Inorg. Chem. **1994,** *33,* 5940−5945

Syntheses and Characterizations of $Au_2MNT(PR_3)_2$ (R = Me, Et, OPh, Cy). Study of Structural Features of Open Ring Complexes as a Function of Tertiary Phosphine and Phosphite Cone Angle

Rosa M. Dávila, Richard J. Staples, Anabel Elduque, Michele M. Harlass, Lorraine Kyle, and John P. Fackler, Jr.*

Laboratory for Molecular Structure and Bonding, Department of Chemistry, Texas A&M University, College Station, Texas 77843-3255

Received February 3, 1994[⊗]

Dinuclear gold(I) "open ring" complexes of the type $[Au_2(MNT)(PR_3)_2]$ (MNT = 1,2-dicyanoethene-1,2-dithiolate-*S,S'*) have been synthesized. The tertiary phosphines and phosphite used include PMe_3, **1**, $P(OPh)_3$, **2**, PEt_3, **3**, and PCy_3, **4**. The molecular structure of these complexes as determined through X-ray crystallography show an MNT unit bridging two gold(I) centers and a trialkylphosphine or triphosphite ligand coordinated to each gold(I) atom. One of the gold centers exhibits a linear two-coordinate geometry while the other gold(I) atom is an irregular three coordinate center in each of these MNT complexes. While remaining unsymmetrical, the steric bulk of the tricyclohexylphosphine prevents a close Au••Au contact from forming, causing the two gold atoms to be positioned on opposite sides of the ligand plane. Solution $^{31}P\{^1H\}$ NMR for each of these compounds gives only one signal from room temperature to −80 °C for these compounds. Au••Au contacts are found with the less bulky phosphines which are positioned on the same side of the MNT ligand plane. Pertinent crystal data are as follows: Compound **1** crystallizes in the monoclinic space group $P2_1$, with $a = 9.261(2)$ Å, $b = 10.544(3)$ Å, $c = 10.007(4)$ Å, $\beta = 113.59(2)°$, $Z = 2$ and $V = 895.4(5)$ Å^3. Compound **2** crystallizes in the triclinic space group $P\bar{1}$ with $a = 12.220(2)$ Å, $b = 12.465(2)$ Å, $c = 14.272(3)$ Å, $\alpha = 80.48(1)°$, $\beta = 67.85(1)°$, $\gamma = 81.86(1)°$, $Z = 2$ and $V = 1978(1)$ Å^3. Compound **3** crystallizes in the space group $P2_1/n$ with $a = 7.464(2)$ Å, $b = 28.832(7)$ Å, $c = 11.221(3)$ Å, $\beta = 93.46(2)°$, $Z = 4$ and $V = 2410(1)$ Å^3. Compound **4**·THF crystallizes in the triclinic space group $P\bar{1}$ with $a = 9.734(2)$ Å, $b = 15.797(3)$ Å, $c = 16.79(1)$ Å, $\alpha = 111.54(5)°$, $\beta = 92.00(5)°$, $\gamma = 99.65(1)°$, $Z = 2$ and $V = 2355(2)$ Å^3.

Introduction

Recently we reported[1a] the synthesis and characterization of $[Au_2\mu\text{-}(MNT)(PPh_3)_2]$ and $[Au_2(\mu\text{-}S_2C_6H_4)(PPh_3)_2]$. Schmidbaur also reported the latter compound.[1b] These dinuclear gold(I) complexes exhibit unsymmetrical coordination around the gold(I) centers. Coordination of $[AuPPh_3]^+$ to the bridging 1,2-dithiolate ligand (MNT) produces a two-coordinate center as well as an irregular three coordinate center.[2] These results were different from what had been observed previously for analogous 1,1-dithiolate gold(I) complexes.[3] The latter display symmetrical linear two-coordination around each gold(I) atom. The structural differences observed for the two dithiolate systems are thought to arise from electronic differences in the dithiolates rather than from steric effects. In our previous report[1a] we discussed and outlined a scheme to explain the structures which involved an electron delocalization taking place in the 1,2-dithiolene system. To rule out the possibility that steric bulk from the phosphine is responsible for the structural characteristics observed, we have synthesized complexes analogous to $[Au_2\mu\text{-}(MNT)(PPh_3)_2]$, progressively increasing the size of the cone angle of the tertiary phosphine ligand. The synthesis and characterization of the series $[Au_2(\mu\text{-}MNT)(PR_3)_2]$ (R = Me, **1**; R = OPh, **2**; R = Et, **3**; R = Cy, **4**) is reported here. We have examined specifically the changes in metal-metal distances and in the Au−S interactions as a function of increasing cone angle.

Experimental Section

All reactions were carried out in oven-dried Schlenk glassware by using standard inert-atmosphere techniques. Infrared spectra (KBr pellets) were recorded on a Perkin-Elmer 783 infrared spectrophotometer. NMR were recorded on a Varian XL-200 Fourier transform spectrometer. The $^{31}P\{^1H\}$ NMR were referenced against external H_3PO_4. Na_2MNT was prepared according to literature procedures.[4] The compounds $AuPR_3(Cl)$ (R = Me, Et, OPh, Cy) were prepared by displacement of THT (THT = tetrahydrothiophene) from AuTHT(Cl)[5] with the appropriate phosphines. All phosphines and phosphite (PR_3; R = Me, Et, OPh, Cy) were purchased from Strem Chemical Corp. Microanalyses were performed by Gallbraith Laboratories and National Chemical Consulting Inc.

