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Self-Association in Gold Chemistry: A Tetragold(I) Complex Linked by Both Aurophilic and Hydrogen Bonding

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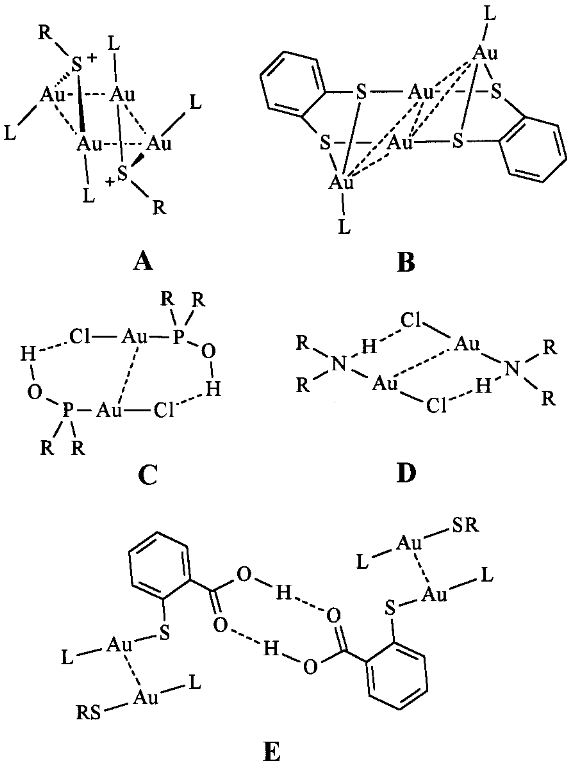
Introduction

The supramolecular chemistry of gold(I) complexes has become an intriguing subject, because many d^{10} gold(I) compounds display interesting photochemistry that may be dependent on the state of aggregation and that has potential applications in electronic, optical, or sensing devices.[1] Self-assembly of gold(I) compounds may be aided by the existence of Au···Au aurophilic attractions, which may have a strength comparable to hydrogen bonding (7−11 kcal/mol).[2] These interactions have a profound influence on the properties, structures and conformations of gold complexes.[3,4] Theory suggests that these Au···Au attractions arise from relativistic London forces, with relative strength predicted to increase with the softness of the ligands,[5] and this is supported by the observation that, in the series of complexes Me$_2$PhPAuX, the Au···Au distances decrease in the order (X = Cl > Br > I).[6] Some developments that are relevant to the present work are described below.

Chart 1



Several complexes of the form [{RS(AuL)$_2$}$_2$]$^{2+}$, with L = a tertiary phosphine ligand, assemble into centrosymmetric six-membered dicationic rings through short Au···Au contacts with thiolate ligands bridging opposite edges above and below the molecular plane, forming a V/ inverted-V configuration (**A**, Chart 1).[7] Furthermore, difunctional alkylthiols have been used to link analogous cationic six-membered rings together to generate extended structures,[8] and eight-membered rings, with S$_4$Au$_4$ cores **B**, were constructed using the dithiols 3,4-dimercaptotoluene and benzene-1,2-dithiol.[9] The complementary forces of Au···Au and hydrogen bonding have resulted in the assembly of dimers, tetramers, chains, and two-dimensional networks such as **C** − **E**.[10,11] Several gold(I) complexes of the P-donor ligands phosphinite, R$_2$(O)P$^-$, and phosphite, (RO)$_2$(O)P$^-$, have been synthesized by fortuitous oxidation or hydrolysis of precursor molecules.[12] Complexes containing the S−Au−P group have been used in gold drugs for the treatment of rheumatoid arthritis, so water-stable complexes of this kind have added interest.[13] Many gold(I) drugs used in chrysotherapy are thought to be oligomers with sulfur atoms in bridging positions,[1,14] and so there is increasing interest in analogous gold

