Structural Isomers of $[Au(CH_2)_2PPh_2]_2Br_4$. 2.[1] Crystal Structures of *cis/cis*-$[Au(CH_2)_2PPh_2]_2Br_4$ and the Cationic A-Frame $[(\mu\text{-}Br)(Au(CH_2)_2PPh_2)_2Br_2][IBr_2]$

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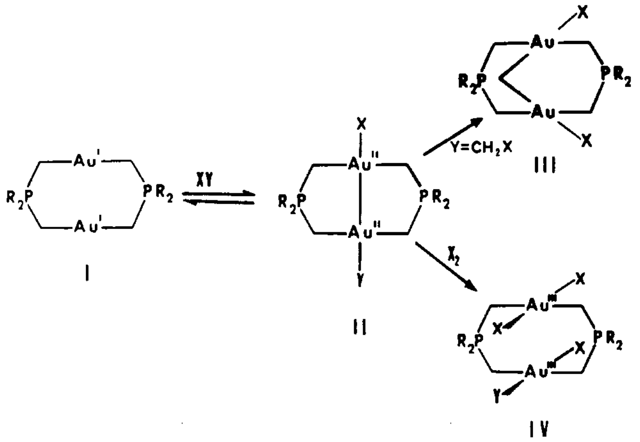
Two new structural forms of Au^{III} dimers, each derived from the oxidation of the parent compound $[Au^I(CH_2)_2PPh_2]_2$, have been characterized crystallographically. $[(\mu\text{-}Br)(Au(CH_2)_2PPh_2)_2Br_2][IBr_2]$ (**1**) is an A-frame cationic species with a bridging halogen atom. *cis/cis*-$[Au(CH_2)_2PPh_2]_2Br_4$ (**2**) is an Au^{III} dimer with a cis geometry for both metal centers. Data for **1**: Monoclinic, $P2_1/c$ (No. 14), $a = 9.582(5)$ Å, $b = 32.551(9)$ Å, $c = 12.634(5)$ Å, $\beta = 109.91(3)°$, $V = 3705(2)$ Å^3, $Z = 4$, $R = 0.084$ for 156 parameters (phenyl rings refined as fixed hexagons). Data for **2**: Monoclinic, $P2_1/c$ (No. 14), $a = 8.068(2)$ Å, $b = 16.815(10)$ Å, $c = 11.991(4)$ Å, $\beta = 108.96(2)°$, $V = 1539(1)$ Å^3, $Z = 2$, $R = 0.046$ for 69 parameters (phenyl rings refined as fixed hexagons). A reaction scheme stressing the role of these new species in the redox chemistry of the dinuclear gold ylide system is proposed.

Introduction

The chemistry of the digold complex[2] $[Au(CH_2)_2PR_2]_2$ (**I**), R = Me, Et, *t*-Bu, and Ph, is now well established (Scheme I), particularly in the case of R = Ph, several derivatives of which have been examined crystallographically. It undergoes oxidative addition reactions with a variety of small molecules XY to form, in the first step, Au^{II} metal-metal-bonded species **II**.[3] When X = halogen and Y = CH_2X a further intramolecular redox rearrangement[3e] generates the $(\mu\text{-}CH_2)Au^{III}_2$ A-frame complexes **III**.[3d,4] Oxidation of complexes **II** by halogens yields the type **IV** Au^{III} dimers. To this date only four of the latter complexes have been structurally characterized: X = Cl, Y = CCl_3;[3g] X = Br, Y = $CHCl_2$;[5a] X = Y = Cl;[5b] X = Y = Br.[1,6] Some reactions involving opening of the organometallic ring also have been reported.[7]

Dimeric Au^{III} complexes possessing one metal atom with a trans and one with a cis geometry were obtained from the reactions[1,5] of $[Au(CH_2)_2PPh_2]_2Cl_2$ with $SnCl_2$ and $[Au(CH_2)_2PPh_2]_2(CH_2CF_3)I$ with Br_2. In neither case is it known whether the structurally characterized cis/trans products were formed directly from the reaction or subsequently from the isomerization of their corresponding trans/trans analogues. The isomerization of $[Au(CH_2)_2PPh_2]_2Br_4$ from trans/trans to cis/trans geometry has been observed[1,8] in $CDCl_3$.

Scheme I



An interesting aspect of the chemistry of the type **IV** tetrahalide species is their 2-electron reduction, which can lead to Au^{II} products or mixed-valence, Au^I/Au^{III}, species, depending on the reducing agent.[9,10]

Continuing our investigation of the properties of the +3 oxidation state complexes of this system, we have identified and characterized two novel structural forms: a cationic species with a bridging bromide atom $[(\mu\text{-}Br)(Au(CH_2)_2PPh_2)_2Br_2][IBr_2]$ (**1**) and the *cis/cis*-$[Au(CH_2)_2PPh_2]_2Br_4$ (**2**). With knowledge of these structures, as well as those of the recently described[6,10] *trans/trans*-$[Au(CH_2)_2PPh_2]_2Br_4$ (**3**) and $Au^I[\mu\text{-}(CH_2)_2PPh_2]_2Au^{III}Br_2$, we propose a reaction scheme that may provide some further understanding of the chemistry of these digold systems.