Syntheses. $Au_2(MNT)(PMe_3)_2$, 1. To a THF (5 mL) solution of $Au(PMe_3)Cl$ (0.0899 g, 0.291 mmol), Na_2MNT (0.0271 g, 0.146 mmol) was added. The solution changed from colorless to yellow. After stirring for 1 h the THF was evaporated under vacuum leaving a yellow solid. The solid was dissolved in CH_2Cl_2 and NaCl was filtered off. The CH_2Cl_2 solution was concentrated under vacuum and a yellow solid was precipitated upon addition of Et_2O (10 mL). The solid was filtered off, washed with Et_2O and dried under vacuum. Yield = 0.0421 g (42.4%). IR: 2190 cm^{-1} (b, C≡N). $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = -5.47$ ppm (s). ^1H NMR ($CDCl_3$): $\delta = 1.60$ ppm (d, $J_{P-H} = 10.8$ Hz,

---

[⊗] Abstract published in *Advance ACS Abstracts,* November 1, 1994.

(1) (a) Dávila, R. M.; Elduque, A.; Grant, T.; Staples, R. J.; Fackler, J. P. *Inorg. Chem.* **1993,** *32,* 1749. (b) Nakamoto, N.; Hiller, W.; Schmidbaur, H. *Chem. Ber.* **1993,** *126,* 605.

(2) Jones, P. G. *Gold Bull.* **1981,** *14,* 102.

(3) Khan, M. N. I.; Wang, S.; Heinrich, D. D.; Fackler, J. P., Jr. *Acta Crystalogr., Sect. C* **1988,** *C44,* 822.

(4) Locke, J.; McCleverty, J. A. *Inorg. Chem.* **1966,** *5,* 1157.

(5) Usón, R.; Laguna, A.; Laguna, M. *Inorg. Synth.* **1989,** *26,* 85.

0020-1669/94/1333-5940$04.50/0

Table 1. Crystallographic Data

	1	**2**	**3**	**4**
formula	$C_{10}H_{18}N_2P_2S_2Au_2$	$C_{30}N_2O_6P_2S_2Au_2$	$C_{16}H_{30}N_2P_2S_2Au_2$	$C_{40}H_{66}N_2P_2S_2Au_2{*}C_4H_8O$
fw	686.28	1154.7	770.44	1167.10
space group	$P2_1$ (No. 4)	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)
a, Å	9.261(2)	12.220(2)	7.464(2)	9.734(2)
b, Å	10.544(3)	12.465(2)	28.832(7)	15.797(3)
c, Å	10.007(4)	14.272(3)	11.221(3)	16.79(1)
α, deg	90.00	80.48(1)	90.00	111.54(5)
β, deg	113.59(2)	67.85(1)	93.46(2)	92.00(5)
γ, deg	90.00	81.86(1)	90.00	99.65(1)
V, Å^3	895.4(5)	1978(1)	2410(1)	2355(2)
Z	2	2	4	2
d_{calc}, g/cm^3	2.538	1.938	2.123	1.646
μ(Mo Kα), cm^{-1}	167.3	76.23	124.4	64
λ(rdiation),[a] Å	0.710 73	0.710 73	0.710 73	0.710 73
temp, °C	20	20	20	20
transm factor: max, min	0.9679, 0.8640	0.955, 0.713	0.840, 0.580	1.000, 0.648
R,[b] R_w[c]	0.0399, 0.0490	0.0323, 0.0373	0.045, 0.055	0.038, 0.048

[a] Graphite-monochromated Mo Kα. [b] $R = \sum||F_o| - |F_c||/\sum F_o$. [c] $R_w = \{[\sum w(F_o - F_c)^2]/[\sum w(F_o)^2]\}^{1/2}$; $w^{-1} = [\sigma^2 F + gF^2]$.

CH_3). Anal. Calcd for $C_{10}H_{18}N_2P_2S_2Au_2$: C, 17.50; H, 2.62; N, 4.08; Found: C, 15.54; H, 2.28; N, 3.17. (Analysis indicates that not all of the NaCl was filtered out. The C:H:N ratio is in agreement with the chemical formula. The percentages indicate ca. 10–12% residual NaCl by weight.)

Compounds **2**–**4** were synthesized in an analogous way as that described above. Specific reaction details and characterization data follow.

$Au_2(MNT)[P(OPh)_3]_2$, 2. To a CH_2Cl_2 solution of $Au[P(OPh)_3]Cl$ (0.0777 g, 0.143 mmol), $Na_2(MNT)$ (0.0133 g, 0.0715 mmol) was added. The reaction was allowed to stir for 6 h. Yield = 0.0529 g (54.3%). IR: 2900, 2830 (s, C–H), 2190 (s, C≡N), 1440 (s, C=C) cm^{-1}. $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ = 77.01 ppm (s). Anal. Calcd for $C_{40}H_{30}N_2O_2P_2S_2Au_2{\cdot}CH_2Cl_2$: C, 41.89; H, 2.74; N, 2.38. Found: C, 41.48; H, 2.28; N, 2.31.

$Au_2(MNT)(PEt_3)_2$, 3. To a THF solution of $Au(PEt_3)Cl$ (0.2273 g, 0.0324 mmol), Na_2MNT (0.0604 g, 0.0324 mmol) was added. The reaction was allowed to stir for 16 h. Yield = 0.162 g (64.%). IR: 2180 cm^{-1} (s, C≡N). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ = 35.38 ppm (s). ^1H NMR ($CDCl_3$): δ = 1.18 ppm (m, $PCH_2\mathbf{CH_3}$, J_{H-H} = 7.51 Hz, J_{P-H} = 18.94 Hz), δ =1.82 ppm (m, $P\mathbf{CH_2}CH_3$, J_{P-H} = 9.68 Hz).

