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Sulfur-Containing Gold(III) Chelates and Their Use in Heterovalent Dimer Synthesis: Crystal Structures of $Au^{III}[CH_2P(S)Ph_2]_2Br$, $[Au^{III}[S_2P(OH)Ph]_2]Cl$, and $Au^{III}[CH_2P(S)Ph_2][S_2CN(Et)_2]_2$†

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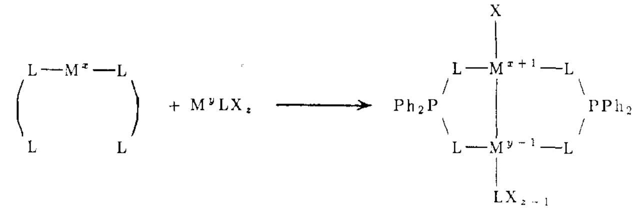
The oxidation of $[PPN][Au(CH_2P(S)Ph_2)_2]$ with Br_2 in CH_2Cl_2 gives the neutral Au^{III} complex $Au[CH_2P(S)Ph_2]_2Br$ (Au(MTP)$_2$Br), containing one chelating and one dangling $[CH_2P(S)Ph_2]^-$ (MTP) ligand. The sulfur atom of the chelating MTP ligand is trans to the Br. From ^1H NMR studies, the complex in solution is undergoing a dynamic rearrangement on the NMR time scale that exchanges the methylene resonances. The reaction of Au(MTP)$_2$Cl with Au(THT)Cl gives a 2:1 ratio of the heterovalent Au^I/Au^{III} complex C_s-$[Au^IAu^{III}(MTP)_2Cl_2]$ and the homovalent Au^{II}–Au^{II} complex C_i-$[Au(MTP)Cl]_2$. The reaction of Au(THT)Cl with $NaS_2P(OR)Ph$, R = Et and H, in THF gives $[Au[S_2P(OR)Ph]_2]Cl$. The Au^{III} complex with R = OH has been characterized crystallographically; in the solid state both the cis and trans isomers are observed. In solution, via ^1H NMR spectroscopy, cis and trans interconversion is facile. The reaction of tetraethylthiuram disulfide with $[Au(MTP)]_2$ cleaves the dimer giving $Au(MTP)(S_2CN(Et)_2)_2$, a single-center, two-electron-oxidation product, rather than a two-center, two-electron-oxidation product. In this complex the MTP is a dangling ligand, carbon bound to the metal atom. One diethyldithiocarbamate ligand is also dangling with the other chelating. Crystal data for Au(MTP)$_2$Br: $P\bar{1}$ (No. 2), $a = 11.672$ (4) Å, $b = 12.814$ (3) Å, $c = 10.143$ (4) Å, $\alpha = 109.26$ (3)°, $\beta = 110.65$ (3)°, $\gamma = 71.98$ (2)°, $V = 1307.7$ (7) Å^3, $Z = 2$, $R = 0.0700$, $R_w = 0.0732$ for 1738 reflections with $I > 3\sigma(I)$ and 238 parameters. Crystal data for $[Au[S_2P(OH)Ph]_2]Cl$: $C2/c$ (No. 15), $a = 23.736$ (12) Å, $b = 13.807$ (6) Å, $c = 20.555$ (7) Å, $\beta = 104.25$ (3)°, $V = 6558$ (5) Å^3, $Z = 12$, $R = 0.0569$, $R_w = 0.0612$ for 190 parameters with 2551 reflections with $I > 3\sigma(I)$. Crystal data for Au(MTP)(DTC)$_2$: $P\bar{1}$ (No. 2), $a = 11.820$ (1) Å, $b = 14.462$ (2) Å, $c = 10.167$ (2) Å, $\alpha = 104.41$ (1)°, $\beta = 110.90$ (2)°, $\gamma = 102.61$ (2)°, $V = 1479.2$ (6) Å^3, $Z = 2$, $R = 0.038$, $R_w = 0.049$ for 3743 reflections with $I > 3\sigma(I)$ and 289 parameters.

Introduction

Recently we demonstrated[1] that the *metallachelate* (transition-metal-containing chelate) $[PPN][Au(MTP)_2]$ reacts with $^1/_2$ molar equiv of *cis*-$PtCl_2(SEt_2)_2$ in CH_2Cl_2 to give $Au_2Pt(MTP)_4$, a neutral, linear, trinuclear, heterometallic complex. Various dimeric heterometallic complexes have been synthesized by others.[2] Such heteronuclear complexes are of interest as models of various catalytic processes such as the Fischer-Tropsch synthesis.[3] Darensbourg and co-workers[4] have demonstrated that some heterobimetallic systems react in a way that is different from the simple sum of the reaction of the individual metal atoms. Forcing or allowing interactions of one metal center with another has led to substances having unique chemical reactivities.[5] Sinfelt and co-workers[6] have demonstrated an increase in the selectivity of catalytic reactions such as dehydrogenation and isomerization of hydrocarbons when bimetallic heterogeneous systems are employed. Independent coordination of dissimilar components at both metal centers in activated heterometallic dimers also may lead to unique reactivities.[6] In such systems the heterobimetallic complex can serve as a template for facilitating bimolecular reactions.

While studying the utility of the *metallachelate* [PPN][Au(MTP)$_2$] as a starting material in the synthesis of heterometallic complexes, we reacted it in a 1:1 ratio with Au(THT)Cl. We obtained the previously characterized[7] dimeric complex C_i-$[Au(MTP)]_2$ (containing a S-Au-C linkage). This demonstrated that dimer formation was possible; however, it was also apparent that isomerization occured under the conditions used. The reaction of other metal salts, e.g., $CuBr_2$, $NiCl_2(PPh_3)_2$, etc., with [PPN][Au(MTP)$_2$] also gave, among other things, the digold dimer C_i-$[Au(MTP)]_2$.

Scheme I[a]



[a] Key: x and y, formal oxidation states of M; X = halide; L = bidentate ligand.

From preliminary work it became apparent that an important aspect of the chemistry of these systems was the presence of two MTP ligands on one metal center. Therefore, we oxidized the metallachelate anion with Br_2, expecting a Au^{III} complex that still contained the desired two MTP ligands. This Au^{III} complex then could be reacted with Au^I complexes or other easily oxidized complexes to form metal-metal-bonded dimers. As Balch,[8] Shaw,[9] and Maitlis[10] have ably demonstrated, the reaction of organometallic complexes in high oxidation states with metals in low oxidation states can give metal-metal-bonded[3] complexes (Scheme I). Such reactions work best with precursors that undergo facile

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† Abbreviations used: C_i = point group of dimer with center of inversion, C-Au-S linkage; C_s = point group of dimer with a mirror plane through the two gold centers, C-Au-C and S-Au-S linkage; dppm = bis(diphenylphosphino)methane; DTC = S_2C-$N(Et)_2^-$, diethyldithiocarbamate; DTP = $S_2P(OH)Ph^-$, phenyldithiophosphonate; MTP = $CH_2P(S)Ph_2^-$, diphenylmethylphosphine sulfido; PPN = $N(PPh_3)_2^+$, bis(triphenylphosphine)nitrogen(1+) cation; py = pyridine; THF = $O(CH_2)_4$, tetrahydrofuran; THT = $S(CH_2)_4$, tetrahydrothiophene.

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oxidation and reduction. The stability of the newly formed metal–metal-bonded dimers also appears important.

Here we present the full report of the single-crystal X-ray structure determinations of three gold(III) mononuclear complexes with two sulfur-containing chelate ligands. The Cl analogue of one of these complexes, $Au(MTP)_2Cl$, has been used in the synthesis of the heterovalent, noncentrosymmetric Au^I/Au^{III} ylide dimer C_s-$[Au^IAu^{III}(MTP)_2Cl_2]$. These Au^{III} complexes may be useful precursors to heterobimetallic gold-containing dimers. Their complete characterization and comparison with other Au^{III} chelate complexes is necessary to develop this chemistry.

