* Calcd. for $C_8H_{22}S_2Au_2$: C, 16.72; H, 3.83; S, 11.15. Found: C, 16.86; H, 3.87; S, 11.07.

Sodium ethyltrithiocarbonate solution

Ethanethiol (1 ml excess) was added to a suspension of sodium hydride (0.08 g in THF) at 0 °C under nitrogen. A white suspension of the mercaptide salt was formed and carbon disulfide (3 ml) was added dropwise. A yellow solution of the ligand was obtained.

Reaction of sodium ethyltrithiocarbonate with dimethylgold(III) iodide

To the above solution, dimethylgold(III) iodide (0.4 g in 10 ml THF) was added with stirring. After filtration, evaporation of the solvent resulted in a white residue which was purified chromatographi-

cally (ethanol on silica gel). This compound was identified by ^{1}H, ^{13}C NMR and IR spectroscopy as di-(μ-ethylmercapto)tetramethyldigold(III).

Sodium dithiobenzoate [21]

Two ml of CS_2 was added to a Grignard solution made up of 4 g of chlorobenzene and 0.7 g of magnesium in 50 ml of anhydrous ethyl ether. After cooling followed by 12 hr of standing at room temperature, the mixture was decomposed with ice and aqueous HCl. Dithiobenzoic acid was extracted with ethyl ether and shaken with an aqueous solution containing a stoichiometric amount of Na_2CO_3. The sodium dithiobenzoate formed was isolated from the aqueous layer by vacuum evaporation.

Dimethyl(dithiobenzoato)gold(III)

To a suspension of sodium dithiobenzoate (0.25 g in 20 ml THF), dimethylgold(III) iodide (0.4 g in 10 ml THF) was added with stirring. After filtration and removal of the excess solvent under vacuum, the orange residue was purified chromatographically (C_2H_5OH on silica gel). M.p. 92-94 "C. The ^{1}H and ^{13}NMR spectral data are given in Tables I and II, respectively. Yield 73%. Orange-red powder, very soluble in organic solvents. It is an air-stable complex. the IR absorption frequencies are given in Table IV. **Anal.** Calcd. for $C_9H_{11}S_2Au$: C, 28.43; H, 2.90. Found: C, 29.03; H, 3.2.

Reactions of *dimethylgold(III)dithiolates* with phosphines

$(CH_3)_2AuS(C_2H_5)P(CH_3)_2C_6H_5$. To a 2 ml solution of di(μ-ethylmercapto)tetramethyldigold(III)

(0.3 *M* in CDCl$_3$), 2 ml of a solution of dimethylphenylphosphine (0.3 *M* in CDCl$_3$) was added. The ^{1}H NMR spectrum of the adduct is given in Table IV.

Using the same method, the dimethyl(N,N-dimethyldithiocarbamato)gold(III) dimethylphenylphosphine, dimethyl(ethyldithiophosphato)gold(III) dimethylphenylphosphine, and dimethyl(O-ethylxanthato)gold(III)dimethylphenylphosphine adducts were prepared. The ^{1}H NMR chemical shifts of the adducts are given in Table V.

ESCA Studies of Organogold Dithiolates

ESCA (Electron Spectroscopy for Chemical Analyses) has been recognized as a powerful technique for obtaining new insight into structural and bonding problems in organometallic chemistry [22,23]. A well-established relationship exists between core-level bonding energy (En) with the formal oxidation of the metal. An increase of the positive charge on the atom produces an increase of the binding energies for the core level. Table III gives the binding energies of the $Au_{4f_{7/2}}$ and $S_{2p_{3/2}}$ levels for two different organogold dithiolates and the gold and sulfur binding energies of some reference complexes for comparison.