$Au_2(MNT)(PCy_3)_2$, 4. To a THF solution of $Au(PCy_3)Cl$ (0.0936 g, 0.1826 mmol), Na_2MNT (0.0171 g, 0.0913 mmol) was added. The reaction was allowed to stir for 18 h. Yield = 0.0593 g (59.3%). $^{31}P\{^1H\}$ NMR (CH_2Cl_2) δ = 57.16 ppm (s), ^1H NMR δ = 1.36 ppm (m, broad), 1.71 ppm (s, broad), 1.90 ppm (m, broad). Anal. Calcd for $C_{40}H_{66}N_2P_2S_2Au_2{\cdot}C_4H_8O$: C, 45.28; H, 6.39; N, 2.40. Found: C, 45.77; H, 6.54; N, 2.13.

X-ray Crystallography

Crystals of **1** and **3** suitable for X-ray diffraction analysis were obtained from the slow diffusion of an Et_2O layer into a CH_2Cl_2 solution of **1** and **3** respectively. For **2** light yellow rectangular crystals were obtained from the slow diffusion of a hexane layer into a THF solution of **2**. Yellow needle-like crystals of **4** were obtained using a similar solvent system as that for **2**. Crystals used for X-ray diffraction analysis were mounted on glass fibers with epoxy cement in a random orientation. Unit cell dimensions for all structures were determined from 25 machine-centered reflections obtained from rotation photographs and confirmed by axial photographs and Delaunay reduction. Data was collected on a Nicolet R3m/E diffractometer controlled by a Data General Nova 4 minicomputer using graphite monochromated Mo Kα radiation (λ = 0.71073 Å) at ambient temperature over the range 4 < 2θ < 45° for the four compounds. The data was corrected for decay, absorption, Lorentz and polarization effects. Semiempirical absorption correction was applied using psi scan data. Data processing was performed by a Data General Eclipse S140 minicomputer using the SHELXTL crystallographic computational package (version 5.1) and Siemens SHELXTL PLUS (MicroVAX II).

Table 2. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for $Au_2(MNT)(PMe_3)_2$ (**1**)

	x	y	z	U(eq)[a,b]
Au(1)	5772(1)	8515	4026(1)	44(1)
Au(2)	3883(1)	10174(2)	5389(1)	49(1)
S(1)	3126(7)	8081(6)	3426(8)	39(3)
S(2)	2459(10)	11339(7)	3263(8)	53(3)
P(1)	8215(9)	9141(9)	4292(9)	53(3)
P(2)	5184(9)	9686(7)	7748(8)	46(3)
N(1)	1709(42)	7817(30)	−562(32)	78(16)
N(2)	885(32)	11416(31)	−684(32)	76(15)
C(1)	2249(38)	9020(31)	1862(32)	57(14)
C(2)	2034(26)	10298(33)	1814(28)	49(12)
C(3)	1911(32)	8316(31)	501(37)	53(13)
C(4)	1380(31)	10966(26)	376(35)	39(12)
C(5)	8792(91)	8211(74)	3175(76)	212(36)
C(6)	8183(77)	10729(67)	3614(81)	180(29)
C(7)	9576(46)	9341(44)	5981(41)	82(11)
C(8)	4710(46)	8127(35)	8222(43)	78(10)
C(9)	7452(37)	9732(34)	8422(39)	65(9)
C(10)	4741(42)	10687(35)	9003(38)	73(9)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor. [b] Estimated standard deviations are given in parentheses.

All structures were determined using direct methods. Compound **1** crystallized in the space group $P2_1$, as suggested by the systematically absent data and confirmed by successful refinement, R = 0.0399; R_w = 0.0490. Refinement of the enantiomorph of **1** produced poorer statistics. Structure **2** was solved in $P\bar{1}$. Final R values for **2** were R = 0.0323; R_w = 0.0373. Compound **3** crystallized in the space group $P2_1/n$. R values after final refinement were R = 0.045 and R_w = 0.055. Compound **4**·THF crystallized in the space group $P\bar{1}$. An interstitial (noninteracting) THF molecule was found in the asymmetric unit. Final R values for **4** were R = 0.038; R_w = 0.048.

The final cycles of refinement were performed with hydrogen atoms placed in idealized SHELXTL PLUS generated positions. All non-hydrogen atoms were refined anisotropically (with the exception of carbon atoms in compound **1**. Crystal data and details of the crystallographic experimental parameters are given in Table 1. Atomic coordinates and equivalent isotropic thermal parameters for **1**–**4** are presented in Tables 2, 4, 6 and 8 respectively. Relevant bond distances and angles are presented in Tables 3, 5, 7 and 9 respectively.

Table 3. Relevant Bond Lengths (Å)[a] and Angles (deg) for $Au_2(MNT)(PMe_3)_2$ (**1**)

	Bond Lengths		
Au(1)−Au(2)	3.145(2)	C(1)−C(2)	1.36(5)
Au(1)−S(1)	2.323(7)	C(1)−C(3)	1.47(5)
Au(1)−P(1)	2.268(9)	C(2)−C(4)	1.50(4)
Au(2)−S(2)	2.351(7)	P(1)−C(7)	1.67(3)
Au(2)−S(1)	2.849(7)	P(2)−C(8)	1.81(4)
Au(2)−P(2)	2.240(7)	P(2)−C(9)	1.93(3)
S(2)−C(2)	1.73(3)	P(2)−C(10)	1.81(4)
P(1)−C(5)	1.73(9)	N(1)−C(3)	1.13(5)
P(1)−C(6)	1.80(7)	N(2)−C(4)	1.08(4)
	Bond Angles		
S(1)−Au(1)−P(1)	170.8(3)	Au(2)−P(2)−C(10)	115(1)
S(2)−Au(2)−P(2)	160.8(3)	S(1)−C(1)−C(2)	127(2)
Au(1)−S(1)−C(1)	101(1)	S(1)−C(1)−C(3)	113(2)
Au(2)−S(2)−C(2)	107(1)	C(2)−C(1)−C(3)	120(3)
Au(1)−P(1)−C(5)	108(3)	S(2)−C(2)−C(1)	128(2)
Au(1)−P(1)−C(6)	111(2)	S(2)−C(2)−C(4)	112(2)
Au(1)−P(1)−C(7)	118(2)	C(1)−C(2)−C(4)	120(3)
Au(2)−P(2)−C(8)	114(1)	N(1)−C(3)−C(1)	176(4)
Au(2)−P(2)−C(9)	114(1)	N(2)−C(4)−C(2)	178(3)