Experimental Section

Synthesis. All solvents were distilled and dried according to standard methods.[11] All reactions were carried out in an atmosphere of argon with the rigorous exclusion of oxygen and water using Schlenk techniques.[12] The complexes Au(THT)Cl, $[Li][CH_2P(S)Ph_2]$, $[PPN][Au(MTP)_2]$ and $[Au(MTP)_2]$ were synthesized according to published procedures.[1,7,13,14] Proton NMR spectra were obtained in $CDCl_3$ at 36 °C at 90 MHz with a Varian EM-390 instrument, Me_4Si internal standard, or with a Varian XL-200 instrument at 20 °C unless otherwise stated. No attempt was made to obtain the sign of the coupling constants.

$[PPN][Au(MTP)_2]$ (1). To 2.0 mmol of $[Li][CH_2(S)PPh_2]$ (0.43 g of $Ph_3P(S)$ and 1.25 mL of 1.6 M MeLi) in dry THF in an inert atmosphere at −10 °C was added 0.32 g (1.0 mmol) of Au(THT)Cl. After 45 min of stirring, the cooling bath was removed and the reaction slowly equilibrated to room temperature. After 1 h the solvent was reduced in vacuo to approximately one-fourth of its original volume. To this was added an equimolar amount of [PPN][Cl] in a dry THF/methanol solution. After 10 min of stirring a white precipitate, **1**, was formed. Cooling of the reaction mixture followed by removal of the THF/LiCl solution gave 0.89 g of **1** (75% yield; ^1H NMR ($CDCl_3$), 22 °C, 200 MHz, $\delta(CH_2)$ 1.516, J_{HP} = 15.1 Hz).

$Au(MTP)_2Br$ (2). To a CH_2Cl_2 solution containing 25 mg (0.02 mmol) of $[PPN][Au(MTP)_2]$ was added 0.5 mL of 0.02 M Br_2 in CH_2Cl_2. The bromine colored solution quickly (~5 min) changed to a yellow solution, which was taken to dryness in vacuo and remained under vacuum for 2 h. The solid remaining behind was triturated with a minimal amount of CH_2Cl_2, filtered, and used in crystallization by allowing diethyl ether to vapor diffuse into the CH_2Cl_2 in a closed system. Red X-ray quality crystals were obtained in this manner: ^1H NMR ($CDCl_3$), 22 °C, 200 MHz, $\delta(CH_2)$ 1.72, broad singlet (unresolved), $w_{1/2}$ = 54 Hz.

$[Au(S_2P(OH)Ph)_2]Cl$ (3). To 0.160 g (0.5 mmol) of AuCl(THT) in 10 mL of THF at −78 °C was added 0.240 g (7.0 mmol) of $NaS_2P(OR)Ph$ (R = Et, H), and the mixture was stirred for 3 h, allowing the solution to reach room temperature very slowly. The solution became yellow with the formation of a white precipitate. The solution was filtered and taken to dryness in vacuo. Single orange crystals, suitable for an X-ray diffraction study, were obtained by dissolving the product in acetone and allowing diethyl ether to slowly diffuse into the acetone solution of the product in a closed system at −25 °C over 3 weeks time.

$Au(MTP)(DTC)_2$ (4). (a) A solution of tetraethylthiuram disulfide, $[S_2CN(Et)_2]_2$ (14 mg, 0.057 mmol), in toluene (~2 mL) was added to a toluene suspension of $[Au(MTP)]_2$ (0.019 g, 0.022 mmol) at ambient temperature. The resulting orange solution intensified to a dark brown over a period of 4 h. Dark red crystals formed after approximately 1 month at −20 °C (22 mg, 0.033 mmol); mp 156 °C. The ^1H NMR spectrum exhibited resonances at δ 4.05 (J = 9 Hz, d), 3.72 ($-CH_2$, J = 7 Hz, q), 3.35 ($-CH_2$, J = 10 Hz, d), and 1.30 ($-CH_3$, J = 6 Hz, t).

(b) A solution of tetraethylthiuram disulfide, $[S_2CN(Et)_2]_2$ (0.08 mg, 0.027 mmol), in toluene (~2 mL) was added to a toluene suspension of $[Au(MTP)]_2$ (0.022 g, 0.026 mmol) at room temperature. An orange solution gradually formed, although a large portion of $[Au(MTP)]_2$ remained undissolved. Approximately 40% of the starting material $[Au(MTP)]_2$ was recovered. The isolated product proved to be identical with the compound obtained above.

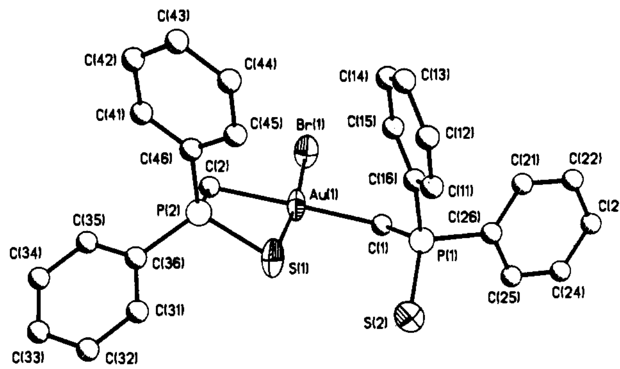

Figure 1. Perspective drawing of $Au(MTP)_2Br$ (**2**) showing the crystallographic numbering scheme. Gold, sulfur and bromine atoms are drawn as ellipsoids of 50% probability, hydrogen atoms are omitted, and carbon and phosphorus atoms are drawn with arbitrary radii for clarity.

C_i-$[Au(MTP)Cl]_2$ (7). To a CH_2Cl_2 solution of C_i-$[Au(MTP)]_2$ (30 mg, 0.035 mmol) was added 9 mg (0.035 mmol) of $PhI{\cdot}Cl_2$. After 30 min of stirring at room temperature, the yellow solution was taken to dryness in vacuo, extracted with CH_2Cl_2, filtered, and crystallized from CH_2Cl_2 via vapor diffusion (ether). Large yellow-orange crystals were obtained and were shown to be C_i-$[Au(MTP)Cl]_2$ by comparison of the unit cell constants with a crystallographically characterized sample. The ^1H NMR spectra taken of similarly shaped and colored crystals gave δ 7.8–7.6 (m, Ph) and 3.014 (d, J = 8.8 Hz, $Au-CH_2-P$).

Collection and Reduction of X-ray Data for $Au(MTP)_2Br$, $[Au(S_2P(OH)Ph)_2]Cl$, and $Au(MTP)(DTC)_2$. The structures of both neutral complexes, **2** and **4**, and the cationic dithiophosphonate complex **3** reported here were determined from intensity data collected at room temperature by using single, well-formed crystals. Complexes **2** and **4** were sealed inside 0.5-mm glass capillaries, while **3** was mounted atop a glass fiber in a random orientation. Data collection for **2**–**4** was carried out on a Nicolet R3m/E automated diffractometer, with the ω scanning technique in bisecting geometry (all data collected with graphite-monochromated Mo Kα radiation). Triclinic symmetry was suggested for **2** and **4** on the basis of interaxial angles and confirmed by using a Delaunay reduction procedure. Complex **3** was monoclinic and confirmed similarly. The axial lengths for **2**–**4** were verified by measuring the interlayer spacing observed in axial photographs, and refined cell parameters were obtained from the setting angles of high-angle reflections. The data were corrected for standard decay, absorption, and Lorentz and polarization effects. Absorption corrections were estimated empirically on the basis of azimuthal scans of medium-intensity reflections spanning a range of 2θ values. Crystal data and details of the crystallographic experimental parameters for the three Au^{III} complexes **2**–**4** are summarized in Table I.