X-Ray Structure

Intensities were measured on the Syntex P2$_1$ diffractometer, with graphite-monochromatic MoKα radiation ($\lambda = 0.71069$ A). The $\theta-2\theta$ scan mode with stationary background count was used to collect data. 3253 data ($2\theta \leqslant 55$") were collected of which 1752 data had I/u(I) $\geqslant$ 3.0. The atoms

TABLE V. ^{1}H NMR Spectra of the Phosphine **Adducts.**^{d}

Adducts^a	CH$_3$–Au^b	–CH$_2$–	C–CH$_3$	P–CH$_3$	N–CH$_3$	C$_6$H$_5$
$(CH_3)_2AuS(C_2H_5)P(CH_3)_2C_6H_5$	*cis* 0.6 $^3J_{P-H} = 9^c$ *trans* 0.93 $^3J_{P-H} = 9.2$	2.83(9)	1.25(t)	1.8 $^2J_{P-H} = 10.2$		
$(CH_3)_2AuS_2P(OC_2H_5)_2P(CH_3)_2C_6H_5$	*cis* 0.95 $^3J_{P-H} = 9$ *tram* 1.25 $^3J_{P-H} = 9.5$	4.25(9)	1.34(t)	2.0 $^2J_{P-H} = 10.5$		1.1
$(CH_3)_2AuS_2COC_2H_5 \cdot P(CH_3)_2C_6H_5$	*cis* 0.9 $^3J_{P-H} = 8.8$ *trans* 1.21 $^3J_{P-H} = 9$	4.49(9)	1.4(t)	1.99 $^2J_{P-H} = 10.5$		1.6
$(CH_3)_2AuS_2CN(CH_3)_2 \cdot P(CH_3)_2C_6H_5$	*cis* 0.85 $^3J_{P-H} = 9$ *trans* 1.95 $^3J_{P-H} = 9.3$			2.02 $^2J_{P-H} = 10.3$	3.48	7.6

^{a}Using CDCl$_3$ as a solvent. ^{b}Chemical shifts in 6 units. ʿCoupling constants in Hz. ^{d}All spectra were taken at -40 °C.

were located by direct methods (MULTAN) which was consistent with the Patterson result. The isotropic refinement resulted in $R = 0.158$ and $R_w = 0.197$. The anisotropic refinement of 2 Au and 2 S and isotropic refinement of 8 C resulted in $R = 0.104$ and $R_w = 0.090$. Final refinement gave $R = 0.078$, $R_w = 0.085$ (see Table VI). The atomic scattering factors for neutral atoms were taken from Cromer and Waber [24]. The atomic position and thermal parameters are presented in Table VII, and the resulting bond distances and angles in Table VIII. Figure 1 shows the structure of the molecule.

TABLE VI. Summary of Refinement.

	Data Used	Weighting Scheme	R*	R_w**
1.	1752	$w_i = [2^* scale^* |F^2|/\sigma(I)]^2$	0.116	0.146
2.[a]	1752	$w_i = \dfrac{1}{[R \times G_i(F)]^2}$	0.104	0.090
3.[b]	1752	$w_i = \dfrac{1}{[G_i(F)]^2}$	0.105	0.133
4.[c]	1396	$w_i = \dfrac{1}{[G_i(F)]^2}$	0.078	0.085

$$*R = \Sigma \| F_o | - |F_c \| / \Sigma | F_o |$$

$$**R_w = \left\{ w(|F_o| - |F_c|)^2 / \Sigma w |F_o|^2 \right\}^{1/2}$$

[a] A check on agreement factors (based on refinement 1) as function of fixed h, k, 1, $\sin\theta/\lambda$ and F_o revealed that the h = 0, 6 and 7 layers had the high R values $R = 0.239, 0.188$ and 0.347 respectively. The weighting scheme was modified to $w_i = 1/[R \times G_i(F)]^2$ (the R was normalized before use, they are 3.9, 1.90, 1.70, 1.39, 1.0, 1.2, 3.1 and 5.63 for h = 0, 1, 2, 3, 4, 5, 6, and 7 layers). The refinement 2 shows significant improvement on refinement 1. [b] The structural results of refinement 3 are identical with refinement 3. [c] The result of AGREE analysis and the unit cell packing diagram suggest that the h = 0, 6 and 7 layers have the absorption and secondary extinction problems. Due to the sites, Au atoms are very closed to bc plane (see Fig. 2). Excluding these three layers, the refinement results in the $R = 0.078$ and $R_w = 0.085$. The structural results are identical with refinement 2 and 3.