[a] Estimated standard deviations are given in parentheses.

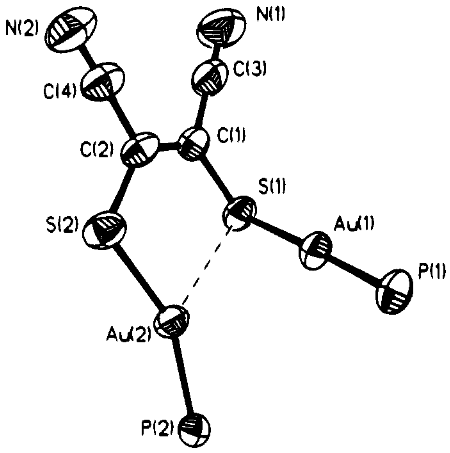


Figure 1. Basic framework of $Au_2(MNT)(PR_3)_2$ complexes.

Results

The basic route for the synthesis of complexes **1**−**4** was the reaction of one equivalent of Na_2MNT with two equivalents of the corresponding $AuPR_3(Cl)$ complex. All the products precipitate as yellow solids in moderate yields of 40−60%. The complexes are stable at room temperature.

The complexes were characterized initially through IR spectroscopy, ^1H and $^{31}P\{^1H\}$ NMR, and later through X-ray diffraction methods as described above. A general observation made for the characterization of all of the complexes is the appearance of a strong band around 2190 cm^{-1} in the infrared corresponding to the C≡N stretch from the MNT ligand. The $^{31}P\{^1H\}$ NMR of complexes **1**−**4** shows only a singlet from room temperature to −80 °C. ^1H NMR characterization of the complexes shows a downfield shift of the signals upon coordination of the ligand to the gold(I) centers compared with the spectrum of the starting $Au(PR_3)Cl$.

Table 4. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for $Au_2(MNT)[P(OPh)_3]_2$, **2**

	x	*y*	*z*	*U*(eq)[a,b]
Au(1)	3395(1)	3441(1)	8401(1)	43(1)
Au(2)	5291(1)	4947(1)	7902(1)	43(1)
S(1)	3224(2)	4691(1)	9503(1)	43(1)
S(2)	4220(2)	6384(2)	7251(1)	54(1)
P(1)	3591(2)	2280(1)	7302(1)	47(1)
P(2)	6925(2)	3928(1)	7921(1)	40(1)
O(1)	3388(7)	2774(5)	6288(5)	93(4)
O(2)	2757(6)	1325(5)	7600(4)	81(3)
O(3)	4886(5)	1734(5)	6934(5)	78(3)
O(4)	6878(4)	3084(4)	8900(3)	49(2)
O(5)	7451(4)	3222(3)	6993(3)	44(2)
O(6)	7995(4)	4539(3)	7910(3)	47(2)
N(1)	292(7)	6196(7)	10374(7)	98(4)
N(2)	1434(7)	8004(6)	7660(6)	81(4)
C(1)	2387(6)	5792(5)	9078(6)	46(3)
C(2)	2810(6)	6443(5)	8182(5)	46(3)
C(3)	1203(7)	6019(6)	9790(7)	63(4)
C(4)	2010(7)	7325(6)	7907(6)	57(3)
C(10)	2965(7)	3867(6)	6101(6)	58(4)
C(11)	3653(8)	4448(7)	5219(6)	64(4)
C(12)	3278(9)	5523(8)	4991(8)	81(5)
C(13)	2285(10)	5992(8)	5631(8)	83(5)
C(14)	1609(8)	5422(8)	6494(9)	82(5)
C(15)	1924(7)	4306(7)	6765(7)	67(4)
C(20)	2265(7)	794(6)	8605(6)	53(3)
C(21)	1490(7)	1366(7)	9348(7)	68(4)
C(22)	1002(10)	817(12)	10284(9)	113(7)
C(23)	1337(15)	−293(16)	10496(10)	143(10)
C(24)	2070(12)	−803(10)	9716(12)	112(8)
C(25)	2592(8)	−297(7)	8741(9)	78(5)
C(30)	5434(6)	930(6)	6273(6)	51(3)
C(31)	5582(7)	−107(7)	6705(6)	65(4)
C(32)	6224(7)	−899(7)	6089(8)	75(4)
C(33)	6683(8)	−636(8)	5031(8)	77(5)
C(34)	6523(8)	425(10)	4625(7)	80(5)
C(35)	5876(7)	1212(7)	5244(6)	65(4)
C(40)	5848(6)	2550(5)	9475(5)	39(3)
C(41)	5233(7)	2821(6)	10436(6)	53(3)
C(42)	4227(7)	2283(7)	11025(6)	66(4)
C(43)	3860(8)	1525(7)	10681(8)	72(4)
C(44)	4487(8)	1262(6)	9715(8)	70(5)
C(45)	5506(7)	1777(6)	9104(6)	51(3)
C(50)	8337(6)	2342(5)	6859(5)	41(3)
C(51)	8141(7)	1473(6)	6481(7)	65(4)
C(52)	8976(8)	596(7)	6304(8)	78(4)
C(53)	9966(8)	572(7)	6521(7)	78(4)
C(54)	10163(7)	1430(8)	6879(6)	70(4)
C(55)	9337(6)	2342(6)	7066(6)	54(3)
C(60)	8351(6)	5514(5)	7257(6)	48(3)
C(61)	8521(8)	5616(7)	6251(6)	72(4)
C(62)	8927(9)	6563(9)	5618(8)	92(5)
C(63)	9128(8)	7401(7)	6060(9)	85(5)
C(64)	8946(7)	7294(7)	7069(8)	78(5)
C(65)	8548(6)	6328(6)	7689(6)	60(3)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor. [b] Estimated standard deviations are given in parentheses.