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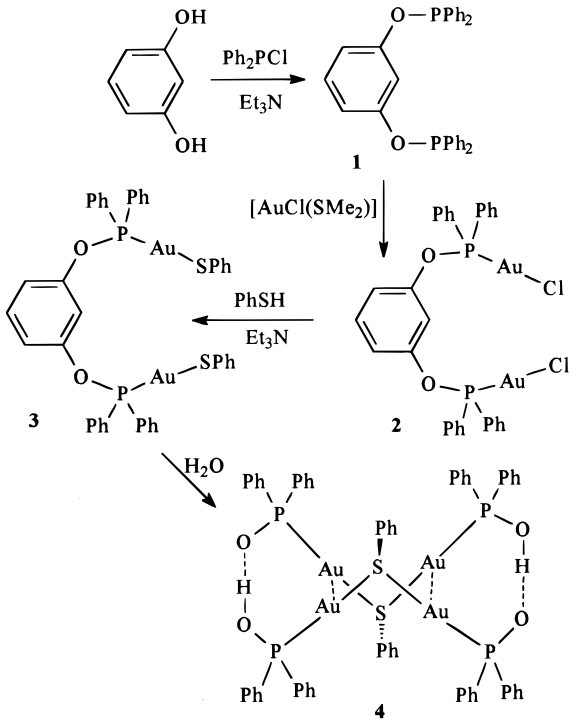
Scheme 1



complexes that include functional groups that are capable of hydrogen bonding.[7,10,12]

This article describes the synthesis of a tetranuclear gold(I) metallacycle containing bridging thiolate ligands, with Au··Au bonding analogous to that in **A**. However, a phosphinous acid/phosphinite ligand combination is also present and gives additional bridging through strong hydrogen bonding between these groups. This combination gives the first neutral complex of type **A** (Chart 1).

Results and Discussion

Reaction of two equivalents of chlorodiphenylphosphine with resorcinol in the presence of triethylamine as base gave the ligand 1,3-bis(diphenylphosphinito)benzene, **1**, as a pale-yellow oil, as expected by analogy with similar syntheses.[15,16] The ^{31}P NMR spectrum of **1** gave a singlet resonance at $\delta = 111.8$, in agreement with the literature values for similar arylphosphinite derivatives,[17] and the mass spectrum gave a parent ion at 478.124 amu, consistent with the expected structure.

The bis(phosphinite) ligand, **1**, reacted with $[AuCl(SMe_2)]$, with displacement of dimethyl sulfide, to form the binuclear gold phosphinite complex, **2**, as illustrated in Scheme 1. Complex **2** was obtained as a colorless crystalline solid, and was characterized by its NMR spectra [$\delta(^{31}P) = 116.7$] and by an X-ray structure determination (Table 1). The structure of **2** is shown in Figure 1, and selected bond distances and angles are presented in Table 2.

Table 1. Crystal Data for Complexes **2** and **4**

	complex **2**	complex **4**
empirical formula	$C_{30}H_{24}Au_2Cl_2O_2P_2$	$C_{90}H_{78}Au_6O_6P_6S_3$
fw	943.27	2719.32
temp	150(2) K	200(2) K
wavelength	0.71073 Å	0.71073 Å
cryst syst, space group	Triclinic, $P\bar{1}$	monoclinic, $P2_1/c$
unit cell dimensions	$a = 10.262(2)$ Å $b = 11.308(2)$ Å $c = 13.882(3)$ Å $\alpha = 69.51(3)°$ $\beta = 77.52(3)°$ $\gamma = 74.99(3)°$	$a = 18.5609(3)$ Å $b = 21.4281(3)$ Å $c = 21.2130(4)$ Å $\alpha = 90°$ $\beta = 90.6420(10)°$ $\gamma = 90°$
volume	1443.4(5) Å^3	8436.4(2) Å^3
Z	2	4
D (calcd)	2.170 mg/m^3	2.141 mg/m^3
abs coeff	10.476 mm^{-1}	10.637 mm^{-1}
F(000)	884	5112
independent reflns	5859 [R(int) = 0.1080]	18517 [R(int) = 0.0980]
data/restraints/param	5859/0/343	18517/0/1003
goodness of fit on F^2	1.046	1.069
R [$I > 2\sigma(I)$]	$R1 = 0.0569$, $wR2 = 0.1585$	$R1 = 0.0530$, $wR2 = 0.1306$

$R1 = \sum||F_o| - |F_c||/\sum|F_o|$. $wR2 = \{\sum[w(F_o^2 - F_c^2)^2/\sum F_o^4\}^{1/2}$

