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Synthesis of a Mixed-Valence Au^I/Au^{III} Complex, $[Au(CH_2)_2PPh_2]_2Br_2$, and Its Characterization by X-ray Crystallography and X-ray Photoelectron Spectroscopy

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The mixed-valence Au^I/Au^{III} complex $[Au(CH_2)_2PPh_2]_2Br_2$ has been prepared by two methods: reduction of $[Au(CH_2)_2PPh_2]_2Br_4$ with AgCN; oxidation of $[Au(CH_2)_2PPh_2]_2(CN)_2$ by Br_2, followed by spontaneous reduction. The CH_2Cl_2 solvate of the mixed-valence complex was characterized crystallographically: orthorhombic, *Pcmn* (nonstandard setting of *Pnma*, No. 62), $a = 11.404$ (2) Å, $b = 12.627$ (2) Å, $c = 23.355$ (3) Å, $V = 3363$ (1) $Å^3$, and $Z = 4$. It consists of an eight-membered metallacycle containing a two-coordinate Au^I and a four-coordinate Au^{III} centers. The X-ray photoelectron spectroscopy study of this complex along with its Au^I/Au^I and Au^{III}/Au^{III} congeners confirmed the crystallographic results.

Introduction

The oxidation reactions of cofacial multinuclear complexes with a variety of small molecules often result in transannular addition with metal–metal-bonded products. Examples involving dinuclear,[1] trinuclear,[2] and tetranuclear[3] species have been reported.

Two-electron oxidative addition reactions of the dinuclear Au^I/Au^I complex[4] $[Au(CH_2)_2PPh_2]_2$ (**1**) invariably give the homovalent Au^{II}/Au^{II} analogues containing an Au–Au single bond (Scheme I). A further two-electron oxidation yields the corresponding Au^{III}/Au^{III} products.[1h,5] A conproportionation of the Au^I/Au^I and Au^{III}/Au^{III} compounds to produce 2 molar equiv of the Au^{II}/Au^{II} species has been reported.[6] The two-electron oxidation of the Au^I/Au^I complex could lead, in principle, to a mixed-valence Au^I/Au^{III} product. This has not been observed.

In contrast to the oxidation reactions, the two-electron reduction of the Au^{III}/Au^{III} complexes does not always result in homovalent products. Schmidbaur and co-workers reported[7] that the reaction of the Au^{III}/Au^{III} complex $[Au(CH_2)_2PMe_2]_2Br_4$ with MeLi gives initially the tetramethyl analogue, which eliminates C_2H_6 spontaneously to form a mixed-valence Au^I/Au^{III} complex, $[Au(CH_2)_2PMe_2]_2Me_2$. The latter complex was characterized by its ^1H NMR spectrum. Alternatively, a mixed-valence product can be formed from an intramolecular disproportionation of an Au^{II}/Au^{II} material. Disproportionation has been suggested upon combining[7] $[Au^{II}(CH_2)_2PMe_2]_2Br_2$ with MeLi. Recently,[8] a similar disproportionation has been shown to occur in the reaction of $[Au(CH_2)_2PPh_2]_2I_2$ with CH_2PR_3 (R_3 = Me_3, $MePh_2$, Ph_3), yielding the Au^I/Au^{III} product $[Au(CH_2)_2PPh_2]_2(CH_2PR_3)_2^{2+}$ characterized[8,9] by its ^1H NMR and ^{197}Au Mössbauer spectra. A third way[10] to synthesize the mixed-valence complex $[Au(CH_2)_2PMe_2]_2Me_2$ is described by reacting the "A-frame" complex $(\mu\text{-}CH_2)[Au(CH_2)_2PMe_2]_2X_2$ (X = Br, I) with 2 equiv of MeLi.

To date, no structural data exist for these Au^I/Au^{III} complexes. A similar mixed-valence dimeric system, $[Au(CH_2)PPh_2(S)]_2I_2$ (A), has been characterized[11] by X-ray crystallography. A mixed-valence digold complex containing one bridging and one chelating $(CH_2)_2PPh_2^-$ ligand, $[Au(CH_2)_2PPh_2]_2Cl_2$ (B), is also known[12] (Chart I). The formation of each of these products is influenced by the choice of solvent.

Here we report the synthesis of the mixed-valence, symmetrically bridged Au^I/Au^{III} complex $[Au(CH_2)_2PPh_2]_2Br_2$ (**2**), its X-ray crystal structure, and an X-ray photoelectron spectroscopy (XPS) study confirming the Au^I/Au^{III} result. To our knowledge, this is the first reported XPS study of a mixed-valence gold complex. The XPS results for the homovalent complexes $[Au^I(CH_2)_2PPh_2]_2$ (**1**) and $[Au^{III}(CH_2)_2PPh_2]_2Br_4$ (**3**) are also reported.