Results and Discussion

The M_2S_2 rhombus

Structural studies of species containing the M_2S_2 rhombus have focused [25] on complexes of Fe(III), Co(III), Ni(II), Pd(II) and Pt(II). The structure reported here of $[(CH_3)_2AuSC_2H_5]_2$ is the first known Au_2S_2 moiety with a *syn*–endo configuration. In the related Ni_2S_2 complexes [11] some

TABLE VII. Positional Parameters, Thermal Parameters and Estimated Standard Deviations of $[(CH_3)_2AuSC_2H_5]_2$.[a]

Atom	x	y	z	β_{11} or B	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Au¹	0.0560(2)	0.1663(2)	0.2419(1)	0.0174(5)	0.01624(4)	0.0066(2)	0.0033(2)	0.0009(2)	0.0000(2)
Au²	-0.2233(2)	0.5350(2)	0.2724(1)	0.191(5)	0.0133(3)	0.0073(2)	0.0011(2)	0.00072(2)	0.0008(2)
S1	-0.0142(13)	0.4136(14)	0.1534(8)	0.0203(27)	0.0179(22)	0.0059(7)	-0.0007(16)	0.00259(7)	0.0020(10)
S2	0.143(13)	0.3689(13)	0.3672(8)	0.0174(25)	0.0148(20)	0.0054(7)	-0.0005(15)	-0.0011(8)	0.0001(19)
C1	0.1011(63)	-0.0039(60)	0.1277(35)	5.4(10)					
C2	0.1137(61)	0.0419(62)	0.3269(34)	5.2(9)					
C3	-0.4150(69)	0.6981(71)	0.1897(40)	6.1(11)					
C4	-0.3916(66)	0.6266(67)	0.3813(37)	5.4(10)					
C5	-0.2096(74)	0.3614(74)	0.0510(41)	6.4(12)					
C6	-0.3973(66)	0.2430(67)	0.0854(37)	6.2(10)					
C7	-0.1449(69)	0.2686(70)	0.4532(39)	6.5(11)					
C8	-0.3623(67)	0.1711(68)	0.4035(38)	6.1(10)					

[a] The form of the thermal ellipsoid is: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.
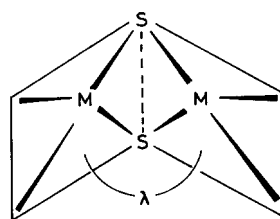
TABLE VIII. Significant Intramolecular Bond Distances and Angles of $[(CH_3)_2AuSC_2H_5]_2$.

Bond	Length (A)	Angles	Values	Nonbond	Length (A)
Au1–S1	2.414(11)	Au1–S1–Au2	91.2(5)	Au1···Au2	3.457(2)
Au2–S1	2.425(11)	Au1–S2–Au2	91.7(5)	C1···C2	2.935(72)
Au1–S2	2.410(11)	S1–Au1–S2	81.6(5)	C3···C4	2.875(80)
Au2–S2	2.408(10)	S1–Au2–S2	81.4(5)	C1···S1	3.393(48)
Au1 -Cl	2.136(49)	S1–Au1–Cl	96.2(16)	C2···S2	3.344(49)
Au1–C2	2.120(50)	C1–Au1–C2	87.2(21)	S1···S2	3.152(16)
Au2–C3	2.134(53)	S2–Au1–C2	94.9(16)	C3···S1	3.456(51)
Au2–C4	2.082(51)	S1–Au2–C3	98.4(19)	C4···S2	3.299(48)
S1–C5	1.879(54)	S2–Au2–C4	94.3(18)		
C5 –C6	1.583(71)	C3–Au2–C4	85.9(24)		
S2–C7	1.835(55)	Au1–S1–C5	111.9(21)		
C7-C8	1.633(63)	Au2–S2–C5	106.6(21)		
		S1–C5–C6	106.5(34)		
		Au1–S2-C7	109.6(20)		
		Au2–S2–C7	108.4(20)		
		S2–C7–C8	110.1(33)		
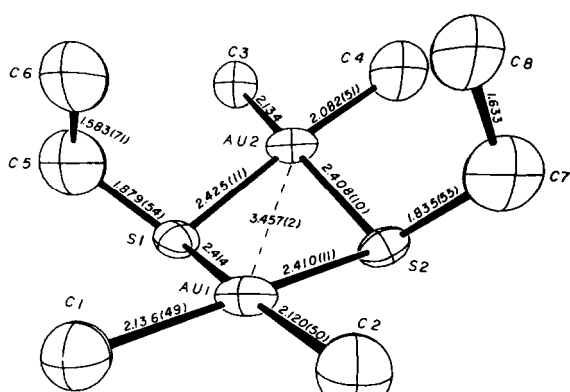
Fig. 1. ORTEP thermal ellipsoid view (50% probability) and numbering scheme of $[(CH_3)_2AuSC_2H_5]_2$.