Crystal Structure Description

The basic framework for complexes **1**−**4** is shown in Figure 1 (R groups have been omitted for clarity). The same labelling scheme has been applied in all cases. The two gold atoms are bridged by an MNT ligand bonded through the sulfur atoms. Each gold(I) center is coordinated to a PR_3 unit. In general, the coordination about Au(1) is approximately linear (smallest S−Au−P angle 170.8°). However, the coordination about Au(2) deviates considerably from linear with bonding interactions observed between Au(2) and S(1). A summary of important relevant distances and angles associated with the irregular three coordinate geometry of Au(2) is presented in Table 10. Data for the Ph_3P derivative reported previously[1a] also is included for comparison.

Discussion

The structural results described here show that the unsymmetrical coordination around the gold(I) centers reported for $[Au_2(\mu\text{-}MNT)(PPh_3)_2]$ is maintained even as the cone angle of

Table 5. Relevant Bond Lengths (Å)[a] and Angles (deg) for Au$_2$(MNT)[P(OPh)$_3$]$_2$, **2**

Bond Lengths			
Au(1)−Au(2)	2.991(1)	S(2)−C(2)	1.734(6)
Au(1)−S(1)	2.327(2)	N(1)−C(3)	1.13(1)
Au(1)−P(1)	2.232(2)	N(2)−C(4)	1.12(1)
Au(2)−S(1)	2.709(2)	C(1)−C(2)	1.356(9)
Au(2)−S(2)	2.343(2)	C(1)−C(3)	1.441(9)
Au(2)−P(2)	2.216(2)	C(2)−C(4)	1.47(1)
S(1)−C(1)	1.759(7)		

Bond Angles			
Au(2)−Au(1)−P(1)	118.7(1)	Au(2)−S(1)−C(1)	96.8(2)
S(1)−Au(1)−P(1)	178.1(1)	Au(2)−S(2)−C(2)	104.7(2)
Au(1)−Au(2)−S(2)	92.2(1)	S(1)−C(1)−C(2)	124.4(5)
S(1)−Au(2)−S(2)	85.4(1)	S(1)−C(1)−C(3)	115.0(5)
Au(1)−Au(2)−P(2)	107.4(1)	C(2)−C(1)−C(3)	120.5(6)
S(1)−Au(2)−P(2)	120.0(1)	S(2)−C(2)−C(1)	128.7(5)
S(2)−Au(2)−P(2)	154.4(1)	S(2)−C(2)−C(4)	112.3(5)
Au(1)−S(1)−Au(2)	72.4(1)	C(1)−C(2)−C(4)	119.0(6)
Au(1)−S(1)−C(1)	100.9(3)	N(1)−C(3)−C(1)	178.(1)

[a] Estimated standard deviations are given in parentheses.

the coordinating phosphine is changed substantially. One exception to this statement is the observation that the Au(1)−S(1)−C(1)−C-(2) torsion angle (Figure 1) expands to 155.0-(6)° in the PCy$_3$ complex from about ±70−80° with the other phosphines. Column **2** in Table 10 lists important changes which occur as the cone angle[6] changes from 118° in the case of PMe$_3$, **1**, to 170° for PCy$_3$, **4**. As presented in Table 10, the following trends are observed:

Au···Au separation:

$$\mathrm{PCy_3 > PMe_3 > PPh_3 > PEt_3 > P(OPh)_3}$$

$$\mathrm{Au(2){-}S(1){:}\ PMe_3 > PCy_3 > PPh_3 > P(OPh)_3 > PEt_3}$$

S(2)−Au(2)−P(2) angle:

$$\mathrm{PCy_3 > PMe_3 > PPh_3 > P(OPh)_3 > PEt_3}$$

No direct relationship is established between the increasing cone angle and the Au(2)−S(1) or Au···Au distances in these structures. In fact, the extremes in phosphine cone angle, PMe$_3$ (118°) and PCy$_3$ (170°), appear to produce similar Au(2)−S(1) distances. The shortest distances for Au(2)−S(1) are formed in **2** and **3**. These compounds also show the shortest Au···Au distances although their phosphine cone angles are both larger than the cone angle of PMe$_3$, **1**. These two complexes are the only ones in the series that allow for twisting away of the second atom in the phosphine ligands. The shorter Au(2)−S(1) and Au···Au distances observed for **2** and **3** appear to result from this bend of the R group. Brown and co-workers[7] have found that, for the phosphite derivatives of Cr(CO)$_5$ complexes, steric repulsions are absorbed more readily through bond bending, an effect which may be at work here also.