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Table I. Crystallographic Data for **1** and **2**

	1	**2**
formula	$C_{28}H_{28}Au_2Br_5IP_2$	$C_{28}H_{28}Au_2Br_4P_2$
fw	1346.56	1139.76
space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
a, Å	9.582(5)	8.068(2)
b, Å	32.551(9)	16.815(10)
c, Å	12.634(5)	11.991(4)
β, deg	109.91(3)	108.96(2)
V, Å^3	3705(2)	1539(1)
Z	4	2
d_{calc}, g cm^{-3}	2.41	2.46
μ(Mo Kα), cm^{-1}	147.7	147.8
radiation (λ, Å)	monochromated in Mo Kα (0.710 69)	
temp, K	293	293
trans factors, max, min	0.055, 0.032	0.864, 0.520
R,[a] R_w[b]	0.084, 0.083	0.046, 0.055

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = [\Sigma\sqrt{w}(|F_o| - |F_c|)]/\Sigma\sqrt{w}|F_o|$; $w^{-1} = [\sigma^2(|F_o|) + g|F_o|^2]$.

Experimental Section

All reactions were carried out under an argon atmosphere using Schlenk techniques.[11] All solvents were dried and distilled before use. The ^{1}H-NMR spectra were recorded on a Varian XL-200 at 20 °C in $CDCl_3$ solvent.

$[(\mu$-Br)(Au(CH$_2$)$_2$PPh$_2$)$_2$Br$_2$][IBr$_2$] (1). Single crystals of **1** were obtained by slow Et_2O diffusion into the CH_2Cl_2 reaction mixture of $[Au(CH_2)_2PPh_2](CH_2CF_3)I$ and Br_2.[5a] However, the major products of this reaction, which has been described elsewhere,[5a] are **3** and *cis/trans*-$[Au(CH_2)_2PPh_2]_2(CH_2CF_3)Br_3$.

***cis/cis*-[Au(CH$_2$)$_2$PPh$_2$]$_2$Br$_4$ (2). Method a.** To 20 mg of $[Au^{II}(CH_2)_2PPh_2]_2I_2$[3b] in 2 mL of CH_2Cl_2 was added an equimolar amount of Br_2 dissolved in CH_2Cl_2. The reaction mixture was stirred for 12 h. At the end of this period, the solvent was removed and the orange product dried under vacuum. Slow evaporation (ca. 4 weeks) of a 3-mL CH_2Cl_2 solution of this product afforded approximately equal amounts of red crystals of $[Au^{II}(CH_2)_2PPh_2]_2Br_2$ (by ^{1}H NMR[2b]) and yellow crystals of complex **2**, which could be separated physically using visual selection in 30% yield. Data for **2**: ^{1}H NMR δ 7.35–7.95 (m, Ph), 3.27 ppm (d, $-CH_2-$, J_{HP} = 11.2 Hz).

Method b. To a CH_2Cl_2 solution of 20 mg of complex **3** was added approximately 0.01 mol of I_2. The dark red solution was stirred for 2 h, and the solvent as well as the excess of I_2 were removed under vacuum. Slow diffusion of diethyl ether into a CH_2Cl_2 solution of this product afforded orange crystals of *cis/trans*-$[Au^{III}(CH_2)_2PPh_2]_2Br_4$ (by a unit cell determination[1]). The crystals were placed in an NMR tube and dissolved in $CDCl_3$. The ^{1}H NMR spectrum, recorded immediately after dissolution, contained resonances between 2.73 and 3.45 ppm. The solution was kept in the NMR tube, and its spectrum was recorded again 5 days later, showing only one doublet, centered on 3.27 ppm, attributed to complex **2**.

Method c. A 20-mg amount of complex **3** and 15 mL of CH_2Cl_2 were placed in a round-bottomed flask fitted with a reflux condenser. The mixture was heated and held at reflux temperature for 6 h. The solvent was removed under vacuum, the yellow product was dissolved in $CDCl_3$, and its ^{1}H NMR spectrum was recorded: $[Au^{II}(CH_2)_2PPh_2]_2Br_2$ to *cis/cis*-$[Au(CH_2)_2PPh_2]_2Br_4$ ratio 2:1 (by integration of the respective resonances at 1.90 and 3.27 ppm) plus some minor unidentified decomposition products.

X-ray Crystallography

The X-ray analyses of **1** and **2** were carried out with a Nicolet R3m/E automated four-circle diffractometer and SHELXTL 5.1 software implemented on an Eclipse S140 minicomputer. Single crystals appropriate for X-ray study were mounted atop glass fibers at random orientation for data collection. Initial cell parameters were determined by using orientation reflections obtained from photographic data and were confirmed by axial photographs and a Delaunay reduction. Accurate unit cell dimensions were calculated from the setting angles of high-angle reflections. The intensity data were corrected for Lorentz and polarization effects and standard decay. An empirical absorption correction based on azimuthal scans of reflections spanning a range of 2θ values was applied. Systematically absent data suggested the monoclinic space group $P2_1/c$ for both structures, and this was confirmed by successful refinement. The only suitable crystal of **1** was of marginal quality, as it had been exposed to a range of temperatures and pressures, which precluded data collection beyond 2θ = 40°. Initial gold atom positions were determined from sharpened Patterson maps; all other non-hydrogen atoms were found in Fourier difference maps. Hydrogen atoms were included in the structure of **2** at calculated positions (C–H = 0.96 Å) and were refined with fixed thermal parameters. All gold, halogen, and phosphorus atoms of **1** and **2** were refined anisotropically. Phenyl groups were refined as regular hexagons (C–C = 1.395 Å) for **1**. Unfortunately, the poor crystal quality makes light-atom positions less well determined than desirable. This is reflected in Tables II and IV. However, a better crystal was not available. Crystallographic data pertaining to **1** and **2** are listed in Table I. Atomic coordinates and equivalent isotropic thermal parameters for **1** and **2** are listed in Tables II and III, while important angles and distances are listed in Tables IV and V.