M···M interaction is suggested. However, the present structure has a long Au···Au distance of 3.457(3) A, 0.56 A longer than the Au···Au distance in metallic gold [2]. Structural studies [26] of [Au-$(CH_2)_2P(CH_3)_2]_2$ and $[AuI(CH_2)_2P(CH_3)_2]_2$ show Au···Au distances of 3.005 and 2.660 Å respectively, the latter indicating a strong metal-metal bond. On going from the d^{10} to the d^9 system, a metal-metal bond is formed. In isoelectronic d^8 complexes, Au(III), Ni(II), Pd(II), and Pt(II), only the Ni(II) complexes have a small dihedral angle between the NiS$_2$ planes, the λ hinge angle [25a], I, suggesting some M···M interaction.

The M···M distance ratio between the different complexes is about the same as the ratio of λ angles (see Table IX). An increase in the M-S-M angle is proportional to the opening up of the λ angle. The ratios of the M···M distances (Au···Au/ Pd···Pd = 1.05) and the M-S bond distances (Au-S/ Pd-S = 1.04) indicate that increasing the M-S dis-

tance causes the increased M···M distance. This observation leads us to conclude that three structural features influence the M···M distance: (1) the hinge angle λ which is related to the M-S-M angle, (2) the M-S distance, and (3) the S···S distance. In these d^8–d^8 systems then, all three factors must be considered when attempting to deduce M···M bonding from structural observations.

Solution Studies

Tobias[30] has pointed out that many organogold-(III) complexes undergo inter- or intramolecular exchanges in solution. For example, by mixing $[(CH_3)_2AuI]_2$ with $[(CH_3)_2AuCl]_2$, an exchange of the halides has been observed. Dimethyl[2,4-pentanedionato] gold(III)[31] has been found to show exchange between bound and free acetylacetone. Organogold(III) 1,1-dithiolates do not appear to exchange ligands on the NMR time scale. ^{1}H NMR resonances of the spectrum are sharp at all temperatures.

Reaction of dimethylgold(III) iodide with sodium ethyltrithiocarbonate produces. di-μ-ethylmercapto-bis-dimethyldigold(III) (eqn. 2).

This compound also was obtained by reacting sodium ethylmercaptide with dimethylgold iodide. Although thioxanthate complexes of copper(II) with tertiary phosphines as stabilizing ligands have been

TABLE IX. Comparison of Some Distances and Angles in Hinged M_2S_2 Moiety.

(a)

	M···M Distance (Å)	M-S Bond Dist	S···S Distance	Dihedral Angle (deg.)	M-S-M Angle	S-M-S Angle	Stereochemistry	Ref.
1. [(CH₃)₂AuSC₂H₅]₂	3.457(3)	2.418	3.158(25)	141.3	91.3(8)	81.5(8)	*Syn*–endo	This work
2. Pd₂[S₂CN(S₂H₅)₂]₂[S₂CS(CH₃)₂]₂	3.288(2)	2.326(3)	3.060(4)	139.5	90.0(2)	82.3(2)	*Syn*–endo	28
3. Pd₂[SC(CH₃)₂]₂[S₂CS(CH₃)₂]₂	3.162(1)	2.320(3)	3.088(5)	131.8	85.9(1)	83.4(1)	*Anti*	10a
4. Ni₂(CSCH₂C₆H₅)₂(S₂CSCH₂C₆H₅)₂	2.795(3)	2.188(4)	2.862	114.3	79.5	81.7	Syn –Endo	10a
5. Ni₂(SC₂H₅)₂(S₂CSC₂H₅)₂	2.763	2.183	2.84		78.4	81.6	*Syn*–Endo	27