There are some special structural features observed for **2** and **4** which deserve elaboration. The structure of **2** shows the same general geometry of the other "open ring" complexes but with a very short distance between the two metal centers, Au(1)−Au(2) = 2.991(1) Å. This distance suggests the presence of a stronger metal-metal interaction when compared to the other "open ring" complexes. It is also interesting to observe that complex **2** shows the shortest Au−P distances of the "open ring" series, Au(1)−P(1) = 2.232(2) Å and Au(2)−P(2) = 2.216(2) Å. Structural evidence presented by Verkade[8] has shown that the presence of electronegative substituents on a phosphine ligand in a metal complex causes a decrease in the metal-phosphorus bond length. Related work[9] with triphenylphosphite gold(I) complexes suggests that this shortening of the Au−P length is caused by a contraction of the phosphorus donor orbital on the phosphite ligand.

Table 6. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for Au$_2$(MNT)(PEt$_3$)$_2$, **3**

	x	*y*	*z*	*U*(eq)[a,b]
Au(1)	4829(2)	1101(1)	9177(1)	50(1)
Au(2)	7658(2)	1860(1)	8820(1)	60(1)
S(1)	6014(10)	1586(2)	10718(6)	54(3)
S(2)	10136(9)	1417(3)	9625(6)	60(3)
P(1)	3668(10)	611(2)	7739(7)	61(3)
P(2)	6565(10)	2346(3)	7380(7)	63(3)
N(1)	7080(36)	892(9)	13451(26)	98(9)
N(2)	11791(39)	700(10)	12147(25)	105(9)
C(1)	7783(31)	1252(8)	11376(21)	45(7)
C(2)	9430(37)	1203(9)	10945(24)	65(8)
C(3)	7414(43)	1065(11)	12525(30)	85(10)
C(4)	10743(44)	921(11)	11676(29)	82(10)
C(5)	5319(39)	213(10)	7219(28)	85(10)
C(6)	6908(44)	459(12)	6661(30)	114(13)
C(7)	1876(43)	209(11)	8325(29)	97(11)
C(8)	2504(40)	−23(11)	9451(27)	94(11)
C(9)	2570(46)	911(11)	6537(28)	99(11)
C(10)	1835(50)	578(13)	5473(32)	139(15)
C(11)	4159(59)	2362(19)	7120(44)	205(24)
C(12)	2881(51)	2249(13)	7763(33)	124(14)
C(13)	7137(85)	2184(22)	5898(51)	249(32)
C(14)	8194(66)	1844(17)	5620(45)	202(24)
C(15)	7316(65)	2938(16)	7553(42)	166(18)
C(16)	8070(52)	3151(14)	8544(35)	143(16)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor. [b] Estimated standard deviations are given in parentheses.

Table 7. Relevant Bond Lengths (Å)[a] and Angles (deg) for Au$_2$(MNT)(PEt$_3$)$_2$, **3**

Bond Lengths			
Au(1)−Au(2)	3.085(2)	S(2)−C(2)	1.72(3)
Au(1)−S(1)	2.355(7)	N(1)−C(3)	1.19(4)
Au(1)−P(1)	2.276(7)	N(2)−C(4)	1.12(4)
Au(2)−S(1)	2.642(7)	C(1)−C(2)	1.36(4)
Au(2)−S(2)	2.382(7)	C(1)−C(3)	1.44(4)
Au(2)−P(2)	2.253(8)	C(2)−C(4)	1.48(4)
S(1)−C(1)	1.76(2)		

Bond Angles			
Au(2)−Au(1)−P(1)	125.6(2)	Au(2)−S(2)−C(2)	104(1)
S(1)−Au(1)−P(1)	177.9(3)	S(1)−C(1)−C(2)	126(2)
Au(1)−Au(2)−S(2)	95.2(2)	S(1)−C(1)−C(3)	114(2)
S(1)−Au(2)−S(2)	85.5(2)	C(2)−C(1)−C(3)	121(2)
Au(1)−Au(2)−P(2)	108.2(2)	S(2)−C(2)−C(1)	127(2)
S(1)−Au(2)−P(2)	126.7(3)	S(2)−C(2)−C(4)	117(2)
S(2)−Au(2)−P(2)	147.7(3)	C(1)−C(2)−C(4)	116(2)
Au(1)−S(1)−Au(2)	76.0(2)	N(1)−C(3)−C(1)	177(3)
Au(1)−S(1)−C(1)	102.8(8)	N(2)−C(4)−C(2)	175(3)
Au(2)−S(1)−C(1)	97.4(9)		

[a] Estimated standard deviations are given in parentheses.

The molecular structure of complex **4** is shown in Figure 2. The interesting feature of this structure is that the Au···Au interaction is broken but the "extra" Au(2)−S(1) interaction remains. As shown by the Au(1)−S(1)−C(1)−C(2) torsional angle, Table 10, the two gold atom are on opposite sides of the dithiolate ligand plane in **4**. The distance of 4.883(3) Å between the metal centers shows the longest Au···Au separation in this "open ring" series. The Au(2)−S(1) interaction at a distance

---

(6) Tolman, C. A. *Chem. Rev.* **1975**, *77*, 313.

(7) Brown, T.; Lee, K. *Inorg. Chem.* **1992**, *31*, 289.

(8) Verkade, J. G. *Coord. Chem. Rev.* **1972**, *9*, 1.

(9) Hitchcok, P.; Pye, P. L. *J. Chem. Soc., Dalton Trans.* **1977**, 1457.