Table II. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) for $[(\mu$-Br)(Au(CH$_2$)$_2$PPh$_2$)$_2$Br$_2$][IBr$_2$] (**1**)[a]

atom	x	y	z	U_{iso}[b]
Au(1)	9550(4)	1539(1)	2224(4)	122(2)*
Au(2)	6994(5)	1001(1)	2280(4)	150(3)*
Br	7370(12)	1309(4)	589(8)	155(7)*
Br(3)	466(16)	1927(4)	−173(11)	212(9)*
Br(1)	11925(24)	1784(6)	3420(17)	336(16)*
Br(2)	5617(29)	710(7)	3461(22)	404(21)*
Br(4)	3899(14)	652(6)	−422(11)	234(10)*
I	2240(8)	1293(3)	9658(6)	179(5)*
P(1)	6943(29)	1977(7)	2960(19)	107(15)*
P(2)	10207(33)	555(9)	2571(22)	147(18)*
C(1)	8315(79)	2066(22)	2376(56)	83(27)
C(2)	10728(95)	1053(25)	1923(70)	123(32)
C(3)	5801(97)	1562(29)	2285(72)	139(34)
C(4)	8217(89)	479(25)	1979(69)	126(33)
C(11)	6004(64)	2687(32)	3437(57)	184(45)
C(12)	5192(64)	3049(32)	3334(57)	171(41)
C(13)	3942(64)	3116(32)	2382(57)	144(37)
C(14)	3504(64)	2820(32)	1534(57)	305(75)
C(15)	4316(64)	2457(32)	1638(57)	518(138)
C(16)	5566(64)	2391(32)	2589(57)	153(39)
C(21)	6639(60)	1696(21)	4939(84)	160(39)
C(22)	7108(60)	1646(21)	6105(84)	213(50)
C(23)	8521(60)	1777(21)	6772(84)	128(34)
C(24)	9464(60)	1957(21)	6273(84)	169(41)
C(25)	8995(60)	2007(21)	5107(84)	213(49)
C(26)	7583(60)	1876(21)	4440(84)	138(35)
C(31)	12066(100)	172(21)	1646(62)	176(44)
C(32)	12726(100)	−162(21)	1307(62)	183(44)
C(33)	12312(100)	−561(21)	1467(62)	216(51)
C(34)	11238(100)	−628(21)	1966(62)	160(40)
C(35)	10578(100)	−295(21)	2306(62)	266(64)
C(36)	10992(100)	105(21)	2146(62)	152(38)
c(41)	12439(97)	455(17)	4717(80)	154(39)
C(42)	13022(97)	532(17)	5872(79)	182(45)
C(43)	12210(97)	761(17)	6393(79)	106(30)
C(44)	10815(97)	914(17)	5760(79)	274(66)
C(45)	10231(97)	837(17)	4606(79)	246(59)
C(46)	11043(97)	608(17)	4084(79)	139(36)

[a] Estimated standard deviations in the least significant digits are given in parentheses. [b] For values with asterisks, the equivalent isotropic U is defined as one-third of the trace of the U_{ij} tensor.

The modeling of $[Au(CH_2)_2PPh_2]_2Br_4$ was done using the CAChe molecular modeling package from TETRONIX (CAChe (Computer Aided Chemistry), CAChe Scientific, Inc., a TEKTRONIX company). The structure of the trans/trans isomer was entered into the molecular editor using the coordinates obtained from the single-crystal X-ray structure. The geometry was then altered to create those of the cis/cis and the cis/trans isomers. All structures were then optimized using the MM2 program in the CAChe package. The augmented MM2 parameters provided by CAChe to handle non-hydrocarbons were used. The conjugate gradient was used for the initial optimization and then the block diagonal method to get the final energy minimum. The final energies show that the trans/trans isomer has the highest energy with the cis/trans being