Scheme I

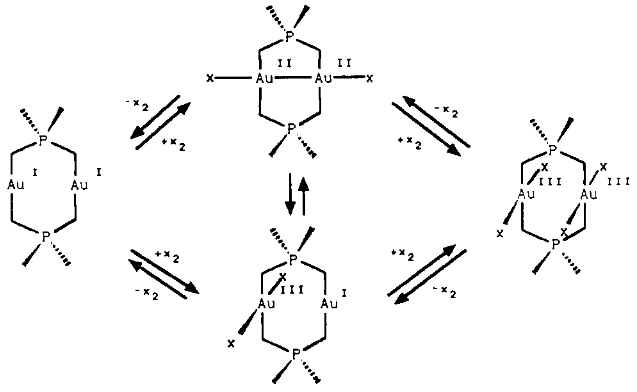
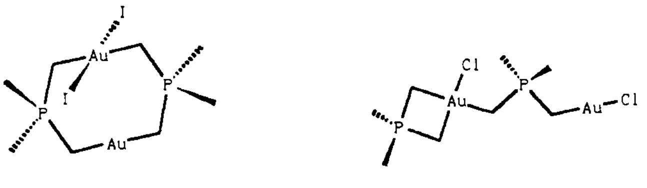


Chart I



A B

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Experimental Section

Synthesis. All reactions were carried out under an argon atmosphere by using Schlenk techniques.[13] All solvents were distilled before use. Published procedures were followed for the syntheses of **1**[4] and **3**.[5b,14]

$[Au(CH_2)_2PPh_2]_2Br_2$ (2). (a) A 12.2-mg (0.091-mmol) amount of AgCN was added to a saturated solution of 20 mg (0.018 mmol) of **3** in 4 mL of CH_2Cl_2. The yellow color of **3** disappeared slowly over a period of 1.5 h. The reaction mixture was stirred for 18 h and allowed to settle, and the colorless supernatant solution was separated by filtration from the white precipitate (soluble in an aqueous KCN solution). The infrared spectrum of an aliquot of the supernatant was recorded (IBM-FTIR/32, 1500–2250 cm^{-1}): 1606 cm^{-1} (s), C–C aromatic. Slow diffusion of $(C_2H_5)_2O$ into this solution afforded crystals of **2** suitable for a crystallographic study. Yield: 3 mg, 17%. Complex **2** in its crystalline form could not be redissolved in CH_2Cl_2, $CHCl_3$, thf, C_6H_6, CH_3COCH_3, CH_3CN, or CH_3OH. To obtain an ^1H NMR spectrum, the reaction as described above was carried out in $CDCl_3$ solvent, which at the end of the reaction period was filtered into an NMR tube. The spectrum, recorded on a Varian XL 200 spectrometer at 20 °C, was of poor resolution and showed a complex pattern containing resonances between 1.70 and 3.45 ppm. These chemical shifts are consistent with an Au^{III}/Au^{III} species.

(b) A 0.1-mL (1.9-mmol) amount of Br_2 was added to a solution of 16 mg (0.018 mmol) of $[Au^{II}(CH_2)_2PPh_2]_2(CN_2)$[1e] in 4 mL of CH_2Cl_2. The solution was stirred for 24 h, and the excess Br_2 was removed under vacuum, leaving a pale yellow solid insoluble in $CDCl_3$. Slow diffusion of $(C_2H_5)_2O$ into a CH_2Cl_2 solution of the product afforded colorless crystals of **2**, as determined crystallographically. An ^1H NMR spectrum was obtained as above with similar results.

X-ray Photoelectron Spectroscopy. The XPS spectra of compounds **1**, **2**, and **3** were collected on a VG Scientific ESCALAB MK II using Mg $K\alpha_{1,2}$ ($h\nu$ = 1253.6 eV) line as an excitation source. All experiments were carried out at a pressure of approximately 5×10^{-10} mbar, both in the chamber of the analyzer and in the region of the source.

The X-ray source was operated at 100 W (10 kV, 10 mA). A constant voltage of either 20 or 50 V was applied through the hemispheres of the electron analyzer, which were operated in the CAE (constant analyzer energy) mode, attaining a value of fwhm (full width at half-maximum) of 1.3 or 1.9 eV, respectively, for the Au $4f_{7/2}$ transition of gold foil.

The samples, which were in powder form, were mounted on 12-mm-diameter stainless steel sample stubs precoated with Scotch 924 transfer tape. The sample stubs were precooled to −125 °C in a specially designed glovebox that allows cooling without frost formation on the sample,[15] then inserted into the spectrometer, and run at liquid nitrogen temperatures (−196 °C). Precooling the samples prevents the "blooming" of mobile components to the surface of the sample under vacuum and reduces the vapor pressure of volatile surface components. Analysis at liquid-nitrogen temperatures also minimizes the decomposition or reduction of surface components by the X-ray beam. The three spectra exhibited some charging due to the mounting procedure but were calibrated, by assuming a C peak due to residual hydrocarbon, to have a binding energy of 285.00 eV or alternatively, by assuming the Au $4f_{7/2}$ peak of gold foil, to have a binding energy of 84.00 eV.