(b)

The Ratio of Bond Distance and Angle Between Different Metal Complexes

	M···M / M···M	M-S / M-S	S···S / S···S	λ / λ	M-S-M / M-S-M	S-M-S / S-M-S
Au (1) / Pd (2)	1.05	1.04	1.03	1.01	1.01	0.99
Au (1) / Pd (3)	1.09	1.04	1.02	1.07	1.06	0.98
Pd (2) / Pd (3)	1.04	1.00	0.99	1.06	1.05	0.99
Pdᵃ(2) / Ni*	1.18	1.06	1.07	1.22	1.14	1.01
Pdᵃ(3) / Ni*	1.14	1.06	1.08	1.15	1.08	1.02

ᵃThe data of Ni* uses the average data of compounds 4 and 5. The numbers in parentheses refers to the compounds in (a).
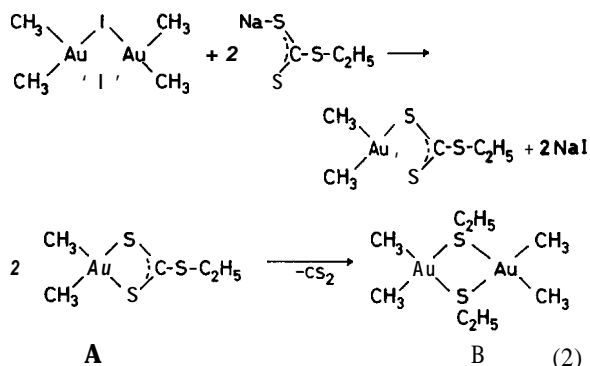
reported, metal thioxanthate complexes generally are unstable. In the case of $Co(III), Fe(III), Ni(II),$ and $Pd(II)$ the complexes lose CS_2 to form mercaptide-bridged dimers [9,32] and trimers. The CS_2 elimination from dimethyl(thioxanthato)gold(III) takes place (reaction 2) rapidly also.

For $(CH_3)_4Au_2(SC_2H_5)_2$ various stereochemistries might be expected, particularly in solution. However, the ^1H NMR spectrum of this complex does not change over in the temperature range $40°$ to -70 °C.

Although metal complexes of cyanodithioformamate are known [33], the reaction of tetraethylammonium cyanodithioformate with dimethylgold(III) iodide produces tetraethylammonium dimethyl-(1,2-dicyanoethylene-1,2-dithiolate)gold(III).

The ^1H and ^{13}C NMR shielding and coupling constants obtained from the spectra of organogold dithiolates are summarized in Tables I and II. Because chemical shifts and coupling constants are solvent and concentration dependent, all ^1H and ^{13}C NMR have been obtained in the same solvent $(CDCl_3)$ and concentration. An examination of the ^1H chemical shifts of the methyl-gold protons in the series of organogold dithiolates suggests the following:

For complexes of the general formula $(CH_3)_2$-AuS_2C-X where $X = -N(CH_3)_2$ [1]; $-OC_2H_5$ [2]; $-C_6H_5$[3], the ^1H chemical shifts of CH_3-Au follow the order: shielding of $1 > 2 > 3$.

It is well known that derivatives of dithioacids show contributions of valence bond structures A, B and C.
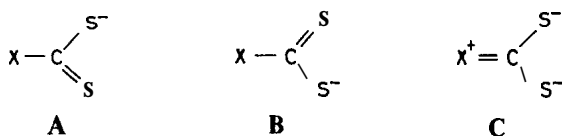
The contribution of the various valence bond structures depend on the X group. The special feature of structure (C) is that additional n-electron density flows from the X-group to the carbon atoms via delocalized π-orbitals.