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Table III. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) for *cis/cis*-$[\mathrm{Au(CH_2)_2PPh_2}]_2\mathrm{Br_4}$ (**2**)

atom	*x*	*y*	*z*	U_{iso}[b]
Au	2055(1)	−16(1)	4307(1)	34(1)*
Br(1)	173(3)	1179(2)	4144(3)	47(1)*
Br(2)	93(4)	−458(2)	2355(3)	55(1)*
P	4959(8)	1102(5)	6341(7)	37(3)*
C(1)	3459(32)	285(17)	5995(24)	43(8)
C(2)	3468(31)	−1020(18)	4461(25)	41(7)
C(11)	3938(20)	2556(11)	5181(13)	34(7)
C(12)	3132(20)	3299(11)	5074(13)	60(9)
C(13)	2243(20)	3518(11)	5849(13)	70(10)
C(14)	2160(20)	2993(11)	6730(13)	52(8)
C(15)	2965(20)	2250(11)	6837(13)	59(9)
C(16)	3854(20)	2032(11)	6062(13)	30(6)
C(21)	7081(22)	1812(9)	8380(15)	46(8)
C(22)	7942(22)	1865(9)	9592(15)	56(8)
C(23)	7853(22)	1235(9)	10328(15)	52(8)
C(24)	6904(22)	552(9)	9852(15)	45(7)
C(25)	6042(22)	499(9)	8640(15)	35(6)
C(26)	6131(22)	1129(9)	7904(15)	35(6)

[a] Estimated standard deviations in the least significant digits are given in parentheses. [b] For values with asterisks, the equivalent isotropic *U* is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

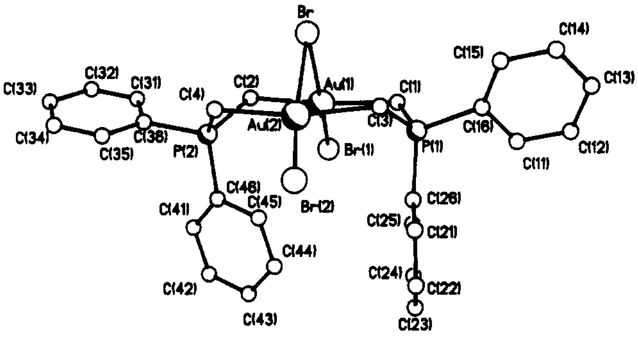

Figure 1. Structure of $[(\mu\text{-Br})(\mathrm{Au(CH_2)_2PPh_2})_2\mathrm{Br_2}][\mathrm{IBr_2}]$ (**2**) with the crystallographic numbering scheme. All atoms have arbitrary radii. The $\mathrm{IBr_2}$ anion is not shown.

about 0.26 kcal below it in energy and the cis/cis being approximately 8.9 kcal below the trans/trans form.

Results

These studies of dimeric $\mathrm{Au^{III}}$ halide complexes derived from the parent compound $[\mathrm{Au(CH_2)_2PPh_2}]_2$ have resulted in the characterization of two structural types novel to the chemistry of this system. Of particular importance is the recognition of the existence of compound **1**, since this cationic A-frame species may be involved in redox and isomerization processes of $\mathrm{Au^{III}}$ dimers. Due to the poor quality of the available crystal, the structural characterization of this complex is not entirely satisfactory with regard to the parameter-to-data ratio, the esd's of measured bonds and angles, and the atomic thermal parameters. However, in view of the importance of this species and the fact that the crystallographic work determines unambiguously its molecular structure, we are presenting here the results obtained.

Structural Description. $[(\mu\text{-Br})(\mathrm{Au(CH_2)_2PPh_2})_2\mathrm{Br_2}][\mathrm{IBr_2}]$ (1). The cationic complex **1** crystallizes in the monoclinic space group $P2_1/c$ with a whole anion–cation pair per asymmetric unit. The organometallic A-frame cation is in a boat configuration (Figure 1) with C_{2v} symmetry, like all other A-frame complexes[3d,13,14] formed from the complex $[\mathrm{Au^I(CH_2)_2PPh_2}]_2$, while the $\mathrm{IBr_2}$ anion is linear. The metal–metal distance, 3.033(7) Å, is the shortest distance measured between two $\mathrm{Au^{III}}$ atoms bridged by $\mathrm{CH_2PR_2CH_2^-}$ ligands. The coordination of the gold atoms (Figure 2) shows significant deviations from a square-planar geometry. A bromine atom bridges symmetrically the two gold centers, Au–(μ-Br) = 2.49(1) and 2.51(1) Å, while the difference between the terminal Au–Br bonds, 2.41(2) and 2.50(3) Å, is within experimental error.

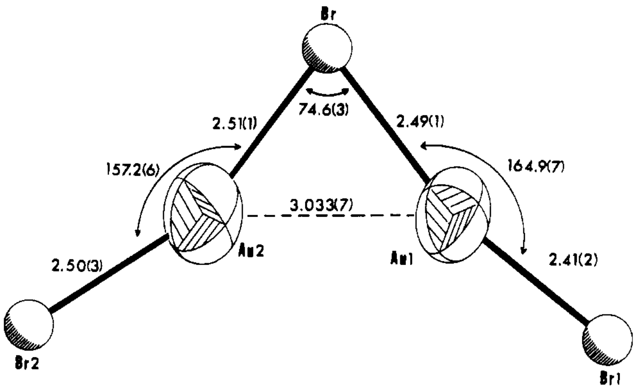

Figure 2. (μ-Br)$\mathrm{Au_2Br_2}$ part of the structure of **2**.