Crystallography. The X-ray analysis of **2** was carried out with a Nicolet R3m/E automated diffractometer and SHELXTL software implemented on an Eclipse S140 minicomputer. A single crystal of **2** appropriate for X-ray study was mounted atop a glass fiber at a 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 25 reflections in the range 25° < 2θ < 40°. Intensity data were collected for 3071 unique reflections (+h,+k,+l) with 0° < 2θ < 50° by using the ω-scanning technique in bisecting geometry. No symmetry-equivalent reflections were measured. The intensity data were corrected for Lorentz and polarization effects and for standard decay (~9%). An empirical absorption correction based on azimuthal scans of reflections spanning a range of 2θ values was applied. Systematically absent data suggested the space groups *Pcmn* and *Pc*2$_1$*n*. The structure was successfully solved and refined in the centrosymmetric space group (the crystals showed a negative qualitative pyroelectricity test). Initial positional parameters for the gold atom were obtained from a sharpened Patterson map. The remaining non-hydrogen atoms were located in difference Fourier maps. An interstitial molecule of CH_2Cl_2 was found on the mirror plane at a position of no chemical significance. Hydrogen atoms were placed in calculated positions (C–H = 0.960 Å) with fixed thermal parameters (U(H) = 0.08 Å^2). All non-hydrogen atoms were refined anisotropically. A low-angle reflection (2,0,2) with extinction problems was omitted from the final refinement. Refinement of 129 parameters using 1389 reflections with $F_o^2 > 3\sigma(F_o^2)$ converged to a conventional R value of 0.057 with a goodness-of-fit indicator of 1.263. The highest peak of residual electron density, 1.82 e/Å^3, appears at 1.09 Å from Au. Refinement in the noncentrosymmetric space group *Pc*2$_1$*n*, with a complete molecule per asymmetric unit, was successful to an R value of 0.057. This, however, required four bromine atoms, two on each Au at 50% occupancy, with two Au–Br bonds short (2.32 Å) and two long (2.69 and 2.95 Å). As refinement in this space group does not change the molecular structure of **2** and does not improve the crystal structure, the centrosymmetric space group *Pcmn* is preferred. Parameters pertaining to data collection and structure refinement are listed in Table I. Atomic coordinates and equivalent isotropic thermal parameters for **2** are given in Table II. Tables of observed and calculated structure factors with their esd values, listings of anisotropic thermal parameters and hydrogen coordinates and isotropic thermal parameters, and complete lists of crystallographic data, bond lengths, and bond angles for **2** have been deposited as supplementary material.

Table I. Crystallographic Data for $[Au(CH_2)_2PPh_2]_2Br_2\cdot CH_2Cl_2$ (**2**)

formula	$C_{29}H_{30}Au_2Br_2Cl_2P_2$	μ(Mo Kα), cm^{-1}	113.3
fw	1064.87	radiation λ, Å (monochromated in Mo Kα)	0.71069
space group	*Pcmn* (No. 62)		
a, Å	11.404 (2)		
b, Å	12.627 (2)	temp, °C	22
c Å	23.355 (3)	transm factors: max, min	0.022, 0.008
V, Å^3	3363 (1)		
Z	4	R^a	0.057
d_{calc}, g cm^{-3}	2.10	$R_w{}^b$	0.059

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

Table II. Atomic Coordinates (×10^4) and Equivalent Isotropic Thermal Parameters for $[Au(CH_2)_2PPh_2]_3Br_2$ (**2**)