ESCA studies have been carried out for $(CH_3)_2$-$AuS_2CN(CH_3)_2$ and $(CH_3)_2AuS_2COC_6H_5,$ to obtain information about the distribution of electron density around the Au and S atoms. The data reveal a pronounced influence of the ligand on the $Au_{4f_{7/2}}$ binding energies. The difference is of the order of 0.4 eV, large enough to distinguish the different electron donor property of the ligands. The $Au_{4f_{7/2}}$ binding energy of dimethyl(N,N-dimethyldithiocarbamato)gold(III) implies a marked increase of electron density on the metal relative to dimethyl(dithiobenzoato)gold(III). The ESCA results thus correlate with ^1H chemical shifts.

Furlani *et* al. [21] have found the following relative d-orbital splittings of the sulfur ligands in the spectrochemical series: $R_2NCS_2^- < ROCS_2^- < R-CS_2^-$. This suggests that the S $\rightarrow$ M n-interaction with the tilled d orbitals on the M is greater in the dithiocarbamate complexes than in the xanthates or dithiocarboxylates. The net increase of electron density on the metal atom in the dithiocarbamates produces the shifts observed in ^1H NMR chemical and ESCA studies. Also the ^{13}C NMR chemical shifts follow the order: ^{13}C shielding of $1 > 2 > 3$ (see Table II).

The ^1H chemical shielding of dimethyl(1,2-dicyano-ethylene-1,2-dithiolate)gold(III) (Table I) is the highest in the entire series of methylgold dithiolates studied. In the ligand (1,2-dicyanoethylene-1,2-dithiolate) the mesomeric shift is essentially complete in this anionic complex. The ^{13}C shielding of gold-methyl carbon also is the highest of the series.

For complexes of the general formula $(CH_3)_2$-AuS_2PXY, the order of ^1H shielding of methyl-gold protons follows the order: ^1H shielding of $X=Y=$ $CH_3 > X=C_6H_5, Y=OC_2H_5 > X=Y=OC_2H_5.$ It is known that the relative position, in the spectrochemical series is [34]; $(CH_3)_2PS_2^- < (C_6H_5)(C_2-H_5O)PS_2^- < (C_2H_5O)_2PS_2^-$. It is also known [34] that the relative positions in the nephelauxetic series are: $(CH_3)_2PS_2^- < C_6H_5(C_2H_5O)PS_2^- < (C_2H_5O)-PS_2^-$. The ^1H NMR chemical shifts obtained for $(CH_3)_2AuS_2P(CH_3)_2,$ $(CH_3)_2AuS_2P(OC_2H_5)C_6H_5$ and $(CH_3)_2AuS_2P(OC_2H_5)_2$ are consistent with the ligand order in the spectrochemical and nephelauxetic series.

The interaction of $(CH_3)_2PC_6H_5$ with the organogold(III) dithiolates has been demonstrated by the changes in the NMR spectra of these complexes upon addition of the phosphine. In all cases the ^1H NMR spectra indicate that the phosphine is bonded to the gold center.The phosphorus methyl coupling constant of the methyl group on the. phosphine has been changed from 3 Hz in the uncomplexed phosphine to 11 Hz in the complex, typical of a tetrahedral phosphorus. The assignment of cis and *trans* methyl groups to the coordinated phosphine was based on the trimethyltriphenylphosphinegold(III) complex

[8]. From the proton NMR relative intensities, the downfield doublet was assigned as due to the methyl group *trans* to phosphine and the upfield doublet *cis* to phosphine.

By adding $(CH_3)_2PC_6H_5$ to a $CDCl_3$ solution of bis(dimethyl)di-(μ-ethylmercapto)digold(III), the cleavage of the mercapto bridge was achieved (eqn. 3).

$$(3)$$
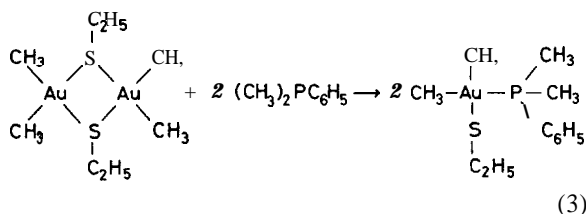
The proton NMR spectrum consists of a quartet ($-CH_2$), triplet ($-CH_3$), a multiplet for p-C_6H_5 and three doublets with relative intensities of 1: 1:2. The positions are given in Table V. This pattern confirms the formation of a *cis* dialkyl planar arrangement of the ligands at the gold center. The doublets observed are easily assigned to the *tram, cis* CH_3Au groups and the $(CH_3)_2PC_6H_5$ ligand. The difference in the δ value (0.4 ppm) between *cis* and *trans*-CH_3Au groups is due to the *trans* effect of the phosphine.