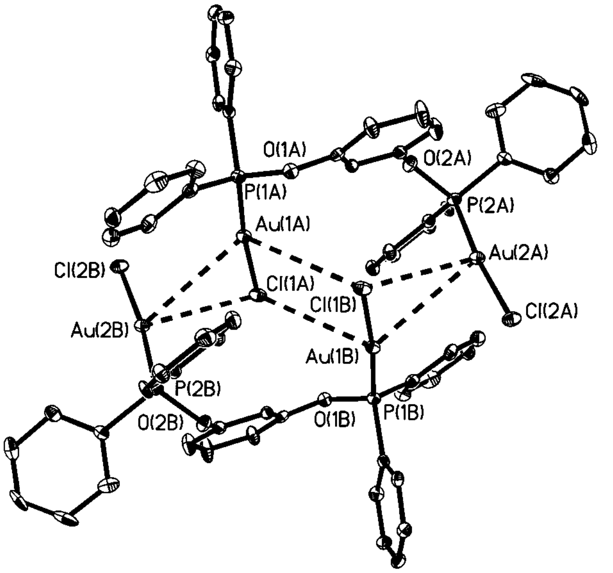


Figure 1. A view of the molecular structure of $[1,3\text{-}C_6H_4(OPPh_2\text{-}AuCl)_2]$, **2**, showing the weakly associated dimers. Hydrogen atoms are omitted for clarity.

Table 2. Selected Interatomic Distances (Å) and Angles (deg) for Compound **2**

Au(1)−P(1)	2.217(3)	Au(2)−P(2)	2.213(3)
Au(1)−Cl(1)	2.284(3)	Au(2)−Cl(2)	2.295(3)
P(1)−O(1)	1.622(8)	P(2)−O(2)	1.618(8)
O(1)−C(1)	1.37(1)	O(2)−C(5)	1.40(1)
P(1)−Au(1)−Cl(1)	173.5(1)	P(2)−Au(2)−Cl(2)	173.6(1)
O(1)−P(1)−Au(1)	113.6(3)	O(2)−P(2)−Au(2)	115.6(3)
C(1)−O(1)−P(1)	123.9(6)	C(5)−O(2)−P(2)	122.1(7)

Molecules of **2** contain two roughly linear gold(I) centers with angles P−Au−Cl = 173.5(1) and 173.6(1)°, and the Au−P [2.217(3) and 2.213(3) Å] and Au−Cl [2.284(3) and 2.295(3) Å] bond lengths are typical of such groupings.[2] The P−O distances of 1.622(8) and 1.618(8) Å are typical for a single bond to oxygen.[18] The molecules form loosely associated dimers, although the shortest gold−gold contact between

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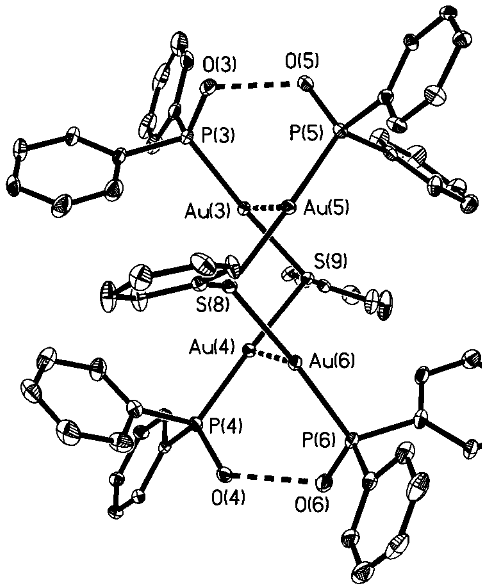

Figure 2. A view of the molecular structure of $[\{Au_2(\mu\text{-}SPh)(PPh_2O)(PPh_2OH)\}_2]$, **4**. Dashed lines indicate the Au··Au and OH··O secondary bonds.

adjacent molecules, d(Au1A··Au2B) = 3.695(1) Å, is slightly longer than the sum of the van der Waals radii (3.6 Å and so is on the edge of the range considered for Au···Au intermolecular bonding.[18] There are also relatively short Au··Cl contacts, Cl1A··Au2B = 3.407(2) Å and Cl1A.··Au1B = 3.616(2) Å, as indicated in Figure 1.