atom	*x*	*Y*	*z*	$U_{iso}{}^a$
Au	841 (1)	8712 (1)	1182 (1)	52 (1)*
Br(1)	−62 (4)	8924 (4)	2134 (2)	59 (2)*
Br(2)	1755 (5)	6165 (5)	225 (3)	80 (2)*
Cl	3863 (14)	3619 (10)	1174 (5)	166 (7)*
P(1)	2979 (8)	7500	1911 (4)	53 (3)*
P(2)	−1309 (8)	7500	452 (4)	50 (3)*
C(1)	2517 (19)	6310 (20)	1548 (9)	59 (7)*
C(2)	9116 (19)	6315 (18)	806 (8)	55 (7)*
C	3829 (67)	2500	1559 (20)	152 (35)*
C(11)	2424 (29)	6548 (24)	2965 (12)	88 (9)
C(12)	2247 (29)	6621 (27)	3541 (14)	96 (10)
C(13)	2199 (40)	7500	3826 (21)	92 (13)
C(16)	2562 (34)	7500	2667 (14)	59 (9)
C(21)	5218 (25)	6546 (20)	1972 (10)	67 (7)
C(22)	6449 (29)	6539 (23)	2073 (12)	87 (9)
C(23)	7080 (46)	7500	2073 (19)	93 (14)
C(26)	4597 (30)	7500	1946 (15)	55 (9)
C(31)	−3505 (27)	6604 (23)	419 (11)	77 (8)
C(32)	−4813 (26)	6600 (22)	325 (11)	75 (8)
C(33)	−5290 (43)	7500	341 (17)	82 (12)
C(36)	7062 (33)	7500	440 (15)	61 (10)
C(41)	−661 (28)	6615 (26)	−586 (14)	94 (10)
C(42)	−457 (28)	6604 (26)	−1143 (13)	90 (10)
C(43)	−359 (32)	7500	−1414 (17)	63)9)
C(46)	9187 (30)	7500	−276 (13)	48 (7)

^{a}Equivalent isotropic U defined as one-third of the orthogonalized U_{ij} for values marked with an asterisk.

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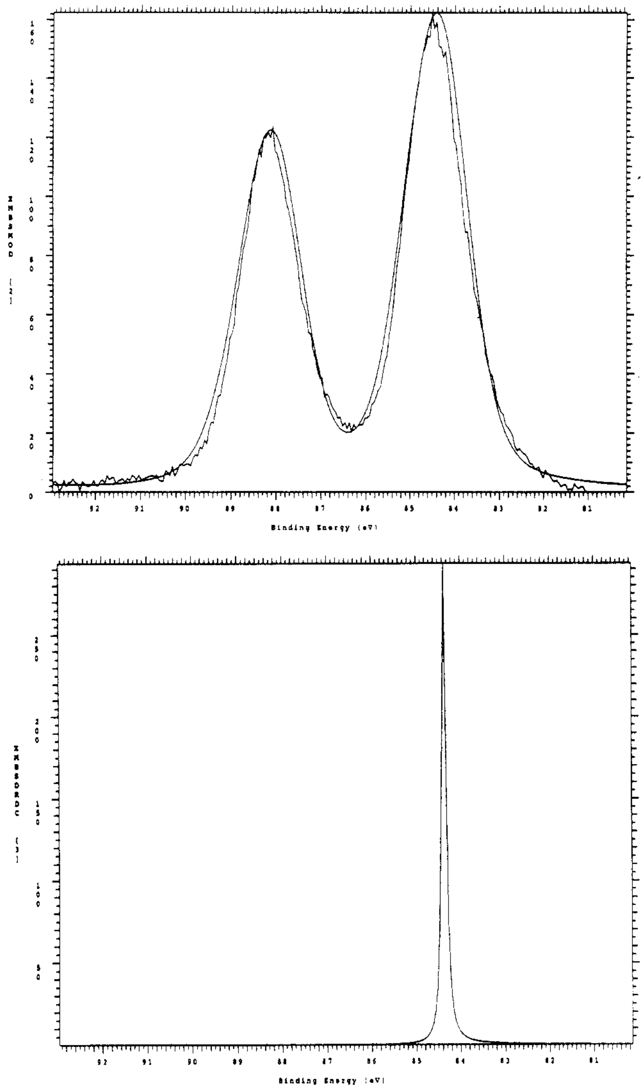

Figure 1. (a) Top: XP (Au $4f_{7/2}$) spectrum of $[Au^{I}(CH_2)_2PPh_2]_2$ (**1**) both unsmoothed and smoothed; scales arbitrary. (b) Bottom: Deconvolution of the spectrum of **1**.