Structural Solution and Refinement. For **2** and **3** all solutions and final refinements were carried out by using the SHELXTL crystallographic software package installed on a Data General Eclipse S140 minicomputer. The solution and refinement of **4** was carried out with the Enraf-Nonius structure determination package (VAXSDP) installed on a VAX-11/780 computer and allowed for full-matrix least-squares refinement. In all cases, the initial Au atom coordinates were determined from the Patterson function listing. From the refinements and difference Fourier listings all non-hydrogen atom coordinates were determined and subsequently refined. All of the non-hydrogen atoms of **2** and **4** as well as all the non-hydrogen or non-carbon atoms of **3** were refined anisotropically, with hydrogen atoms in fixed, idealized positions. In order to maintain a favorable data to parameter ratio, phenyl rings in structure **2** and **3** were refined by using rigid-body constraints (C–C distances of 1.395 Å, C–C–C angle of 120°). In each case refinements converged uneventually, giving conventional R indices of 0.070, 0.057, and 0.038 for 2–4, respectively, leaving only chemically insignificant peaks in the electron density map after the final difference Fourier. Selected bond distances and angles for complexes **2**–**4** are given in Tables II–IV, respectively. Refined atomic fractional coordinates and equivalent isotropic temperature factors for **2**–**4** are given in Tables V–VII, respectively.

Crystal and Molecular Structure Description of $Au(MTP)_2Br$ (2). This neutral four-coordinate square-planar complex is formed rather than the anionic four-coordinate complex $[PPN][Au(MTP)_2Br_2]$ that we originally anticipated from our synthesis.

Complex **2** crystallized in the triclinic space group $P\bar{1}$ with one discrete neutral molecule (Z = 2) in the asymmetric unit. The solid-state crystal structure confirms the existence of one chelating and one dangling (carbon bound) MTP ligand at a four-coordinate Au^{III} center (Figure 1). The fourth coordination site on Au is occupied by Br, which is trans to

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Table I. Crystallographic Data for **2–4**

formula	$C_{26}H_{24}AuBrP_2S_2$	$C_{22}H_{28}Au_{1.5}Cl_{1.5}O_4P_4S_6$	$C_{23}H_{32}AuN_2PS_5$
fw	739.434	990.374	726.72
space group	$P\bar{1}$ (No. 2)	$C2/c$ (No. 14)	$P\bar{1}$ (No. 2)
syst absences		hkl, $h + k = 2n + 1$; $h0l$, $l = 2n + 1$	
a, Å	11.672 (4)	23.736 (12)	11.820 (1)
b, Å	12.814 (3)	13.807 (6)	14.462 (2)
c, Å	10.143 (4)	20.557 (8)	10.167 (2)
α, deg	109.26 (3)		104.41 (1)
β, deg	110.65 (3)	104.28 (3)	110.90 (2)
γ, deg	71.98 (2)		102.61 (2)
V, Å^3	1307.7 (7)	6527 (5)	1479.2
Z	2	12	2
d_{calcd}, g/cm^3	1.88	2.015	1.632
cryst size, mm	0.25 × 0.25 × 0.30	0.3 × 0.25 × 0.3	0.3 × 0.3 × 0.3
$F(000)$, e	711.8	3751.3	716.0
μ(Mo Kα), cm^{-1}	74.68	73.9	53.7
radiation (monochromated in Mo Kα (λ_α = 0.71073 Å) incident beam)			
orientation reflcns: no.; range (2θ), deg	23: 17–30	25: 25–30	25: 25–38
temp, °C	22	22	23
scan method	ω	ω	ω
data collcn range (2λ), deg	0–45	0–45	3–55
no. of unique data; tot. with $F_o^2 > 3\sigma(F_o^2)$	2172; 1738	4610; 2851	6715; 3743
check reflcns	3 every 97	3 every 97	3 every 150
no. of params refined	238	190	289
transmissn factors: max; min	0.081; 0.041	0.160; 0.083	1.0; 0.8 (normalized)
R^a	0.070	0.057	0.038
R_w^b	0.073	0.061	0.049
goodness-of-fit indicator^c	1.145	1.385	0.91
largest shift/esd, final cycle	0.027	0.008	0.15
largest peak, e/Å^3	2.5	1.68	1.28
g	0.00386	0.00204	d

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum(w(|F_o|)^{1/2} - |F_c|)]/\sum(w|F_o|^{1/2}$; $w^{-1} = [\sigma^2(|F_o|) + |g|F_o^2]$. [c] Goodness of fit $= [\sum w(|F_o| - |F_c|)^2/(N_o - N_p)]^{1/2}$. [d] $w = [\sigma^2(|F_o|)]^{-1}$.

Table II. Selected Bond Distances (Å) and Angles (deg) for Au(MTP)$_2$Br (**2**)[a]

Au(1)–Br(1)	2.440 (5)	S(1)–P(2)	2.031 (11)
Au(1)–S(1)	2.361 (13)	S(2)–P(1)	1.972 (13)
Au(1)–C(1)	2.121 (27)	C(1)–P(1)	1.782 (40)
Au(1)–C(2)	2.152 (26)	C(2)–P(2)	1.857 (43)
C(1)–Au(1)–C(2)	175.2 (14)	Au(1)–C(2)–P(2)	91.6 (14)
Br(1)–Au(1)–S(1)	172.3 (2)	Au(1)–C(1)–P(1)	117.2 (21)
Br(1)–Au(1)–C(1)	88.2 (11)	C(2)–P(2)–S(1)	82.8 (11)
Br(1)–Au(1)–C(2)	89.7 (11)	C(1)–P(1)–S(2)	113.7 (11)
S(1)–Au(1)–C(2)	82.8 (11)		
S(1)–Au(1)–C(1)	99.4 (12)		

[a] Estimated standard deviations in parentheses.

Table III. Bond Lengths (Å) and Angles (deg) for [Au(S$_2$P(OH)Ph)$_2$]Cl·$^3/_2$Et$_2$O (**3**)[a]

Au(1)–S(1)	2.344 (5)	S(1)–P(1)	2.055 (7)
Au(1)–S(2)	2.339 (5)	S(2)–P(1)	2.055 (8)
Au(1)–S(3)	2.342 (5)	S(3)–P(2)	2.055 (7)
Au(1)–S(4)	2.342 (5)	S(4)–P(2)	2.058 (7)
Au(2)–S(5)	2.336 (6)	S(5)–P(3)	2.064 (10)
Au(2)–S(6)	2.328 (7)	S(6)–P(3)	2.062 (8)
P(1)–O(1)	1.498 (15)	P(2)–O(2)	1.499 (10)
P(2)–O(2)	1.499 (10)		
P(3)–O(3)	1.478 (16)		
S(1)–Au(1)–S(2)	83.1 (2)	S(1)–P(1)–S(2)	98.2 (3)
S(1)–Au(1)–S(3)	178.5 (2)	S(3)–P(2)–S(4)	98.4 (3)
S(2)–Au(1)–S(3)	97.1 (2)	S(5)–P(3)–S(6)	97.6 (4)
S(1)–Au(1)–S(4)	96.4 (2)	S(1)–P(1)–O(1)	115.9 (6)
S(2)–Au(1)–S(4)	177.2 (2)	S(3)–P(2)–O(2)	113.4 (6)
S(3)–Au(1)–S(4)	83.3 (2)	S(5)–P(3)–O(3)	115.9 (7)
S(5)–Au(2)–S(6)	83.5 (2)		

[a] Estimated standard deviations in parentheses.