Cleavage of mercapto bridges are known for palladium complexes [35]. With dimethylgold(lll), studies have been carried out [36] involving cleavage of thiocyanato, cyanato, selenocyanato bridges with tertiary phosphines, pyridine and triphenylarsine. The difference observed here with the mercapto bridge is that cleavage occurs only with the very basic tertiary phosphines $(C_2H_5)_3P, (CH_3)_3P, (CH_3)_2$-$PC_6H_5$.

By adding excess dimethylphenylphosphine (fivefold) to the phosphine adduct, the proton NMR spectrum is unaffected. The ^1H NMR signals are sharp even at $+60\,°C$ (the upper limit of thermal stability for the compound in solution). The ligand exchange between $(CH_3)_2Au(SC_2H_5)[-P(CH_3)_2$-$C_6H_5]$ and the excess phosphine thus appears to be slow on the NMR time scale.

Slow phosphine exchange is in agreement with the studies of Schmidbaur *et al.* [37], who on the basis of ^1H NMR spectroscopy of a $(CH_3)_3AuP(C_6H_5)_3$ solution containing free phosphine, pointed out that no exchange or at least very slow exchange takes place.

The situation is different for gold(l) complexes. It has been found that $CH_3AuP(C_6H_5)_3$ and free phosphine exchange at a fast rate [37]. The difference in reaction rates for gold(l) and gold(III) complexes has been explained by the difference in the Au-P bond. In gold(III) complexes the Au-P interaction is stronger than in gold(l) complexes. In the exchange studies of $CH_3AuP(C_6H_5)_3$ with

free phosphine, it was observed that small amounts of phosphine (10^{-3}–10^{-2} *M* in phosphine per M of the complex), leads to the loss of the $^3J_{^1HCAu^{31}P}$ coupling but the $^2J_{^1HC^{31}P}$ is unaffected. Further addition of free phosphine affects the $^2J_{^1HC^{31}P}$, and when the complex and the free ligand are present in the molar ratio 1:3.4 a sharp singlet with zero $^2J_{^1HC^{31}P}$ coupling is observed. For the systems $(CH_3)_2AuS_2$-$COC_2H_5/(CH_3)_2PC_6H_5$, and $(CH_3)_2AuS_2P(OC_2H_5)_2/$ $(CH_3)_2PC_6H_5$, the loss of the $^3J_{^1HCAu^{31}P}$ coupling only, at high temperatures, is evidence for little phosphine dissociation compared with $(CH_3)_2Au$-$[S_2CN(CH_3)_2]/(CH_3)_2PC_6H_5$ where both $^3J_{^1HCAu^{31}P}$ and $^2J_{^1HC^{31}P}$ coupling are lost. The more labile interaction of phosphine with the alkylgold dithiocarbamate complex, compared with alkylgold xanthates, and alkylgold dithiophosphates, again relates to the increased electron density at the gold center in the case of alkylgold dithiocarbamates and the apparent stability of the $(CH_3)_2AuS_2CN(CH_3)_2$ product.

Similar results have been obtained for the nickel-(II) complexes. With sulfur chelates of nickel(II) such as xanthates and dithiophosphates, adducts with nitrogenous [38] bases are readily formed. In contrast, the dithiocarbamate complexes of nickel(II) interact with nitrogenous bases only at liquid nitrogen temperatures [39].

Supplementary Material Available

Tables of observed and calculated structure factors (8 pages).Ordering information is given on any current masthead page.

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12 The crystal structure of $[(CH_3)_2AuSC_2H_5]_2$ reveals a *syn*–endo configuration. In these M_2S_2 systems, three isomers (*syn*–endo, syn-exo and anti) can be expected. Variable temperature ^1H NMR studies of this gold complex show a spectrum which does not change, however, in the temperature range 40 to -70 °C. This suggests that while there may be an equilibrium between these three isomers, one species dominates throughout this temperature range.

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