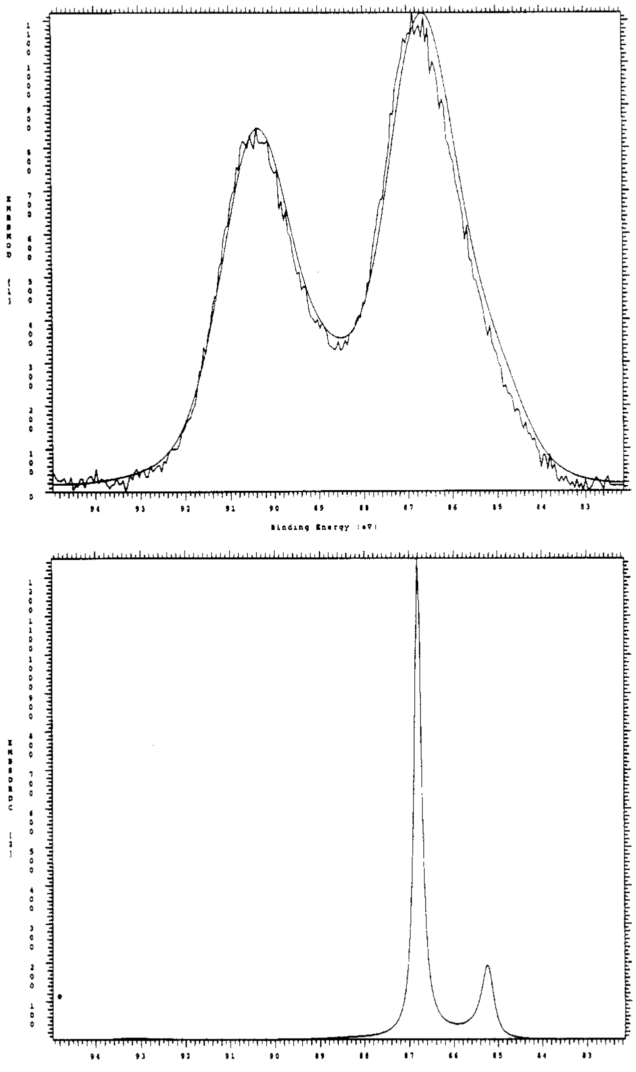

Figure 2. (a) Top: XP (Au $4f_{7/2}$) spectrum of $[Au^{III}(CH_2)PPh_2]Br_4$ (**3**) both unsmoothed and smoothed; scales arbitrary. (b) Bottom: Deconvolution of the spectrum of **3**.

Results and Discussion

Characterization of the mixed-valence complex **2** was hampered by its insolubility. Of the available techniques that utilize solid samples, ^{197}Au Mössbauer spectroscopy requires a relatively large amount of sample (in view of the low-yield synthesis of this complex), while CP/MAS ^{13}C NMR spectroscopy of the solid was unable to detect the resonances of the methylene carbons. Therefore, the characterization of complex **2** was based on the evidence of the X-ray diffraction study and the interpretation of the XP spectra (Figures 1–3).

The observed binding energies (eV) for compounds **1**, **2**, and **3** were as follows. **1**: Au $4f_{7/2}$, 84.55 ($fwhm_{20}$ = 1.93 eV); Au $4f_{5/2}$, 88.25; C 1s, 285.00; P 2p, 132.60. **2**: Au $4f_{7/2}$, 86.50 ($fwhm_{20}$ = 1.90 eV); Au $4f_{5/2}$, 90.15; C 1s, 285.00; Br 3d, 69.90; P 2p, 133.05. **3**: Au $4f_{7/2}$, 86.80 ($fwhm_{20}$ = 1.62 eV); Au $4f_{5/2}$, 90.45; C 1s, 285.00; Br 3d, 69.65; P 20, 132.95.

The observed Au $4f_{7/2}$ and Au $4f_{5/2}$ peaks were analyzed by applying the maximum-entropy method (MEM) of spectral estimation to deconvolve this spectral region. This method has been applied in the past to XP spectra[16,17] and significantly reduces the amount of subjective judgment introduced into the deconvolution process.[18] When applied to the gold region, the results were as follows (eV). **1**: Au $4f_{7/2}$, 84.35; Au $4f_{5/2}$, 88.00; C 1 s, 285.00. **2**: Au $4f_{7/2}$, 86.70, 85.85, 84.45; Au $4f_{5/2}$, 90.35, 89.50, 88.10; C 1s, 285.00. **3**: Au $4f_{7/2}$, 86.80, 85.25; Au $4f_{5/2}$, 90.50, 88.95; C 1s, 285.00. The deconvolution of the Au $4f_{7/2}$ peak of the dimeric Au^{I} complex gave a single species (Figure 1), while the deconvolution of the Au $4f_{7/2}$ peak of the dimeric Au^{III} complex resulted in two peaks (Figure 2). The primary species at 86.80 eV is due to Au^{III} and accounts for most of the peak area. The other peak at 85.25 eV may be due to Au^{II} that has been reduced by the X-ray beam or could be unreacted starting material left in the sample. Reduction of copper species in the X-ray beam is quite well-known,[19] and this gold species is known to be less stable than the Au^{II} species.

The mixed-valence gold complex gave three peaks (Figure 3), a Au^{III} peak at 86.70 eV, a Au^{II} peak at 85.85 eV, and a Au^{I} peak at 84.45 eV. Agreement between these values and those of Schmidbaur[20] is reasonably good for both the Au^{I} and Au^{III} species. The species at 85.85 eV appears to be due to reduction of the Au^{III} by the X-ray beam, but the difference in binding energy for this species between the mixed-valence compound and the Au^{III}/Au^{III} compound is not understood.