Table IV. Bond Distances (Å) and Angles (deg) for Au(MTP)(S$_2$CNEt$_2$)$_2$ (**4**)[a]

Au–C	2.096 (9)	N(1)–C(31)	1.497 (14)
Au–S(2)	2.342 (2)	N(1)–C(41)	1.493 (13)
Au–S(3)	2.343 (2)	N(2)–C(51)	1.508 (13)
Au–S(5)	2.373 (2)	N(2)–C(61)	1.484 (14)
C(1)–S(5)	1.714 (9)	P–C	1.823 (9)
C(1)–S(3)	1.732 (9)	P–S(1)	1.946 (3)
C(2)–S(2)	1.747 (9)	P–C(11)	1.816 (8)
C(2)–S(4)	1.690 (8)	P–C(21)	1.818 (9)
C(1)–N(1)	1.322 (12)		
C(2)–N(2)	1.322 (11)		
C–Au–S(2)	91.0 (3)	C(1)–N(1)–C(31)	121.1 (8)
C–Au–S(3)	98.6 (3)	C(1)–N(1)–C(41)	120.7 (9)
C–Au–S(5)	173.4 (3)	C(2)–N(2)–C(51)	121.7 (8)
S(2)–Au–S(3)	170.39 (9)	C(2)–N(2)–C(61)	121.8 (9)
S(2)–Au–S(5)	95.61 (9)	C(31)–N(1)–C(41)	118.1 (9)
S(3)–Au–S(5)	74.78 (8)	C(51)–N(2)–C(61)	116.4 (9)
S(3)–C(1)–N(1)	123.6 (7)	Au–C–P	110.1 (5)
S(5)–C(1)–N(1)	124.0 (7)	Au–S(2)–C(2)	100.1 (3)
S(2)–C(2)–N(2)	116.9 (6)	Au–S(3)–C(1)	86.7 (3)
S(4)–C(2)–N(2)	122.5 (7)	Au–S(5)–C(1)	86.1 (3)

[a] Estimated standard deviations in parentheses.

the S atom of the chelating MTP ligand. The gold-coordinated C and Br atoms are found to be at normal distances from the central atom and compare well with related complexes. The Au(1)–S(1) (sulfur from chelating MTP) distance of 2.361 (13) Å is approximately 0.02 Å longer than the Au–S distance observed in **3**. The gold–sulfur distance of the dangling MTP ligand is found to be 4.254 Å in the solid state. This is so long that no Au–S interaction of any chemical significance is inferred. Nevertheless, an examination of the angles C(2)–Au(1)–S(1) and C(1)–Au(1)–S(1) (82.3 and 94.8°, respectively) suggests that the chelating ligand is compressed while the ideal 90.0° angle of the C(1)–Au(1)–S(1) of four-coordinate square-planar complexes has been expanded to 94.8°. Note that the Au(1)–Br(1) bond makes nearly right angles with the coordinating C(2) and C(1) atoms.

From this structural data it appears that the sulfur atom of the dangling MTP is sterically crowded between C(1) and S(1); S(1) has compensated for this by forming an acute angle, S(1)–Au–C(2). All atoms coordinated to Au(1) are nearly coplanar; even S(2) of the dangling MTP is part of this plane. The phosphorus–sulfur distances are consistent with a P═S double bond for the dangling ligand and a P—S single bond for the chelating MTP ligand, 1.972 (13) and 2.031 (11) Å, respectively;

Table V. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters (Å^2 × 10^3) for $Au(MTP)_2Br$

	x	*y*	*z*	*U*[a]
Au(1)	975 (1)	1703 (1)	2873 (1)	52 (1)
Br(1)	191 (3)	1474 (3)	4674 (4)	79 (2)
S(1)	1969 (8)	1987 (8)	1394 (10)	78 (5)
S(2)	−604 (8)	1720 (7)	−1600 (9)	70 (4)
P(1)	−1378 (7)	2362 (6)	20 (9)	61 (4)
P(2)	3301 (7)	2306 (7)	3336 (10)	79 (5)
C(1)	−799 (27)	1541 (30)	1333 (34)	82 (18)
C(2)	2794 (26)	1724 (24)	4442 (35)	83 (18)
C(11)	−1352 (18)	4523 (20)	111 (21)	82 (20)
C(12)	−1285	5659	775	95 (25)
C(13)	−1174	6091	2264	97 (23)
C(14)	−1131	5387	3088	83 (19)
C(15)	−1198	4251	2424	59 (16)
C(16)	−1309	3819	935	51 (14)
C(21)	−3944 (17)	3309 (12)	−163 (20)	79 (19)
C(22)	−5216	3282	−636	80 (18)
C(23)	−5622	2315	−1618	67 (17)
C(24)	−4757	1374	−2127	83 (19)
C(25)	−3484	1401	−1654	56 (15)
C(26)	−3078	2368	−672	47 (14)
C(31)	5093 (19)	1312 (18)	1822 (24)	84 (21)
C(32)	6283	721	1682	84 (22)
C(33)	7242	453	2898	72 (19)
C(34)	7011	777	4253	77 (19)
C(35)	5821	1368	4393	76 (19)
C(36)	4862	1635	3177	66 (16)
C(41)	4124 (19)	4109 (20)	5562 (26)	96 (23)
C(42)	4103	5254	6267	118 (22)
C(43)	3224	6092	5616	118 (29)
C(44)	2365	5785	4259	124 (30)
C(45)	2386	4640	3553	97 (21)
C(46)	3265	3802	4205	87 (21)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

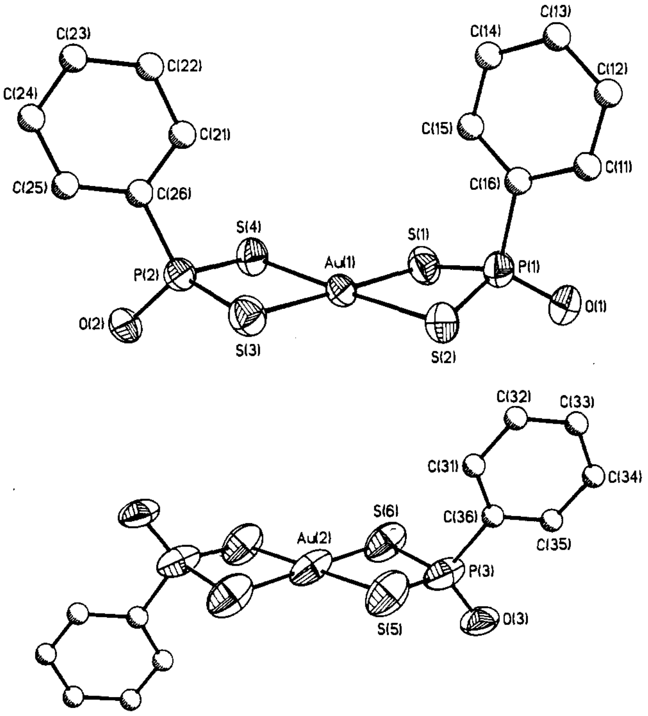

Figure 2. Perspective view of $[Au(S_2P(OH)Ph)_2]Cl\cdot{}^2/_3Et_2O$ (3) showing both the cis (top) and centrosymmetric trans (bottom) isomers. Both isomers are found in the unit cell. The crystallographic numbering scheme used is shown here. All non-carbon atoms are drawn as ellipsoids of 50% probability, hydrogen atoms are omitted, and carbon atoms are drawn with arbitrary radii for clarity. Ether is not shown.

however, the former is a little long compared to the P=S bond found in **1**.