Treatment of **2** with benzenethiol in the presence of triethylamine gave complex **3** as a pale-yellow crystalline powder, as shown in Scheme 1. Complex **3** was characterized by its spectroscopic properties [$\delta(^{31}P) = 124.6$] and by microanalysis. Reaction of **3** with a stoichiometric amount of water in acetone solution led to hydrolysis of the P−O bonds to yield benzenethiol, resorcinol, and the gold(I) complex derivative $[\{Au_2(\mu\text{-}SPh)(PPh_2O)(PPh_2OH)\}_2]$, **4**, as depicted in Scheme 1. It was isolated as colorless prisms, which were stable to air and moisture. Complex **4** was sparingly soluble in nitrobenzene/CH_2Cl_2 solution but insoluble in other common organic solvents and in water. The complex gives $\delta(^{31}P) = 82.4$, in the expected region for a phosphinite gold(I) derivative with P═O···H−O−P bonding.[11] The IR spectrum of **4** shows the presence of a strong absorption band characteristic of the ν(P═O) stretching vibration at 1025 cm^{-1}, which is absent in the IR spectra of **2** and **3**. Complex **4** was also characterized by an X-ray structure determination (Table 1).

The structure of **4** is shown in Figure 2, and selected bond distances and angles are presented in Table 3. The hydrolysis product **4** can be considered to comprise two $Au_2(\mu\text{-}SPh)(PPh_2O)(PPh_2OH)$ units linked by both Au··Au and OH··O secondary bonds. Within each unit, the P−Au−S angles range from 177.37(8) to 175.38(8)°, only a little distorted from linearity. The Au−S [2.335(2) − 2.348(2) Å] and Au−P [2.263(2) − 2.272(2) Å] bond lengths are unremarkable.[19] The angles AuSAu = 97.85(7) and 102.52(8)° are somewhat less than the tetrahedral angle, and the corresponding intramolecular Au···Au distances [3.538(1) and 3.645(1) Å, respectively] suggest a weak aurophilic attraction. The intermolecular Au···Au distances [3.0733(5) and 3.0756(5) Å] are considerably shorter and indicate a much stronger aurophilic attraction between these atoms. Overall, the four gold atoms are arranged in a distorted square, and the Au_4S_2 core gives a six-membered ring in the chair conformation. The P−O bond lengths are all equivalent within experimental error [1.544(6) to 1.558(7) Å], which indicates P−O$^-$···H−O−P bonding such that the P−O bond lengths are intermediate between those in diphenylphosphinite complexes [1.499(4) − 1.52(1) Å][10,12] and the single P−O bonds [1.62(1) Å] found in complex **2**, and considerably longer than a P═O bond [1.49(1) Å].[20] Thus, the tetranuclear gold(I) complex bears two neutral diphenylphosphinous acid groups, Ph_2POH, and two anionic diphenylphosphinite ligands, Ph_2PO^-, each bound to a gold(I) center through the phosphorus atom. These groups combine intermolecularly by P−O···H−O−P bonding, thus forming two peripheral seven-membered rings (Figure 2). The distances between oxygen atoms O(5)−O(3) and O(6)−O(4) [2.40(1) and 2.42(1) Å, respectively] are in the middle of the range of O−O separations [2.2−2.5 Å] that is considered diagnostic of a strong hydrogen bond.[21] The hydrogen atoms were tentatively located in the structure determination, but it should be noted that the formulation is based on the presence of the neutral tetranuclear complex, which requires the presence of only two Ph_2PO^- ligands. It is this combination of intermolecular Au··Au and OH··O secondary bonding effects that gives the neutral gold(I) complex **4** its unique character when compared to the cationic complexes studied previously.[7,8] It is noted that the structure of **4** contains two independent dimers and that they have very similar structures and bond parameters, indicating that the structure observed is rather rigid and not much influenced by crystal packing forces.