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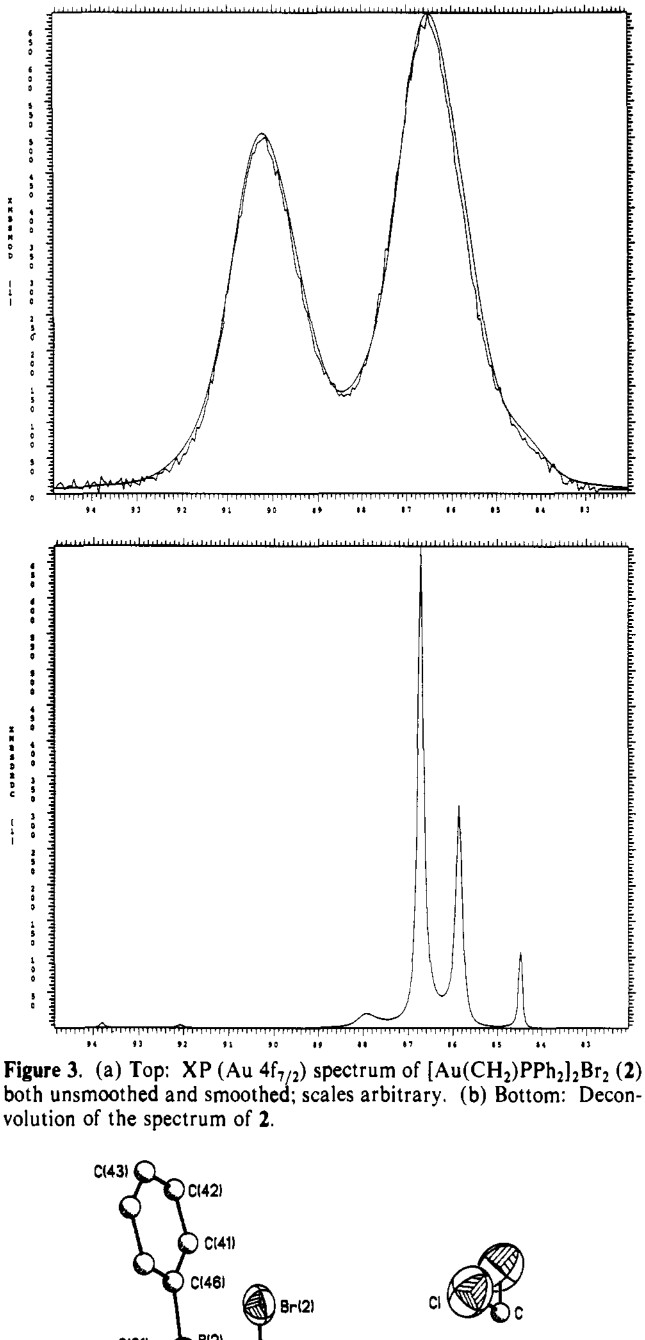

Figure 3. (a) Top: XP (Au $4f_{7/2}$) spectrum of $[Au(CH_2)PPh_2]_2Br_2$ (**2**) both unsmoothed and smoothed; scales arbitrary. (b) Bottom: Deconvolution of the spectrum of **2**.

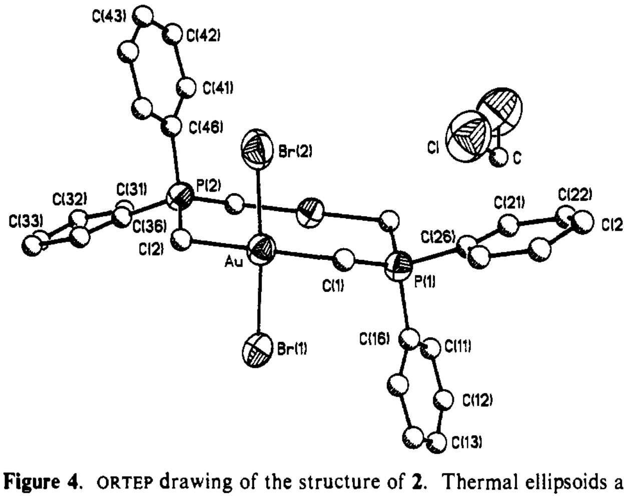

Figure 4. ORTEP drawing of the structure of **2**. Thermal ellipsoids are drawn at the 50% probability level. Carbon atoms of arbitrary radii are given for clarity.

The gold:bromine atomic ratio based upon the atomic sensitivity factors supplied by VG Instruments is 1.77:1.0, suggesting that the mixed-valence compound is slightly bromine deficient. The results of this work are in agreement with the XPS study[21] of the Au^I_3 and Au^I_2/Au^{III} complexes $[Au(\mu\text{-}3,5\text{-}Ph_2pz)]_3$[22] and $[Au(\mu\text{-}3,5\text{-}Ph_2pz)]_3Cl_2$[23] (pz = pyrazolato anion), which showed widths at half-height of 1.41 and 2.01 eV, respectively.