Table VI. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters (Å^2 × 10^3) for $[Au(S_2P(OH)Ph)_2]Cl\cdot{}^2/_3Et_2O$

	x	*y*	*z*	*U*
Au(1)	805 (1)	673 (1)	4930 (1)	43 (1)*
Au(2)	0	5000	0	78 (1)*
Cl(1)	324 (3)	2306 (6)	1882 (3)	99 (3)*
Cl(2)	0	279 (8)	2500	101 (4)*
S(1)	838 (2)	−873 (4)	5408 (2)	57 (2)*
S(2)	633 (2)	1161 (4)	5953 (2)	54 (2)*
S(3)	800 (2)	2220 (4)	4460 (2)	51 (2)*
S(4)	1026 (2)	180 (4)	3931 (2)	52 (2)*
S(5)	783 (3)	5145 (5)	941 (3)	94 (3)*
S(6)	369 (3)	3448 (5)	−53 (3)	91 (3)*
P(1)	897 (2)	−196 (4)	6313 (2)	50 (2)*
P(2)	1036 (2)	1611 (4)	3654 (2)	44 (2)*
P(3)	971 (3)	3702 (5)	842 (3)	78 (3)*
O(1)	545 (5)	−633 (10)	6751 (6)	59 (5)*
O(2)	623 (5)	1838 (9)	2994 (5)	46 (4)*
O(3)	953 (6)	3074 (11)	1419 (7)	75 (6)*
O(4)	0	3793 (21)	2500	114 (14)*
O(5)	0	1451	7500	118 (11)*
C(1)	542 (16)	4332 (27)	2713 (20)	135 (12)
C(2)	690 (24)	4467 (40)	3424 (30)	238 (24)
C(3)	9906	2089	7134	161
C(4)	427	2324	7656	242
C(11)	1769 (5)	28 (10)	7456 (6)	61 (5)
C(12)	2345	51	7831	79 (7)
C(13)	2797	−69	7514	98 (8)
C(14)	2672	−212	6821	99 (8)
C(15)	2096	−235	6446	97 (8)
C(16)	1644	−115	6763	48 (5)
C(21)	2209 (6)	1775 (11)	4191 (5)	87 (7)
C(22)	2774	2030	4175	82 (7)
C(23)	2881	2439	3597	80 (7)
C(24)	2422	2592	3034	97 (8)
C(25)	1857	2337	3049	64 (6)
C(26)	1750	1928	3628	47 (5)
C(31)	2055 (8)	2891 (11)	1041 (8)	98 (8)
C(32)	2621	2814	962	138 (12)
C(33)	2818	3458	544	102 (9)
C(34)	2449	4180	204	105 (9)
C(35)	1883	4257	282	113 (10)
C(36)	1686	3613	701	76 (6)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Crystal and Molecular Structure of $[Au(S_2P(OH)Ph)_2]Cl\cdot{}^2/_3Et_2O$ (3). Complex **3** crystallized in the monoclinic space group *C*2/*c* with 12 molecules per unit cell. Its crystal structure consists of a cocrystallized mixture of the cis and trans isomers in a 2:1 ratio (cis and trans refer to the relative orientation of the phenyl rings) (Figure 2). Specifically, the asymmetric unit contains a whole cis cation and half of the trans cation, the latter having its gold atom located on a crystallographic center of symmetry. The AuS_4 units of both isomers have identical geometries and are perfectly planar. All the Au–S bond length fall within the 2.328 (7)–2.342 (5)-Å range. The S–Au–S angles formed by each chelating ligand are 83.1–83.7° while the S–Au–S angles formed between two $S_2P(OH)Ph$ ligands are 96.3–97.0°. The sum of the S–Au–S angles around each Au atom is the required 360.0°. The four membered AuS_2P rings for both isomers are very close to being planar. The distances of P(1), P(2), and P(3) from the AuS_4 planes are 0.40, 0.10, and 0.08 Å, respectively, resulting in a "boat"-like conformation for the cis isomer and a "chair"-like conformation for the trans isomer. The phenyl rings within each isomer are parallel to each other and perpendicular to the AuS_4 plane. The P–O bond lengths, 1.469–1.498 Å, are typical of P–O single bonds. The hydrogen atoms of the –OH groups were not located, but their positions can be inferred from the short O···Cl$^-$ distances assuming a linear arrangement of the O–H bond and the H···Cl$^-$ hydrogen bond. The chloride ion associated with the trans isomer, Cl(1), is located on a 2-fold axis and is bridging almost symmetrically the trans and cis isomers by two hydrogen bonds (Cl(1)···O(3) = 2.221 Å and Cl(1)···O(1) = 2.334 Å). The chloride associated only with the cis isomer, Cl(2), occupies a general position and is found at a distance of 2.653 Å from O(2). Two half-molecules of Et_2O of crystallization per asymmetric unit are present with oxygen atoms sitting on a 2-fold axis and at positions of no chemical significance.

Crystal and Molecular Structure of $Au(MTP)(S_2CNEt_2)_2$ (4). The structural characterization of $Au(MTP)(S_2CNEt_2)_2$ confirms the existence of the monodentate carbon bound coordination of the MTP ligand (Figure 3). The sum of the angles between adjacent atoms coordinated

Table VII. Atom Coordinates and Isotropic Temperature Factors (Å^2) for Au(MTP)(S$_2$CNEt$_2$)$_2$

atom	*x*	*y*	*z*	*B*^{a}
Au	0.29053 (3)^b	0.20941 (2)	0.46194 (3)	3.874 (6)
C	0.1468 (7)	0.2531 (6)	0.5079 (9)	4.9 (2)
P	0.0134 (2)	0.2360 (1)	0.3330 (2)	3.89 (5)
S(1)	0.0633 (2)	0.2895 (2)	0.1965 (3)	5.68 (6)
S(2)	0.4294 (2)	0.3782 (2)	0.5738 (2)	5.11 (6)
S(3)	0.1800 (2)	0.0343 (2)	0.3426 (2)	5.11 (6)
S(4)	0.4531 (2)	0.2901 (2)	0.8145 (2)	5.43 (6)
S(5)	0.4372 (2)	0.1404 (2)	0.3995 (2)	4.98 (5)
C(1)	0.3188 (7)	0.0245 (6)	0.3280 (8)	4.2 (2)
N(1)	0.3314 (6)	−0.0626 (5)	0.2678 (7)	4.9 (2)
C(2)	0.5074 (7)	0.3848 (5)	0.7594 (7)	3.8 (2)
N(2)	0.6080 (6)	0.4672 (5)	0.8530 (7)	5.2 (2)
C(11)	−0.0769 (6)	0.1008 (5)	0.2490 (8)	3.5 (2)
C(12)	−0.1009 (7)	0.0436 (6)	0.1055 (8)	4.1 (2)
C(13)	−0.1650 (8)	−0.0605 (7)	0.0457 (9)	5.3 (2)
C(14)	−0.208 (1)	−0.1068 (7)	0.127 (1)	6.1 (3)
C(15)	−0.1843 (9)	−0.0521 (7)	0.2735 (9)	6.1 (2)
C(16)	−0.1205 (8)	0.0512 (6)	0.3345 (9)	4.8 (2)
C(21)	−0.0923 (7)	0.2929 (6)	0.3904 (9)	4.6 (2)
C(22)	−0.048 (1)	0.3745 (9)	0.518 (1)	8.0 (3)
C(23)	−0.132 (1)	0.4218 (9)	0.551 (1)	9.0 (4)
C(24)	−0.2547 (9)	0.3874 (9)	0.459 (1)	8.2 (3)
C(25)	−0.302 (1)	0.300 (1)	0.339 (2)	11.4 (5)
C(26)	−0.223 (1)	0.254 (1)	0.302 (1)	10.0 (4)
C(31)	0.220 (1)	−0.1600 (7)	0.195 (1)	6.7 (3)
C(32)	0.226 (1)	−0.2195 (9)	0.299 (1)	8.9 (4)
C(41)	0.4553 (8)	−0.0655 (7)	0.263 (1)	6.1 (2)
C(42)	0.453 (1)	−0.058 (1)	0.114 (1)	9.9 (4)
C(51)	0.6598 (8)	0.5482 (8)	0.800 (1)	6.5 (3)
C(52)	0.596 (1)	0.6281 (7)	0.811 (1)	7.3 (3)
C(61)	0.672 (1)	0.4872 (9)	1.017 (1)	8.2 (4)
C(62)	0.789 (2)	0.448 (1)	1.044 (2)	14.5 (6)

^{a}Equivalent isotropic temperature factor. ^{b}Estimated standard deviations in parentheses.