Table IV. Selected Distances (Å) and Angles (deg) for $[(\mu\text{-Br})(\mathrm{Au(CH_2)_2PPh_2})_2][\mathrm{IBr_2}]$ (**1**)

Distances			
Au(1)···Au(2)	3.033(7)	I–Br(4)	2.64(2)
Au(1)–Br	2.49(1)	P(1)–C(1)	1.77(9)
Au(2)–Br	2.51(1)	P(1)–C(3)	1.77(9)
Au(1)–Br(1)	2.41(2)	P(1)–C(16)	1.81(8)
Au(2)–Br(2)	2.50(3)	P(1)–C(26)	1.81(6)
Au(1)–C(1)	2.11(7)	P(2)–C(2)	1.90(9)
Au(1)–C(2)	2.01(8)	P(2)–C(4)	1.84(9)
Au(2)–C(3)	2.08(9)	P(2)–C(36)	1.78(8)
Au(2)–C(4)	2.15(9)	P(2)–C(46)	1.86(9)
I–Br(3)	2.72(2)		
Angles			
Br–Au(1)–Br(1)	164.9(7)	Br(2)–Au(2)–C(3)	86(3)
C(1)–Au(1)–C(2)	175(3)	Br(2)–Au(2)–C(4)	102(3)
Br–Au(2)–Br(2)	157.2(6)	Au(1)–C(1)–P(1)	116(4)
C(3)–Au(2)–C(4)	171(4)	Au(1)–C(2)–P(2)	113(5)
Br–Au(1)–C(1)	90(2)	Au(2)–C(3)–P(1)	118(4)
Br–Au(1)–C(2)	87(2)	Au(2)–C(4)–P(2)	111(4)
Br(1)–Au(1)–C(1)	96(2)	C(1)–P(1)–C(3)	110(4)
Br(1)–Au(1)–C(2)	87(2)	C(2)–P(2)–C(4)	109(4)
Br–Au(2)–C(3)	84(3)	Br(3)–I–Br(4)	176.7(6)
Br–Au(2)–C(4)	87(3)	Au(1)–Br–Au(2)	74.6(3)

The terminal bromine atoms, Br(1) and Br(2), appear to deviate by 0.23(2) and 0.41(3) Å, respectively, from the Au(1)–μ-Br–Au(2) plane. However, the large errors associated with bond length measurements in this structure (Table IV) do not allow a meaningful discussion of these differences. The trans C–Au–C angles are fairly linear, while the trans Br–Au–Br angles are 164.9(7) and 157.2(6)°. The Br–Au–Br angles approximate the ones observed in both the $C2/c$ and $P2_1/c$ structures[1,6] of *trans/trans*-$[\mathrm{Au(CH_2)_2Ph_2}]_2\mathrm{Br_4}$. The distortions of square-planar geometry cannot be attributed to any intermolecular or anion–cation interactions. Neither can they be explained by intramolecular repulsions since the Br(1)···Br(2) distance is 7.00(3) Å.

The bridging bromine atom forms an Au–Br–Au angle of 74.6(3)°, smaller than the angles of the analogous (μ-$\mathrm{CH_2}$)$\mathrm{Au_2}$ species[3d,13,14] but within the expected range for a d^8-metal A-frame. There are no examples of structurally characterized μ-Br A-frame d^8-metal complexes for comparison. The corresponding angles measured for (μ-X)[M(dppm)]$_2$ complexes are 82.38(5)° for X = Cl and M = $\mathrm{Rh^I}$ with Rh···Rh = 3.1520(8) Å,[15] 67.9(2)° for

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(13) (a) Murray, H. H.; Raptis, R. G.; Porter, L. C.; Fackler, J. P., Jr. The Crystal Structure of (μ-$\mathrm{CH_2}$)$[\mathrm{Au(CH_2)_2PPh_2}]_2\mathrm{Br_2}\cdot[\mathrm{Au(CH_2)_2PPh_2}]_2\mathrm{I_2}$. To be submitted for publication. (b) Raptis, R. G.; Porter, L. C.; Fackler, J. P., Jr. The Crystal Structures of (μ-$\mathrm{CH_2}$)$[\mathrm{Au(CH_2)_2PPh_2}]_2\mathrm{I_2}$ and (μ-$\mathrm{CH_2}$)$[\mathrm{Au(CH_2)_2PPh_2}]_2\mathrm{I_2}\cdot\mathrm{I_2}$. To be submitted for publication.

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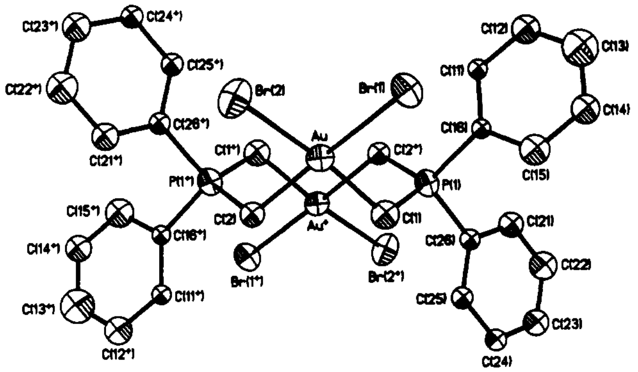


Figure 3. ORTEP drawing of *cis/cis*-$[Au(CH_2)_2PPh_2]_2Br_4$ (**2**) with the crystallographic numbering scheme. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are not shown for clarity.