Table III. Selected Distances (Å) and Angles (deg) for $[Au(CH_2)_2PPh_2]_2Br_2$ (**2**)

Au···Au′	3.061 (2)	P(1)-C(1)	1.81 (3)
Au-Br(1)	2.464 (5)	P(1)-C(16)	1.83 (4)
Au-Br(2)	2.470 (5)	P(1)-C(26)	1.85 (4)
Au-C(1)	2.09 (2)	P(2)-C(2)	1.78 (2)
Au-C(2)	2.15 (2)	P(2)-C(36)	1.86 (4)
		P(2)-C(46)	1.79 (3)
Br(1)-Au-Br(2)	170.2 (2)	Au-C(1)-P(1)	118 (1)
C(1)-Au-C(2)	178 (1)	Au-C(2)-P(2)	117 (1)
Br(1)-Au-C(1)	90.8 (6)	C(1)-P(1)-C(1)′	113 (2)
Br(1)-Au-C(2)	89.3 (5)	C(1)-P(1)-C(16)	112.2 (9)
Br(2)-Au-C(1)	89.1 (6)	C(1)-P(1)-C(26)	108.2 (9)
Br(2)-Au-C(2)	91.0 (5)	C(16)-P(1)-C(26)	103 (2)
Br(1)-Au-Au′	96.2 (1)	C(2)-P(2)-C(2)′	115 (1)
Br(2)-Au-Au′	93.6 (1)	C(2)-P(2)-C(36)	106.2 (9)
		C(2)-P(2)-C(46)	110.8 (9)
		C(36)-P(2)-C(46)	108 (2)

The structure of **2** consists of an eight-membered organometallic ring in a chair configuration (Figure 4) containing a two-coordinate Au^I and a four-coordinate Au^{III} center. Even though the actual symmetry of this complex is only C_2, a more efficient packing is achieved when the molecule is in a position of higher, crystallographically imposed symmetry. The molecule crystallizes on a mirror plane running through the phosphorus atoms and bisecting the phenyl rings. The crystallographic disorder requires that the bromine atoms be refined with 50% site occupancy. The bond lengths and angles of the organometallic ring are unexceptional, particularly as any possible differences between the Au^I and the Au^{III} sides of the complex are averaged by the crystallographic disorder. The coordination of the ylide ligands about Au is linear, C-Au-C = 178 (1)°, while the trans Br-Au-Br angle is 170.2 (2)° with the Au-Br bonds of 2.464 (5) and 2.470 (5) Å. A nonbonding Au···Au distance of 3.061 (2) Å was measured. Table III lists some important distances and angles for **2**.

There are two other plausible interpretations of the crystallographic results: (a) The crystalline sample is a cocrystallized 1:1 mixture of **1** and **3**. (b) The sample is an Au^{III}/Au^{III} complex of the type $[Au(CH_2)_2PPh_2]_2Br_2X_2$, where X is a ligand whose electron density is obscured by the presence of bromine. Both of these possibilities can be rejected on chemical grounds. An equimolar mixture of **1** and **3** conproportionates readily to form the Au^{II}/Au^{II}–dibromide complex.[6] Furthermore, such a mixture should be colored since **3** is yellow and **1** colorless, while **2** is also colorless. Also, considering the various components used in the reaction sequence, only a cyanide ion might pass undetected by X-ray diffraction. However, the crystals of **2** were grown from a solution that showed no C-N stretch in its infrared spectrum. Nevertheless, a model in which two cyanide ions were included in a trial structure at calculated positions with 50% site occupancy was refined. This model gave a poorer final *R* value.

The structure of **2** has the same geometry about Au^I as the metal centers of the Au^I/Au^I complex **1**.[4] In contrast, the coordination about the Au^{III} center of **2** is distinctively different from that of Au^{III} in the Au^{III}/Au^{III} complex **3**. There are two crystallographically characterized conformers of the latter: one[5b] has a Br-Au-Br angle of 164.3 (1)° and Au-Br bonds of 2.411 (3) and 2.440 (3) Å, while the second[14,21] has an even smaller Br-Au-Br angle, 149.5 (2)°, and much longer Au-Br bonds, 2.535 (4) and 2.576 (4) Å. The Au···Au distances in these Au^{III}/Au^{III} tetrabromide complexes are 3.075 (2) and 3.069 (2) Å, respectively. The metal-metal distance in **2**, 3.061 (2) Å, is consistent with the corresponding distances of the heterovalent gold complexes $[Au(CH_2)PPh_2S]_2I_2$,[11] 3.050 (3) Å, and Au_3-