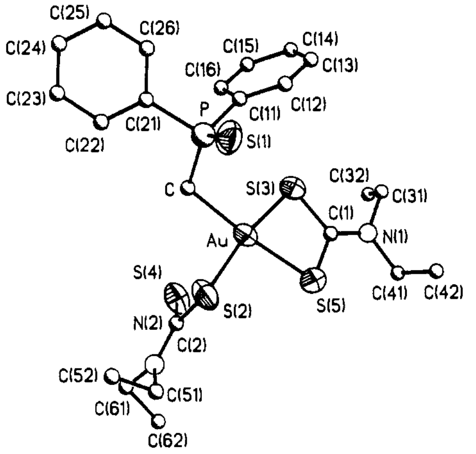

Figure 3. View of Au(MTP)(DTC)$_2$ (**4**) showing the crystallographic numbering scheme. Gold and sulfur atoms are drawn as ellipsoids of 50% probability, hydrogen atoms are omitted, and carbon, nitrogen, and phosphorus atoms are drawn with arbitrary radii for clarity.

to the Au atoms is 360.1°, nearly ideal for a square-planar complex. The geometry of the molecule is quite similar[15] to that of Au(S$_2$CNEt$_2$)$_3$. The Au–S bond lengths in Au(S$_2$CNEt$_2$)$_3$ average 2.342 (8) Å. This is in agreement with the Au–S distances in Au(MTP)(S$_2$CNEt$_2$)$_2$ for the trans S atoms, S(2) and S(3). The noncoordinated sulfur atom S(1) of the MTP ligand of **4** is 3.685 (3) Å away from the Au atom, while the free sulfur atom of the monodentate dithiocarbamate ligand is 0.5 Å closer to the gold atom (3.151 (3) Å). The Au–S(5) bond distance, where there is a *trans*-CH$_2$–Au–S arrangement, is 0.03 Å longer. This illustrates the *trans influence* of carbon compared with that of sulfur. The effect observed here is not nearly as pronounced as has been found for the [Au(CH$_2$)$_2$PR$_2$]$_2$(CH$_3$)X species, where the Au–X distances are increased by as much as 0.2 Å compared to those for the [Au(CH$_2$)$_2$PR$_2$X]$_2$ complexes.[16] Ylidic methylene groups, presumably as a result of their charge center, do not exert as strong a *σ trans influence* as a methyl group.[17]

The nature of the P═S bonding in **4** is noteworthy. The P═S distance is 1.946 (3) Å and compares well with the P═S distance observed in [PPN][Au(MTP)$_2$] (1.966 (4) Å), an anionic complex containing two dangling MTP ligands. Compared to that in **2**, the P═S distance in **4** is substantially shorter than the 1.972 (13) Å found for the dangling sulfur of **2**. When compared to the Au–S–P units of either dimeric or chelating MTP systems, the P–S bond distance, on the other hand, is shorter. The P–S bond length of 1.946 (3) Å is as much as 0.072 Å shorter than that observed for the dimeric and chelating MTP complexes [P–S: 2.018 (3) Å, [Au(MTP)]$_2$; 1.990 (2) Å, Ni(MTP)PPh$_3$Cl]. The S–P–CH$_2$ angle (114.9 (4)°) has closed slightly from that observed for [Au(MTP)]$_2$ (116.2 (3)°). The arithmetic mean of all angles around phosphorus is 109.3°, identical with the mean calculated for similar angles for [Au(MTP)]$_2$ and 1.1° greater than the mean observed for Ni(MTP)PPh$_3$Cl. The coordination mode of the ligand therefore does not greatly change the geometry about the phosphorus atom, but the effect is more pronounced in a chelated configuration. The P–S and P–C bond distances of a monodentate MTP ligand imply less ylene character in this configuration. The ylide/ylene canonical forms invoke both the double bond and zwitterionic nature of the compounds.[18] The chelate and bridge forms of the MTP ligand are as expected delocalized to a greater extent than the monodentate form.

The summation of the S–Au–S and C–Au–S angles in this pseudooctahedral gold complex is 135.3 (5)° due to the long nonbonded Au···S(1) distance and the extreme nonlinearity of the S(1)–Au–S(4) angle. The uncoordinated sulfur atoms of Au(S$_2$CNEt$_2$)$_3$ are similarly situated, located 2.789 (4) and 2.885 (5) Å above and below the AuS$_4$ plane.

Results

Au(MTP)$_2$Br (2). The oxidation of the PPN salt of the anionic Au$^{\mathrm{I}}$ complex Au(MTP)$_2^-$ with Br$_2$ gives, as an isolable product, the neutral Au(MTP)$_2$Br (**2**) and [PPN][Br] (the latter not isolated (eq 1). Complex **2** is a four-coordinate Au$^{\mathrm{III}}$ with trans

$$\underset{\mathbf{1}}{[\mathrm{PPN}][\mathrm{Au(MTP)_2}]} + \mathrm{Br_2} \xrightarrow{\mathrm{CH_2Cl_2}} \underset{\mathbf{2}}{\mathrm{Au(MTP)_2Br}} + [\mathrm{PPN}][\mathrm{Br}] \quad (1)$$

carbon atoms from the MTP anion. One MTP is dangling and one is chelating. The halide is trans to the S atom of the chelating MTP. The broad ^{1}H NMR signal observed at room temperature for the CH$_2$ protons narrows somewhat as the temperature is lowered, consistent with a dynamical process exchanging the methylene resonances. The reaction of the chloro analogue of **2** (obtained via oxidation of **1** with PhI·Cl$_2$) with Au(THT)Cl in CH$_2$Cl$_2$ in a 1:1 mole ratio gives, via ^{1}H NMR analysis, two complexes, A and B (eq 2). In the methylene region of the ^{1}H

$$\mathrm{Au(MTP)_2Cl} + \mathrm{Au(THT)Cl} \xrightarrow{\mathrm{CH_2Cl_2}} \text{A and B in 1:2 ratio} \quad (2)$$

NMR spectrum two doublets at 3.00 and 4.14 ppm (J_{HP} = 8.0 and 5.9 Hz, respectively) in the approximate ratio of 1:2 (A:B) are observed. These same products, A and B are again observed via ^{1}H NMR when AuCl$_3$py and [PPN][Au(MTP)$_2$] are combined in a 1:1 ratio in CH$_2$Cl$_2$. However, the ratio of A:B is now approximately 3:1 (eq 3). The major oxidation product (chloronation via 1 molar equiv of PhI·Cl$_2$) of the independently

$$\mathrm{AuCl_3py} + \underset{\mathbf{1}}{[\mathrm{PPN}][\mathrm{Au(MTP)_2}]} \xrightarrow{\mathrm{CH_2Cl_2}} \text{A and B in 3:1 ratio} \quad (3)$$

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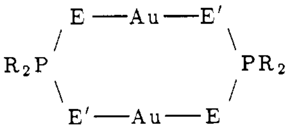
Chart I