Table 3. Selected Interatomic Distances (Å) and Angles (deg) for Compound **4**[a]

Au(3)−P(3)	2.266(2)	Au(3)−S(9)	2.348(2)
Au(4)−P(4)	2.272(2)	Au(4)−S(9)	2.346(2)
Au(3)−Au(5)	3.0733(5)	Au(4)−Au(6)	3.0756(5)
Au(5)−P(5)	2.272(2)	Au(5)−S(8)	2.338(2)
Au(6)−P(6)	2.263(2)	Au(6)−S(8)	2.335(2)
P(3)−O(3)	1.563(7)	P(4)−O(4)	1.545(6)
P(5)−O(5)	1.545(6)	P(6)−O(6)	1.557(7)
S(9)−Au(3)−Au(5)	79.73(5)	P(4)−Au(4)−S(9)	176.80(8)
P(4)−Au(4)−Au(6)	85.84(6)	S(9)−Au(4)−Au(6)	91.91(5)
Au(6)−S(8)−Au(5)	102.52(8)	O(3)−P(3)−Au(3)	113.4(3)
O(4)−P(4)−Au(4)	116.0(3)	P(5)−Au(5)−S(8)	174.87(8)
P(5)−Au(5)−Au(3)	85.71(6)	S(8)−Au(5)−Au(3)	89.23(5)
P(6)−Au(6)−S(8)	175.25(8)	P(6)−Au(6)−Au(4)	100.07(6)
S(8)−Au(6)−Au(4)	76.69(5)	Au(4)−S(9)−Au(3)	97.85(7)
C(8)−S(8)−Au(5)	110.3(3)	C(8)−S(8)−Au(6)	107.4(3)
O(5)−P(5)−Au(5)	115.4(3)	O(6)−P(6)−Au(6)	112.4(3)

[a] There are two independent tetragold molecules in the unit cell. Data are given for only one of them. The second is very similar.

The photophysical properties of complexes **3** and **4** are summarized in Table 4. Complex **3** is brightly luminescent at room temperature in dichloromethane solution, with a peak maximum at 413 nm, in contrast to **2**, which gives only a very weak, broad emission at 367 nm. The emission for **3** is red-shifted to 445 nm as a solid in KBr matrix, and is asymmetric, broad, and featureless. Finely ground single crystals of **4** in a KBr matrix display a broad and featureless luminescence spectrum at room temperature, having a full width at half-

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Table 4. Luminescence Data for **3** and **4**[a]

complex	medium	emission max, nm
3	CH_2Cl_2	413
3	solid	445
4	solid	420

[a] $\lambda_{excitation} = 270$ nm; spectra of solids were obtained in a KBr matrix.

maximum of 100 nm. The peak maximum occurs at 420 nm. Because several gold(I) thiolates are known to give room-temperature emission,[22] whereas the diphosphinite complex $[Au(Ph_2PO)_2]^-$ does not luminesce in solution or as a solid,[11b] it seems clear that the thiolatogold(I) unit is responsible for the observed emission in **3** and **4**. In accord with precedent, the emission is assigned to an excited state arising from a ligand-to-metal charge transfer [from sulfur to gold(I)].[22] The redshift of ca. 30 nm in the emission spectrum of **3** going from solution to the solid state suggests that gold$\cdots$gold interactions are present in the solid state.[22]

Experimental Section

NMR spectra were recorded using a Varian Gemini 300 MHz spectrometer, and chemical shifts are reported relative to TMS (^{1}H) or 85% H_3PO_4 external standard (^{31}P). Mass and IR spectra were recorded using a Finnigan MAT 8320 and a Perkin-Elmer 2000 FTIR, respectively. Emission spectra were recorded at room temperature on a Fluorolog-3 spectrofluorometer using a 3-nm slit width and excitation $\lambda_{max} = 270$ nm. All reactions were conducted under an inert nitrogen atmosphere using standard Schlenk techniques. THF and ether were dried and distilled immediately prior to use. Triethylamine was distilled over KOH. $[AuCl(SMe_2)]$ was prepared according to a literature method.[23]

1,3-$C_6H_4(OPPh_2)_2$, 1. A solution of resorcinol (0.500 g, 4.54 mmol) in diethyl ether (20 mL) was cooled in an ice bath. Triethylamine (1.33 mL, 9.54 mmol) was added, followed by chlorodiphenylphosphine (1.63 mL, 9.08 mmol) to yield a white precipitate of Et_3NHCl. The mixture was stirred for 1 h and filtered through a sintered glass funnel, and the solvent was removed under vacuum. The product was obtained as a clear, yellow oil. Yield: 1.88 g, 86%. NMR ($CDCl_3$): $\delta(^1H) = 6.90-7.60$ [m, Ph]; $\delta(^{31}P) = 111.77$ [s]. EI−MS, *m*/*z*: 478.124; calcd for $C_{30}H_{24}O_2P_2$: 478.125.