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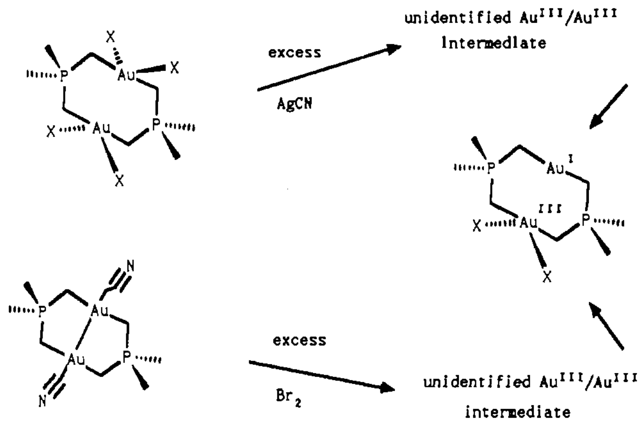
Scheme II



$[(CH_2)_2PPh_2]_4^+$,[8] 3.052 (1) and 3.049 (1) Å.

The 10° deviation of the Br–Au–Br angle of **2** from linearity may be caused by an Au^I–Au^{III} interaction, as the filled $5d_z{}^2$ orbital of the "square-planar" d^8 center is directed toward the electron-rich Au^I atom. In the crystal structure of complex **3**,[14,21] the 149.5 (2)° Br–Au–Br angle was attributed to a relativistic metal–metal interaction, causing an increase in the coordination number of the Au^{III} centers from 4 to 5.

The Au^I/Au^{III} complex **2** has been prepared by two different methods (Scheme II): (1) the reaction of AgCN with the Au^{III}/Au^{III}–tetrabromide complex and (2) the reaction of Br_2 with the Au^{II}/Au^{II}–dicyanide complex. Both reactions showed evidence (^1H NMR) for the involvement of a not yet isolated Au^{III}/Au^{III} species prior to the formation of the final product. In the former reaction, this Au^{III}/Au^{III} intermediate may be the product of a partial cyanide-for-bromide exchange, while in the latter, initial oxidation by Br_2 to form a bromo–cyano complex is possible. It is well established[5c] that halogen addition to Au^{II}/Au^{II} materials in this system leads to Au^{III}/Au^{III} products. The first report[7] of the synthesis of a mixed-valence complex of a gold–ylide dimer also claimed two synthetic procedures leading to the same product: the reaction of MeLi with the Au^{III}/Au^{III}–tetrabromide complex in one case and with the Au^{II}/Au^{II}–dibromide complex in the other.

The participation of cyanide in both reactions 1 and 2 implies that this ion plays an important role in the single-center reduction process. This is reminiscent of the reduction of Cu^{II} salts by cyanides[24a] in a reaction that generates $(CN)_2$ and the reduction of "fulminating gold"[24b] (a Au^{III} species) by 4 equiv of KCN to give the $Au(CN)_2^-$ anion.

It is interesting that even though an excess of AgCN was used in reaction 1, only one Au^{III} center was reduced. Similarly, Schmidbaur's Au^{III}/Au^{III}–tetramethyl complex eliminates C_2H_6 from only one Au^{III} center,[7] while the other Au^{III} center retains its two methyl groups. Furthermore, reductive elimination of alkanes from trans positions of mononuclear alkylgold(III) complexes has been shown[25] to be a forbidden process. However, the possibility exists that a trans to cis isomerization takes place at one gold center, which subsequently undergoes reductive elimination, while the other gold atom retains its trans geometry and its +3 oxidation state. Species containing one Au^{III} atom with trans geometry and one with cis geometry are known[5b,c] in this system. The isomerization of the Au^{III}/Au^{III}–tetrabromide complex from trans/trans to cis/trans geometry has been observed.[26]

At the present time, not all of the steps depicted in Scheme I have been observed. Two-electron oxidative addition reactions involving the Au^I/Au^I dimer are always two-center processes, leading to the homovalent Au^{II}/Au^{II} product. In contrast, the two-electron reduction of Au^{III}/Au^{III} species can result in either homovalent or heterovalent products, depending upon the reducing agent. There has been no report of an intramolecular conproportionation of an Au^I/Au^{III} to an Au^{II}/Au^{II} species, while the synthesis[7] of the Au^I/Au^{III}–dimethyl complex from the Au^{II}/Au^{II}–dibromide one may be an intramolecular disproportionation or may proceed via an Au^{III}/Au^{III} intermediate. Both the homo- and heterovalent products of a similar digold system, $[Au(CH_2)PPh_2S]_2Cl_2$, were identified[27] in the same reaction mixture, but there was not sufficient evidence to indicate whether they were in equilibrium or whether they were products of independent reaction pathways.

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Supplementary Material Available: Tables SI–SV, listing crystallographic data, bond lengths, bond angles, anisotropic thermal parameters, and hydrogen coordinates and isotropic thermal parameters for **2** (5 pages); Table SVI, listing observed and calculated structure factors for **2** (18 pages). Ordering information is given on any current masthead page.

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