5, E = E' = CH_2
6, E = S; E' = CH_2
E = E' = S: dithiophosphinate

prepared C_i-[Au(MTP)]$_2$ dimer has a doublet in the ^{1}H NMR spectrum at 3.00 ppm; a very minor product at approximately $^1/_{20}$th of this concentration is seen as a doublet at 4.14 ppm (eq 4).

$$C_i\text{-}[\mathrm{Au(MTP)}]_2 + \mathrm{PhI{\cdot}Cl_2} \xrightarrow{\mathrm{CH_2Cl_2}} \text{A and B in 20:1 ratio} \quad (4)$$
$$\mathbf{6}$$

Au(MTP)(DTC)$_2$ (4). The reaction of C_i-[Au(MTP)]$_2$ with thiuram disulfide gives, as determined crystallographically, a neutral, four-coordinate Au^{III} monomeric complex, Au(MTP)(DTC)$_2$, (**4**). One of the dithiocarbamate ligands is chelating and one is dangling. The MTP ligand is carbon coordinated and is also a dangling ligand. The dangling ligands are cis due to the chelating DTC. The ^{1}H NMR suggests that at 22 °C, **4** is dynamic in solution.

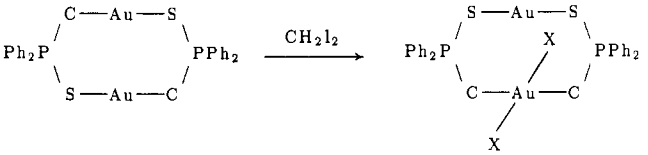
[Au(S$_2$P(OH)Ph)$_2$]Cl (3). From the ^{1}H NMR spectrum of the product of Au(THT)Cl and the sodium salt of $S_2P(R)Ph^-$ (R = OH and OEt), two products in a ~15:1 ratio are observed, as determined from the relative intensity of the resonance for OEt and OH. Only one triplet–quartet pair for a metal coordinated $S_2P(OEt)Ph^-$ complex was observed. Similarly, one $S_2P(OH)Ph^-$ complex was observed. Complex **3** was crystallographically characterized, the Au^{III} complex is square-planar with four sulfur atoms of the dithiophosphonate chelate ligands.

Discussion

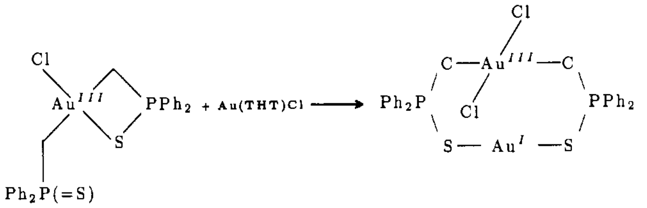
Our studies of the structurally similar dimeric gold complexes [Au(CH$_2$)$_2$PPh$_2$]$_2$ (**5**) and C_i-[AuCH$_2$P(S)Ph$_2$]$_2$ (**6**) (Chart I) have demonstrated significant differences between their chemical properties. The chemistry of complex **5** includes oxidative addition with alkyl halides,[16a,19] halogens[20] and pseudohalogens[21] giving symmetric and asymmetrically substituted dimeric Au^{II}–Au^{II} complexes, Au^{III}–Au^{III} dimeric tetrahalides,[22] alkyl trihalides,[23] and A-frame complexes.[24] Some heterovalent Au^{I}–Au^{III} dimers also have been isolated.[25] These complexes are generated either by rearrangement of the homovalent Au^{II}–Au^{II} complex or reductive elimination from the Au^{III}–Au^{III} system.

Although **6** can be oxidized to give stable symmetric Au^{II}–Au^{II} dihalide species it does not readily react with alkyl halides to give asymmetrically substituted alkyl halide adducts. A-frame complexes are not formed with CH_2X_2 (X = Cl, Br, I). The dimeric nature of **6** is lost when it is reacted at room temperature with thiuram disulfide (vide supra). Further oxidation of **7** to give a Au^{III}–Au^{III} species has not been observed. A heterovalent $Au^{I}\cdots Au^{III}$ diiodide complex has been obtained[7] when **6** was reacted with CH_2I_2. This latter observation is significant because the C_i arrangement of the bridging ligands (having two C–Au^{II}–S linkages) is converted to a C_s arrangement (one C–Au^{III}–C and one S–Au^{I}–S linkage), although, to date, this rearrangement has not been studied in detail. See Scheme II.

Scheme II



Scheme III



A comparison of our ^{1}H NMR results of the reaction products of Au(MTP)$_2$Cl with Au(THT)Cl, reaction 2, with an authentic sample of C_i-[Au(MTP)Cl]$_2$ (**7**) suggests that the heterovalent C_s-[$Au^{I}Au^{III}$(MTP)$_2$Cl$_2$] complex is present. The product distribution from the three reactions (eq 2–4) all run in a 1:1 molar ratio, which indicated that (a) only two products, A and B, were observed and (b) the ratio A:B changed with reaction conditions. We will consider each reaction individually.

In reaction 2 a Au^{III} complex containing trans carbon atoms from the coordinated MTP ligands (one dangling and one chelating) is reacted with a gold(I) chloride in 1:1 ratio. The products A and B in a 1:2 ratio are observed in the ^{1}H NMR spectrum and give rise to doublets at 3.00 and 4.14 ppm, respectively. On the basis of (a) the ^{1}H NMR chemical shifts (A is C_i-[Au(MTP)Cl]$_2$, vide infra), (b) the chemical shift differences of the methylene resonances of **6**, **7**, and B (**6**, Au^{I}, $\delta(CH_2)$ 2.00, J_{HP} = 11.3 Hz; **7**, Au^{II} dichloride, $\delta(CH_2)$ 3.00, J_{HP} = 8.00 Hz; B, Au^{III} dichloride with *trans*-C–Au–C linkage, $\delta(CH_2)$ 4.14, J_{HP} = 5.9 Hz), and (c) the trans carbon atoms of the MTP ligand of **2** it appears that B is the heterovalent $Au^{I}\cdots Au^{III}$ complex C_s-[$Au^{I}Au^{III}$(MTP)$_2$Cl$_2$]; see Scheme III.

In reaction 2, the observation that twice as much of C_s-[$Au^{I}Au^{III}$(MTP)$_2$Cl$_2$] (B) versus C_i-[Au(MTP)Cl]$_2$ (A) is obtained suggests that chelation without isomerization (or redox chemistry) dominates under these reaction conditions.

In reaction 3, AuCl$_3$py, and the two-coordinate Au^{I} anion [Au(CH$_2$P(S)Ph$_2$)$_2$]$^-$, containing two trans dangling MTP ligands, are reacted in a 1:1 molar ratio. The same products A and B are obtained but in a ratio of 3:1. The observation that in this reaction more of the centrosymmetric C_i-[Au(MTP)Cl]$_2$ complex is obtained than the heterovalent C_s isomer infers that the Au^{I} anion **1** dissociates (or isomerizes) a MTP ligand more readily than the Au^{III} complex, thereby allowing for conversion of the C–Au–C linkage to a C–Au–S linkage and formation of the C_i complex. The neutral four-coordinate Au^{III} complex **2** (in reaction 2) must dissociate into [Au(MTP)Br]$^+$[MTP]$^-$ to isomerize, presumably a difficult process. The preference for the homovalent C_i-[Au(MTP)Cl]$_2$ isomer over the heterovalent C_s complex in reaction 3 is therefore reasonable.

Of the five possible isomers one can draw for [Au(MTP)Cl]$_2$ (maintaining two bridging MTP ligands) (Chart II), isomer C is eliminated as an observed product of reactions 2–4 on the basis of symmetry. Complex C would give two doublets (J_{HP}) of equal intensity in the ^{1}H NMR spectrum if it were present. This was not observed in any of the spectra obtained.