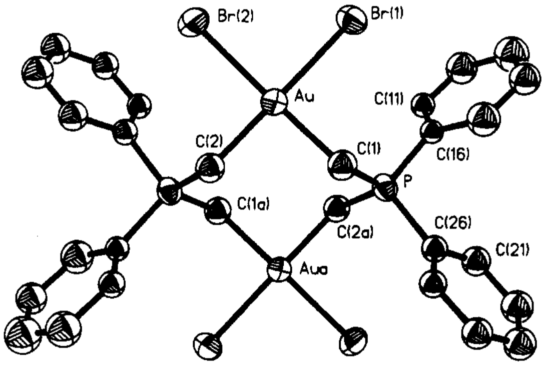


Figure 4. View of the structure of **2** perpendicular to the metal–metal axis depicting the long intramolecular Au···Au distance.

X = I and M = Pd^{II} with Pd–Pd = 3.01(1) Å,[16] and 65.56(5)° for X = I and M = Pt^{II} with Pt–Pt = 2.931(2) Å.[17] An Au–I–Au angle of 55.6(1)° was seen in $(\mu\text{-I})[Au(dppm)]_2[I]$ with an $Au^I \cdots Au^I$ separation of 2.948(2) Å.[18] Two structural features of the Au_2Br_3 unit of complex **1**—the short metal–metal distance and the <180° X–M–X angle (Figure 2)—bear striking similarities to the $(\mu\text{-I})Pd_2(CH_3)I$ portion[16] of the cationic complex $[(\mu\text{-I})Pd_2(dppm)_2(CH_3)I][BF_4]$. A bonding interaction between the two Pd^{II} atoms has been proposed for the latter. Similar structural observations for dinuclear Rh^I complexes have been reported by Cowie.[15]

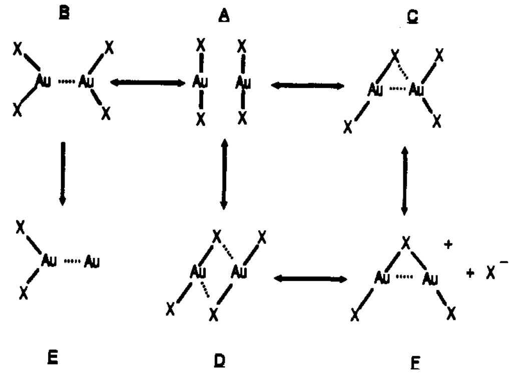
***cis/cis*-$[Au(CH_2)_2PPh_2]_2Br_4$ (2).** The dimeric Au^{III} tetrabromide complex **2** crystallizes in the monoclinic space group $P2_1/c$ with one-half molecule per asymmetric unit. The dimer is positioned on a crystallographic center of symmetry midway between the two gold atoms with bridging ylides cis on each Au^{III} atom. The eight-membered $(\text{-Au-C-P-C-})_2$ ring is twisted into a configuration of C_{2h} symmetry, novel to this system (Figure 3). The intramolecular gold–gold separation, 4.497(4) Å, the longest one seen for any complex derived from $[Au^I(CH_2)_2PPh_2]_2$, is even longer than the intermolecular metal–metal distance, 4.146(4) Å (Figure 4). The coordination of the gold atoms shows insignificant deviations from ideally square-planar geometry (Table V). The AuC_2Br_2 unit is planar within 0.08 Å with cis angles between 89.0(1) and 91(1)° and trans angles between 173(1) and 176(1)°. The two *cis*-AuC_2Br_2 planes of the molecule are parallel to each other but not cofacial. The Au–Br bond lengths, 2.488(4) and 2.475(2) Å, are in good agreement with those measured[5] in the *cis*-$AuBr_2$ part of *cis/trans*-$[Au(CH_2)_2PPh_2]_2(CH_2CF_3)Br_3$, 2.470(3) and 2.476(4) Å.

It should be noted that eight-membered metallocycles with cis/cis geometries have been identified by X-ray crystallography[19] in the structures of $[Pt(dppm)]_2Me_4$ and $[Pt(dmpm)]_2Me_4$ and other molecules.

Table V. Selected Distances (Å) and Angles (deg) for *cis/cis*-$[Au(CH_2)_2PPh_2]_2Br_4$ (**2**)

	Distances		
Au···Au′	4.497(4)	P–C(1)	1.79(3)
Au–Br(1)	2.488(4)	P–C(2)	1.83(3)
Au–Br(2)	2.475(2)	P–C(16)	1.77(2)
Au–C(1)	2.04(3)	P–C(26)	1.80(2)
Au–C(2)	2.01(3)		
	Angles		
Br(1)–Au–Br(2)	88.9(2)	Au(1)–C(2)–P′	119(2)
C(1)–Au–C(2)	90(1)	C(1)–P–C(2)′	110(1)
Br(1)–Au–C(1)	90.3(8)	C(1)–P–C(16)	112(1)
Br(2)–Au–C(2)	90.3(7)	C(1)–P–C(26)	111(1)
Br(1)–Au–C(2)	176.6(8)	C(2)′–P–C(16)	110(2)
Br(2)–Au–C(1)	173.1(9)	C(2)′–P–C(26)	109(1)
Au(1)–C(1)–P	122(1)	C(16)–P–C(26)	103.6(8)

Scheme II



Discussion

The two known crystal structures[1,6] of the *trans/trans*-$[Au(CH_2)_2PPh_2]_2Br_4$ provide an opportunity to study differences in its ground-state structure brought about by slight variations in the environment—crystallization with or without interstitial solvent molecules. As the equilibrium distribution of atoms for a molecule at a given temperature is represented by at least one crystal structure, other structures obtained from crystals produced under a variety of conditions may map deformations associated with reaction pathways. We recognize, of course, that the two crystal structures available here do not constitute even a minimum basis for a structure-correlation analysis.[20] However, when this information is considered along with the structures of complexes **1** and[10] $Au^I[\mu\text{-}(CH_2)_2PPh_2]_2Au^{III}Br_2$ (Scheme II), conclusions leading "from crystal statics to chemical dynamics"[20] can be suggested.