Table 8. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for $Au_2(MNT)(PCy_3)_2 \cdot THF$, **4**

	x	*y*	*z*	*U*(eq)^{a,b}
Au(1)	5242(1)	6703(1)	2394(1)	45(1)
Au(2)	4288(1)	8397(1)	586(1)	49(1)
S(1)	4028(3)	7147(2)	1452(2)	59(1)
S(2)	2195(3)	8685(2)	1129(2)	65(1)
P(1)	6385(3)	6212(2)	3293(2)	46(1)
P(2)	6321(2)	8320(2)	−31(2)	44(1)
N(1)	1609(11)	6737(9)	2998(8)	116(8)
N(2)	−346(12)	8418(11)	2578(9)	143(10)
C(1)	2572(9)	7470(6)	1951(6)	49(4)
C(2)	1863(9)	8083(7)	1790(6)	54(4)
C(3)	2039(11)	7068(8)	2529(8)	73(6)
C(4)	617(12)	8247(9)	2223(7)	75(6)
C(11)	7832(10)	7085(7)	4015(6)	59(4)
C(12)	7682(12)	8071(7)	4160(7)	71(5)
C(13)	8973(14)	8770(9)	4683(8)	94(6)
C(14)	9323(15)	8638(10)	5519(8)	116(8)
C(15)	9481(13)	7684(10)	5364(9)	100(7)
C(16)	8191(10)	6985(7)	4864(6)	64(5)
C(21)	7154(10)	5210(7)	2669(6)	56(4)
C(22)	7969(12)	5370(8)	1986(7)	74(5)
C(23)	8560(14)	4556(10)	1461(8)	95(7)
C(24)	9410(14)	4189(10)	1988(9)	97(7)
C(25)	8562(13)	3995(8)	2654(9)	90(7)
C(26)	7986(11)	4828(7)	3209(7)	68(5)
C(30)	5135(10)	5823(6)	3929(6)	51(4)
C(31)	3989(10)	4995(6)	3335(6)	57(4)
C(32)	2908(10)	4682(7)	3861(7)	64(5)
C(33)	2232(11)	5486(7)	4412(7)	68(5)
C(34)	3351(12)	6288(8)	4984(7)	77(6)
C(35)	4432(11)	6621(7)	4490(6)	64(5)
C(40)	7017(10)	7313(6)	15(7)	55(4)
C(42)	8487(11)	7280(8)	−81(8)	76(6)
C(43)	8892(12)	6493(7)	140(8)	83(6)
C(44)	7949(14)	5570(8)	−409(10)	102(7)
C(45)	6490(14)	5601(8)	−356(10)	104(7)
C(46)	6050(11)	6399(7)	−526(6)	64(5)
C(50)	7675(9)	9336(6)	574(6)	46(4)
C(51)	7348(12)	10241(7)	508(7)	75(5)
C(52)	8538(12)	11054(7)	990(8)	79(6)
C(53)	8779(11)	1189(7)	1915(7)	74(5)
C(54)	9075(10)	10308(7)	1986(6)	65(5)
C(55)	7895(10)	9477(6)	1500(6)	55(4)
C(61)	6148(10)	8310(7)	−1140(6)	58(4)
C(62)	4873(12)	7760(9)	−1668(7)	87(6)
C(63)	4677(11)	7919(9)	−2494(7)	76(6)
C(64)	5943(12)	7807(9)	−2986(7)	75(6)
C(65)	7448(10)	8185(9)	−1616(6)	71(5)
C(66)	7225(12)	8292(11)	−2463(8)	103(8)
O(1)	4821(23)	10913(11)	4279(10)	185(10)
C(71)	6423(26)	10040(17)	3806(16)	190(18)
C(72)	5054(27)	9503(15)	3410(16)	219(17)
C(73)	4092(23)	10053(17)	3705(16)	165(15)
C(74)	6188(27)	10909(16)	4240(19)	215(22)

^{a} Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor. ^{b} Estimated standard deviations are given in parentheses.

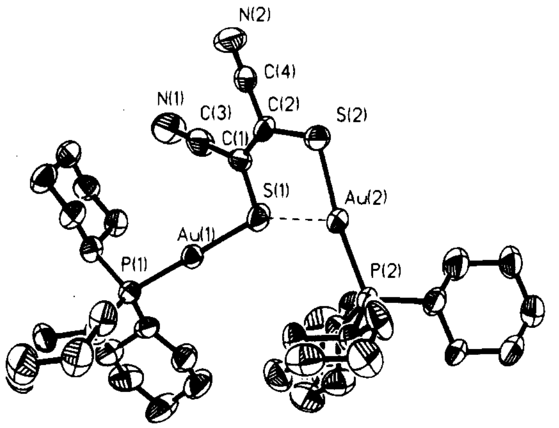


Figure 2. Molecular structure of $Au_2(MNT)(PCy_3)_2$ with thermal ellipsoids drawn at 50% probability.

Table 9. Relevant Bond Lengths (Å)^a and Angles (deg) for $Au_2(MNT)(PCy_3)_2 \cdot THF$, **4**

	Bond Lengths		
Au(1)−Au(2)	4.883(3)	C(1)−C(2)	1.38(2)
Au(1)−S(1)	2.313(4)	C(1)−C(3)	1.41(2)
Au(1)−P(1)	2.271(4)	C(2)−C(4)	1.45(1)
Au(2)−S(1)	2.838(4)	O(1)−C(73)	1.39(2)
Au(2)−S(2)	2.308(3)	O(1)−C(74)	1.34(3)
Au(2)−P(2)	2.266(3)	C(71)−C(72)	1.44(3)
S(1)−C(1)	1.727(9)	C(71)−C(74)	1.36(3)
S(2)−C(2)	1.71(1)	C(72)−C(73)	1.37(4)
	Bond Angles		
S(1)−Au(1)−P(1)	177.8(1)	S(1)−C(1)−C(3)	119.3(9)
S(1)−Au(2)−S(2)	82.8(1)	C(2)−C(1)−C(3)	117.6(9)
S(1)−Au(2)−P(2)	107.3(1)	S(2)−C(2)−C(1)	130.2(8)
S(2)−Au(2)−P(2)	169.9(1)	S(2)−C(2)−C(4)	113.2(9)
Au(1)−S(1)−Au(2)	142.7(1)	C(1)−C(2)−C(4)	117(1)
Au(1)−S(1)−C(1)	104.7(4)	C(73)−O(1)−C(74)	108(2)
Au(2)−S(1)−C(1)	96.3(4)	C(72)−C(71)−C(74)	104(2)
Au(2)−S(2)−C(2)	107.1(4)	C(71)−C(72)−C(73)	108(2)
S(1)−C(1)−C(2)	123.0(9)	O(1)−C(73)−C(72)	107(2)
		O(1)−C(74)−C(71)	112(2)