A preference for isomer B over D (the latter has not been observed to date) is consistent with the relative ease for oxidation of gold centers containing σ-bound carbon atoms versus oxidation of gold centers containing soft σ-donors with good dπ back-bonding

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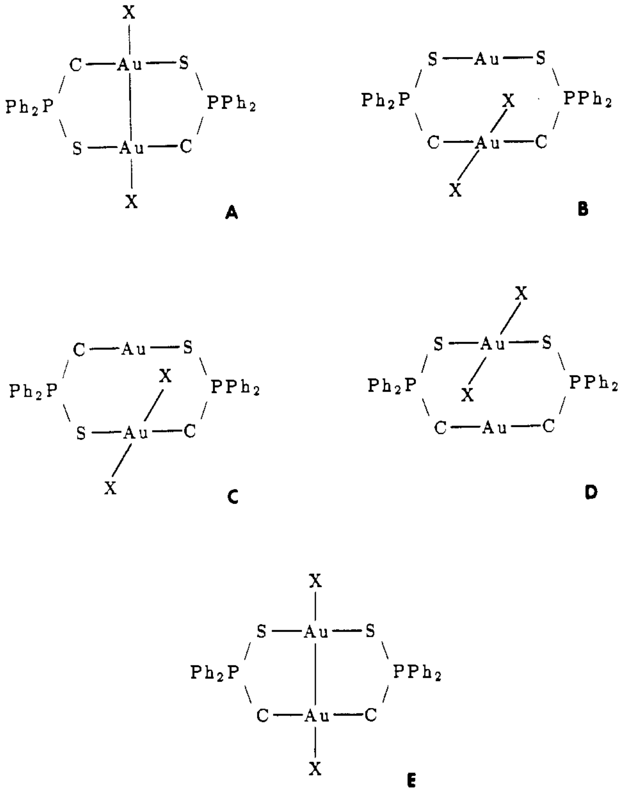
Chart II


A B C D E

capabilities (P and S atoms). The $[Au(dppm)]_2^{2+}$ complexes cannot be easily oxidized, and $[Au(DTC)]_2$ forms Au^{II} metal–metal-bonded dimers upon oxidation that are thermally unstable, eventually giving ionic mononuclear Au^{III} complexes. In the dianionic dimer $[Au(S_2CN(CN)_2)]_2^{2-}$ a stable Au^{II} metal–metal-bonded species has been obtained.[25c] Again, this is consistent with the stronger σ-donating ability of the dianionic $S_2CN(CN)_2^{2-}$ ligand compared with that of the neutral dppm or monoanionic DTC ligand.

The oxidation of the dimeric Au^I complex C_i-$[Au(MTP)]_2$ with the potentially chelating sulfur ligand thiuram disulfide to give the monomeric Au^{III} complex $Au(MTP)(DTC)_2$ (**4**) demonstrates the different reactivity of C_i-$[Au(MTP)]_2$ versus $[Au(ylide)]_2$. Just as **6** has some structural similarities to **5** and dithiophosphate and the dithiocarbamate dimer systems,[26] (see Scheme III), the reaction chemistry also is similar. The reaction[27] between thiuram disulfides and the Au^I dimer $[Au(DTC)]_2$ gives $Au(DTC)_3$. Burmeister and co-workers report[28] that the oxidative addition of Br_2 or Cl_2 to $[Au(DTC)]_2$ initially gives the Au^{II} dimer $[Au(DTC)X]_2$ when carried out at low temperature. (No structural information has been obtained for this Au^{II} species.) Upon warming, the $[Au(DTC)X]_2$ dimer disproportionates to monomeric Au^I and Au^{III} species.[28]

In contrast, thiuram disulfides[29] add to the dinuclear gold(I) phosphorus ylide complexes **5** to yield Au^{II} species rather than cleave the dimer to generate mononuclear species. The reaction of C_i-$[Au(MTP)]_2$ with $[Et_2NC(S)S]_2$ therefore appears to relate more closely to the dithiocarbamate dimer chemistry rather than the chemistry of the phosphorus ylide dimer system.

From the ^1H NMR spectrum of the reaction mixture obtained from $Au(THT)Cl$ and $[Na][S_2P(R)Ph]$ (R = OH, OEt), which gives $[Au(S_2P(R)Ph)_2]Cl$, only one isomer of each is seen. Yet, the solid-state X-ray crystal structure reveals both cis and trans isomers for $[Au(S_2P(OH)Ph)_2]Cl$. Consequently, in solution it appears that mixed-ligand species are not present in detectable amounts. (It is possible that they cannot be distinguished from $[Au(S_2P(R)Ph)_2]Cl$ (R = OH, OEt) due to degenerate ^1H chemical shifts. If the cis and trans isomers are both present in comparable amounts in solution they must be in fast chemical exchange.)

The addition of Lewis bases to four-coordinate d^8 systems containing sulfur chelates (i.e., PR_3 to MS_4) are known to give complexes with a MS_3P coordination geometry.[30] Such complexes have been shown to contain both dangling and chelating ligands and to be in equilibrium with the MS_4 parent complex.[30] Dynamic NMR data are consistent with[31] formation of a five-coordinate d^8 intermediate when M = Pd and Pt. Such a mechanism for **3**, also a four-coordinate d^8 system, would allow cis to trans isomerization; the five-coordinate intermediate would arise from the Cl coordination to the gold center. This intermediate could revert to a four-coordinate complex by displacement of one of the sulfur atoms of $S_2P(OH)Ph^-$. The four-coordinate complex would then contain one chelating and one dangling dithiophosphonate ligand. Structurally, such a species might look very similar to **2**; see Figure 3. Both would be neutral species with a MS_3X coordination geometry. Isomerization of **3** could occur through pseudorotation of a five-coordinate intermediate. Similar structural and dynamic properties are observed[33] with dithiolate complexes of Ni^{II}, Pd^{II}, and Pt^{II}.

Conclusion

The ligand MTP is a versatile, monoanionic, difunctional, three-atom bridge-forming ylide ligand.[32] Three different modes of coordination of the MTP ligand are presented: (a) the carbon-bound dangling MTP ligand as seen in **1**, **2**, and **4**; (b) chelation giving the M–C–P–S four-membered ring as in **2**; (c) the bridging MTP ligand giving a heteroatomic eight-membered ring as in **6** and **7**. We have systematically and logically synthesized the heterovalent C_s-$[Au^IAu^{III}(MTP)_2X_2]$ dimer previously obtained serendipitously. Although this study has addressed only the nature and chemistry of a few monomeric Au^{III} sulfur-containing chelates and their utility in the synthesis of homometallic dimers, the extension to heterobimetallic systems is being pursued.

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Registry No. **1**, 109638-64-4; **2**, 111934-31-7; *cis*-**3**, 111934-30-6; *trans*-**3**, 112018-39-0; **4**, 111934-28-2; **6**, 88272-19-9; **7**, 108503-33-9; C_s-$[Au^IAu^{III}(MTP)_2Cl_2]$, 111934-32-8; $[S_2CNEt_2]_2$, 97-77-8; Au(THT)Cl, 39929-21-0; $AuCl_3py$, 14911-01-4.

Supplementary Material Available: Tables listing bond lengths, bond angles, anisotropic thermal parameters, and derived H atom coordinates for complexes **2–4** (9 pages); tables of observed and calculated structure factors for **2–4** (65 pages). Ordering information is given on any current masthead page.

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(26) Structurally, the dithiocarbamate dimer differs from **6** and **5** in that the Au···Au distance is ~2.78 Å. In **5** and **6** the Au···Au separation is approximately 3.00 Å.

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