Consider the hypothetical Au_2Br_4 species **A** in Scheme II, with an idealized rectangular AuC_2X_2 geometry about each Au^{III} center. (The ylide ligands have been removed in this scheme.) In the plane perpendicular to the C–Au–C axes, there are three deformations which formally require no Au–X stretching motion. They are a "scissors" motion, **A** → **B**, a "windshield wiper" motion **A** → **D**, and the combined motion of rotation and bend at the two Au^{III} centers. The species **B** and **D** represent idealized geometries of the two crystallographically characterized conformers of $[Au(CH_2)_2PPh_2]_2Br_4$, the $P2_1/c$ and $C2/c$ structures, respectively. The deformation leading to species **B** is the vibrational mode

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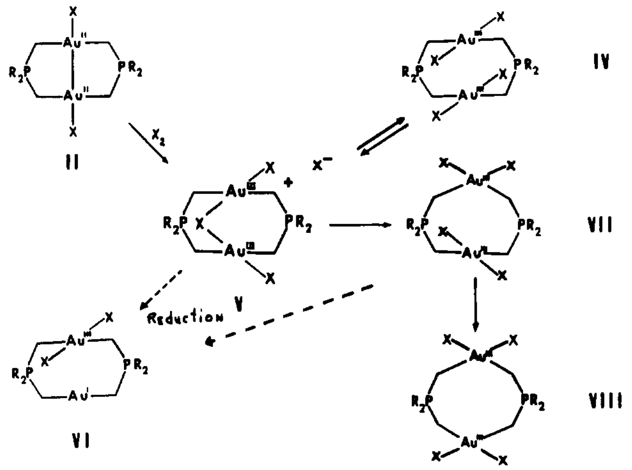
required for the elimination of X_2 from trans positions of a single metal center by a concerted mechanism **B** → **E**. The feasibility of such a process is further supported by the weakening of the Au–X bonds observed in the crystal structure. The reverse process, concerted trans-oxidative addition of halogens to mononuclear Au^I complexes, has been proposed[21] from kinetic studies of the reactions of Cl_2, Br_2, and I_2 at mononuclear Au^I centers. However, even though the synthesis[10] of the Au^I/Au^{III} complex $[Au(CH_2)_2PPh_2]_2Br_2$ was achieved from the *trans/trans*-Au_2Br_4 species, representing an overall process equivalent to **B** → **D**, there is no evidence that this process occurs by a concerted mechanism.

While the **A** → **D** transformation may or may not be productive chemically, the **A** → **C** deformation, a combination of scissors and windshield wiper motions at the two centers, is suggestive[1] of a subsequent formation of a μ-X species **F**. The structural characterization of complex **1** supports this suggestion, particularly as the crystal of this cationic A-frame compound was grown from a solution which also contained the face-to-face Au_2Br_4 species. Interconversions of cofacial and A-frame species have been reported,[17,22,25] in the chemistry of Rh^I–, Ir^I–, Pd^{II}–, and Pt^{II}–dppm dimers. The **A** → **D** process misaligns the filled $5d_{z^2}$ orbitals of the square-planar Au^{III} atoms, thus reducing their overlap. This metal–metal orbital overlap has been proposed[6] to be the cause of the "trigonal-bipyramidal-like" geometry and the long Au–Br bonds of the $P2_1/c$ structure of **3**. Therefore, the $C2/c$ structure[1] of this complex deviates from the ideal semibridging geometry of type **D** only in that it has a Br–Au–Br angle of 164.3(1)° necessary to accommodate the steric requirements of the syn-Br atoms by keeping them at a distance of 3.726(5) Å (the sum of their van der Waals radii). While no species representing the idealized intermediate **C** is known structurally, nucleophilic halide interactions at square-planar d^8 centers are well established kinetically.[26a]

Reactivity studies of group-9 and -10 cationic, μ-halide species have shown[26b] that a common feature of their chemistries is the activation of a variety of small molecules at their endo-site. It is not known whether complex **1** will demonstrate similar chemistry. All attempts to date, by the authors and others,[1] to synthesize systematically $(\mu\text{-}X)Au_2X_2^+$ species from their neutral Au_2X_4 analogues (e.g. reactions with alkali or silver salts) have failed, and the products of these reactions have been, invariably, the reduced $Au^{II}{}_2X_2$ metal–metal-bonded dimers. In fact, the very structure of complex **1**, with the short Au···Au distance and unusual geometry of the Au_2X_3 unit (Figure 2), suggests the formation of a metal–metal bond. It may not be coincidental that the structurally characterized form of this cationic A-frame had an IBr_2^- counterion, which is an excellent oxidizing agent. At the present time, it is not known[5] whether complex **1** was formed by an isomerization of complex **3** or directly from the oxidation of a Au^{II} complex. Both processes are reasonable and have precedence[24,25] in the chemistry of Pt- and Pd–dppm dimers.