[1,3-$C_6H_4(OPPh_2AuCl)_2$], 2. To a solution of $[AuCl(SMe_2)]$ (0.184 g, 0.62 mmol) in THF (5 mL) was added a solution of **1** (0.150 g, 0.31 mmol) in THF (5 mL). The colorless solution was stirred for 1 h, and the solvent was removed under vacuum. The residue was washed with ether and pentane. A white crystalline solid was obtained. Yield: 0.217 g, 74%. NMR (acetone-d_6): $\delta(^1H) = 7.10-7.20$ [m, 3H, H_2, H_4, H_6 of Ar]; 7.40 [t, 1H, H_5 of Ar]; 7.8−8.0 [m, 20H, Ph]. $\delta(^{31}P) = 116.74$ [s]. Anal. Calcd for $C_{30}H_{24}Au_2Cl_2O_2P_2$: C, 38.20; H, 2.56. Found: C, 37.36; H, 2.63%.

[1,3-$C_6H_4(OPPh_2AuSPh)_2$], 3. To a solution of **2** (0.200 g, 0.21 mmol) in THF (20 mL) at 0 °C under nitrogen was added triethylamine (59 μL, 0.42 mmol) and benzenethiol (44 μL, 0.42 mmol). A white precipitate slowly formed. The mixture was stirred for 3 h and filtered through a sintered glass funnel, and the solvent was removed under vacuum. The residue was washed with ether and pentane. A pale-yellow crystalline solid was obtained. Yield: 0.125 g, 54%. NMR (acetone-d_6): $\delta(^1H) = 6.70-7.00$ [m, 4H, Ar]; 7.40−8.00 [m, 30H, Ph]. $\delta(^{31}P) = 124.62$ [s]. Anal. Calcd for $C_{42}H_{34}Au_2O_2P_2S_2$: C, 46.25; H, 3.14; S, 5.88. Found: C, 46.20; H, 3.52; S, 5.58%.

[{$Au_2(\mu$-SPh)(PPh_2O)(PPh_2OH)}$_2$], 4. A solution of **3** (20 mg) was dissolved in wet acetone (1 mL). Colorless prisms were grown by slow diffusion of pentane. NMR (CD_2Cl_2/nitrobenzene-d_5): $\delta(^1H) = 7.1-7.8$ [m, Ph]. $\delta(^{31}P) = 82.43$ (s). Anal. Calcd for $C_{60}H_{52}Au_4O_4P_4S_2$: C, 39.75; H, 2.89. Found: C, 39.30; H, 2.46%.

X-ray Structure Determinations. Crystals of **2** were grown by slow diffusion of ether into an acetone solution. A yellow crystal was mounted on a glass fiber. Data were collected at 150 K using a Nonius Kappa CCD diffractometer using COLLECT software. Crystal cell refinement and data reduction were carried out using the Nonius DENZO package. The data were scaled using SCALEPACK (Nonius, 1998), and no other absorption corrections were applied. The reflection data were consistent with a triclinic system, and the structure was solved successfully in $P\bar{1}$. The SHELXTL 5.03 program package was used to solve the structure by Patterson and successive difference Fouriers. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were calculated geometrically and rode on their respective carbon atoms. The largest residual electron density peak (2.24 e/Å^3) was associated with a gold atom.

Crystals of **4** were grown by slow diffusion of pentane into an acetone solution. A colorless prism was mounted on a glass fiber. Data were collected at 200 K and treated as above. The reflection data and systematic absences were consistent with a monoclinic system, $P2_1/c$. Hydrogen bonding: [H1A$\cdots$O2 = 1.70 Å; H4A$\cdots$O6 = 1.70 Å; H5A$\cdots$O3 1.61 Å]. The largest residual electron density peak (2.051 e/Å^3) was associated with one of the gold atoms.

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Supporting Information Available: Tables of X-ray data for complexes **2** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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