^{a} Estimated standard deviations are given in parentheses.

Table 10. Important Distances (Å) and Angles (deg) of $Au_2(MNT)(PR_3)_2$ Complexes

		dist		angle	
phosphine, compd	cone angle[6]	Au···Au	Au(2)−S(1)	S(2)−Au(2)−P(2) bend	Au(1)−S(1)−C(1)−C(2) torsion
PMe_3, **1**	118	3.145(2)	2.849(7)	160.8(3)	−77(2)
$P(OPh)_3$, **2**	128	2.991(1)	2.709(2)	154.4(1)	−71.5(8)
PEt_3, **3**	132	3.085(2)	2.642(7)	147.7(3)	77(2)
PPh_3[1a,11]	145	3.116(3)	2.811(3)	158.8(2)	70.9(2)
PCy_3, **4**	170	4.8839(3)	2.838(4)	169.9(1)	155.0(6)

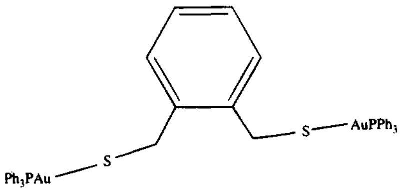
of 2.838(4) Å shows only a slight weakening when compared to complexes **1**−**3**. Complex **4** also shows the smallest deviation from linearity for the three coordinate gold(I) center. In compounds **1**−**3**, Au(1)-S(2) interactions can occur with concommitant Au(2)−S(1) separation with relatively small motions and while maintaining the relatively short Au···Au distance. In **3** either Au(2)−S(1) separation (bond rupture) or pyramidal S(1) inversion must take place to exchange Au−P units. The latter process causes steric strains to develop between the bulky phosphines since both gold atoms become positioned closer together as a result.

The lack of any direct systematic relationship between the phosphine cone angle and the molecular geometry in this series of complexes with a discontinuity appearing when the bulk is large enough to prevent Au···Au interaction appears to confirm the idea that electronic factors, not steric features, are responsible for the irregular geometries observed.[1] Electron delocalization across the 1,2-dithiolene framework appears to be responsible for the formation of the three-coordinate Au center. During the preparation of these complexes[10] it was also found possible to structurally characterize the 1,2-xylenedithiol "open ring" analog, $Au_2[SCH_2(C_6H_4)CH_2S](PPh_3)_2$. The structure of this

---

(10) Dávila, R. M. Ph.D. Dissertation, Texas A&M University, 1993. Details of this result can be obtained from the Texas A&M library or by writing the author. The structure will be published after some further studies are completed of related dithiol compounds. The lack of any intramolecular Au···Au interaction appears surprising in view of a favorable entropy for this to occur but steric constraints and crystal packing forces probably are involved. Appropriate tests are currently underway.

complex shows two S−Au−P chains in a trans orientation (structure **I**). Here the distance between the two gold(I) atoms



I

is 6.243(2) Å with **no** "extra" Au−S interaction present. The shortest Au−Au vector in the structure is 5.54 Å. No intermolecular contacts are detected. The methylene units not only define the orientation of the S−Au−P chains but prevent any electronic delocalization of the type present in the 1,2-dithiolenes. There is no irregularity in the coordination about the Au atoms.

Acknowledgment. This work has been supported by the National Science Foundation, CHE 9300107, the Welch Foundation and the Advanced Research Program of the State of Texas. R.M.D. acknowledges the receipt of a General Electric Teaching Incentive grant, A.P.E. acknowledges a Ministerio de Educacion y Cienca fellowship from the Fulbright Commission and L.K. received funding from the NSF program supporting research for high school teachers administered by the Texas Alliance for Science and Mathematics Education.

Supplementary Material Available: For 1−4, text detailing the structure determination, tables of crystallographic data, atomic coordinates, thermal parameters, and bond distances and angles, and figures showing the structures (36 pages). Ordering information is given on any current masthead page. Tables of F_o and $\sigma(F)$ (64 pages) are available from J.P.F. upon request.

---

(11) **Note Added in Proof.** Since submission of this paper, a crystalline modification of $[Au_2(MNT)PPh_3]\cdot 2THF$ has been found which contains a symmetric disposition of the two phosphine−gold moieties bonded to the MNT. It was crystallized from THF layered with diethyl ether. Important distances and angles found for comparison with those in Table 10: Au⋯Au, 3.092(1) Å; Au−S, 3.273(3) Å; S−Au−P angle, 170.9(1)°; Au−S−C−C torsion, −42(1)°. Crystallographic parameters: Monoclinic, $C2/c$ (No. 15); $a = 23.394(5)$, $b = 14.601(2)$, $c = 16.695(6)$ Å; $\beta = 126.81(1)$°; $V = 4566(1)$ Å^3, $Z = 4$, $d = 1.750$ g/cm^3, $R = 0.0461$, $R_w = 0.0584$.