Besides the **C** → **F** process, the $Au_2X_3{}^+X^- = Au_2X_4$ equilibrium can involve association of the X^- ion with **F** in a manner to generate the *trans/trans*-Au_2X_4 complex **D**. The trans/trans → cis/trans isomerization of the Au^{III}-tetrahalide dimer has been reported[1,8] to occur in $CDCl_3$. The cis/trans → cis/cis isomerization also takes place in $CDCl_3$ over a period of a few days, while the process trans/trans → cis/cis occurs readily in refluxing CH_2Cl_2. It appears that in this solvent the cis/cis isomer is thermodynamically more stable than the trans/trans and cis/trans Au^{III} tetrahalide species. As stated above, molecular modeling calculations involving MM2 programming using the CAChe system suggest that the cis/cis geometry is considerably more stable than the cis/trans and trans/trans geometries. Hence this product is the kinetic and not thermodynamic product of the oxidation of the metal–metal-bonded Au^{II} dimers.

Scheme III



The trans to cis isomerization of mononuclear AuR_3L, L = phosphine, Au^{III} complexes also has been reported.[27] Phosphine dissociation is involved in the process. Assuming with Kochi that a 3-coordinate Au^{III} center is required for cis/trans isomerization, **F** becomes a reasonable intermediate. Rupture of a bridging Au–X bond in **F** leaves one Au^{III} center 3-coordinate making the proposed "T" to "Y" rearrangement about this center facile.

The platinum dimer, *cis/cis*-$[Pt(dppm)]_2Me_4$, which is similar to complex **2**, isomerizes[19a] in the opposite direction, namely cis/cis → trans/trans. A cis/trans isomer has not been found yet in the chemistry of d^8 metal–dppm complexes.[28] The very long Au–Au separation (4.5 Å) of the cis/cis complex **2** frees the gold atoms from any forced interaction as seen in the structure of complex **3**. The gold centers of the cis/cis complex have square-planar geometry typical of mononuclear d^8 metals. The chemistry of the cis/cis isomer is expected to be similar to that of mononuclear Au^{III} complexes, i.e., slow reductive elimination of alkanes[27,29] from an alkylated derivative cis/cis-$[Au(CH_2)_2PPh_2]_2R_4$. A possible 2-electron reductive elimination from a single gold center of complex **2** presents the interesting possibility of forming the cis analogue of the mixed-valence species[10] *trans*-$AuBr_2[\mu\text{-}(CH_2)_2PPh_2]_2Au$, a product not observed to date.

We have recently reported[10] that the reactions of **3** with AgCN and of $[Au^{II}(CH_2)_2PPh_2]_2(CN)_2$ with Br_2 yield the mixed-valence, Au^I/Au^{III}, complex *trans*-$AuBr_2[\mu\text{-}(CH_2)_2PPh_2]_2Au$. In both cases an unidentified Au^{III}/Au^{III} intermediate was observed prior to the formation of the final product. It is possible that this unidentified species is a cationic A-frame and/or a cis/trans type complex containing CN coordination.

Scheme III summarizes current knowledge of the reaction chemistry of this digold system. It ties together the isomers of the $Au^{III}{}_2X_4$ species (**IV**, **V**, **VII**, **VIII**) with the $Au^{II}{}_2X_2$ (**II**) and $Au^I/Au^{III}X_2$ (**VI**) type complexes. The type-**V** complexes appear to play a central role in the chemistry of these d^8 dimers. They

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can be formed by addition of halogens to type-II complexes or by isomerization of type-IV species. The reaction of **3** with I_2, which produces the cis/trans analogue, may have proceeded via the formation of a type-V intermediate with I_2Br as counterion, similar to the crystallographically characterized complex **1**. Depending on the nature of the ligands X and the reaction conditions, reassociation with the counterion X^- can take place either at trans or cis positions[30] (the latter forming the species **VII**). Reductive elimination of X_2 also may occur forming the species **VI**. An X-attack on the μ-X ligand can give X_2 elimination and formation of the known Au^{II} species **II**, present in two of the reactions which formed **2** (vide supra). An X_2 group also can be eliminated from the cis side of type **VII** complexes in a concerted reaction.[29] The reaction of **3** with AgCN which leads to the mixed-valence species may have initially formed a type **V** intermediate by precipitating AgBr. The cis/cis complex **VIII** is the final thermodynamic product of the isomerization process. These types of cis/cis complexes also have been characterized[31] with terminal bidentate chelating dithiolate ligands.

Acknowledgment. We acknowledge the financial support from the National Science Foundation (Grant CHE 8708625) and the Welch Foundation.

Supplementary Material Available: Tables of crystallographic data, bond distances, bond angles, anisotropic thermal parameters, and hydrogen positional parameters for complexes **1** and **2** (7 pages). Ordering information is given on any current masthead page.

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