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Synthesis, Structure, and Reactions of a Binuclear Gold(I)−Gold(III) Complex Containing Bridging and Bidentate (2-Diphenylphosphino-6-methyl)phenyl Groups

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Reaction of the organolithium reagents (C_6H_3-2-PPh_2-6-Me)Li or (C_6H_3-2-PPh_2-5-Me)Li with [AuBr(PEt_3)] gives the corresponding cyclometalated digold(I) complexes [Au_2(μ-C_6H_3-2-PPh_2-*n*-Me)$_2$] ($n = 6$, **1a**; $n = 5$, **1b**), the metal−metal distance in **1a**, 2.861(2) Å, being similar to that in the unsubstituted compound [Au_2(μ-2-$C_6H_4PPh_2$)$_2$]. Both complexes oxidatively add halogens to give metal−metal bonded digold(II) complexes [Au_2X_2(μ-C_6H_3-2-PPh_2-*n*-Me)$_2$] [$n = 6$, X = Cl (**2a**), Br (**3a**), I (**4a**); $n = 5$, X = Cl (**2b**), Br (**3b**), I (**4b**)], and **1b** also adds dibenzoyl peroxide to give the bis(benzoato)digold(II) complex [Au_2(O_2CPh)$_2$(μ-C_6H_3-2-PPh_2-5-Me)$_2$] (**5b**), whereas **1a** is unreactive. The behavior of the 6- and 5-methyl-substituted digold(II) complexes in solution is very different. Complexes **2a**−**4a** isomerize in solution above −20 °C to give gold(I)−gold(III) complexes [XAu^{I}(μ-2-$Ph_2PC_6H_3$-6-Me)-Au^{III}X{η^2-(C_6H_3-2-PPh_2-6-Me)}] [X = Cl (**6a**), Br (**7a**), I (**8a**)], whereas complexes **2b**−**4b** isomerize more slowly in solution by C−C coupling to give digold(I) complexes [Au_2X_2{μ-2,2′-Ph_2P(5,5′-$Me_2C_6H_3C_6H_3$)PPh_2}] [X = Cl (**6b**), Br (**7b**), I (**8b**)] containing (5,5′-dimethyl-2,2′-biphenylyl)bis(diphenylphosphine) (**12b**); the structures of **8a** and **8b** have been determined by X-ray crystallography. Complex **8a** contains linearly coordinated gold(I) and planar coordinated gold(III) atoms separated by 3.4692(7) Å; one arylphosphine group bridges the metal atoms, the other acts as a bidentate chelate ligand to gold(III). Complexes **6a**−**8a** can be oxidized further by halogens to give either gold(I) complexes of (2-halo-3-methylphenyl)diphenylphosphine, [AuX{Ph_2P(C_6H_3-2-X-3-Me)] [X = Br (**10a**), I (**11a**)], arising from electrophilic cleavage of the Au−C bonds, or a binuclear digold(III) complex [Cl_3Au(μ-C_6H_3-2-PPh_2-6-Me)AuCl{η^2-(C_6H_3-2-PPh_2-6-Me)}] (**9a**) in which the gold(III)−carbon bonds are retained. The differences in oxidative addition behavior between the 6- and 5-methyl-substituted series of compounds are believed to be caused mainly by the steric effect of the 6-methyl group adjacent to the gold−gold axis.

Introduction

A wide variety of binuclear compounds containing two gold(I) atoms held in close proximity by a pair of bifunctional ligands is known. Examples of such ligands include dithiocarbamate,[1] bis(diphenylphosphino)methane,[2] (2-pyridyl)dimethylphosphine,[3] methylenethiophosphinate,[4] and phosphorus bis(ylides).[5,6] The digold(I) complexes characteristically undergo oxidative additions with halogens, pseudohalogens, and, in the case of the bis(ylides), alkyl halides to give either metal−metal bonded digold(II) compounds or heterovalent gold(I)−gold(III) compounds; sometimes both can be isolated depending on the conditions.[4−13] Reaction with an additional equivalent of halogen can give binuclear digold(III) compounds.[7,14,15]

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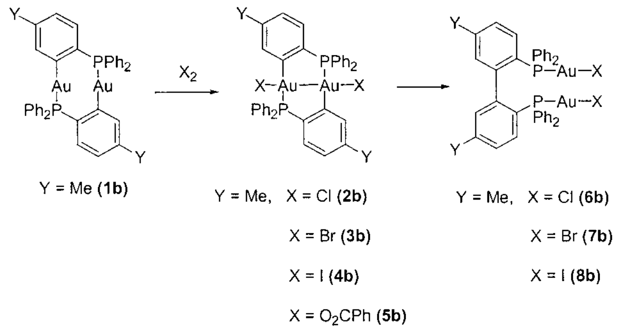
Scheme 1



We have been interested in binuclear cycloaurated complexes $[Au_2(\mu\text{-}2\text{-}C_6H_4PPh_2)_2]$ containing a pair of (2-diphenylphosphino)phenyl ligands, which undergo oxidative addition of halogens or dibenzoyl peroxide to give symmetrical digold(II) compounds $[Au_2X_2(\mu\text{-}2\text{-}C_6H_4PPh_2)_2]$ (X = Cl, Br, I, O_2CPh).[16−18] In the cases of X = Cl, Br, or I, the compounds rearrange spontaneously by coupling of the $C_6H_4PPh_2$ units to give digold(I) complexes of 2,2′-(biphenylyl)bis(diphenylphosphine), $[Au_2X_2(2,2'\text{-}Ph_2PC_6H_4C_6H_4PPh_2)]$ (Scheme 1;Y = H).[17,18] Although the rearrangements (for X = Br, I) are cleanly first-order in digold(II) complex, we suggested[18] that they are multistep processes involving a preliminary isomerization to a heterovalent gold(I)−gold(III) isomer (I). In the second step, the metal−carbon bond of one of the $2\text{-}C_6H_4PPh_2$ groups migrates from gold(I) to gold(III) to give species such as II or III (Figure 1). The $2,2'\text{-}Ph_2PC_6H_4C_6H_4PPh_2$ ligand is then generated in the coordination sphere by reductive elimination of the two σ-bonded aryl groups at the gold(III) center.

We wondered whether the course of these reactions could be modified by steric effects, e.g., by strategic placement of a substituent adjacent to the gold−gold axis of the starting material, or by electronic effects, e.g., by substitution at the position of the aromatic ring para to phosphorus. We have, therefore, studied digold compounds containing as bridging groups (2-diphenylphosphino-6-methyl)phenyl and (2-diphenylphosphino-5-methyl)phenyl, $\mu\text{-}C_6H_3\text{-}2\text{-}PPh_2\text{-}6\text{-}Me$ and $\mu\text{-}C_6H_3\text{-}2\text{-}PPh_2\text{-}5\text{-}Me$, respectively.

Results

The chemistry of the gold complexes containing $C_6H_3\text{-}2\text{-}PPh_2\text{-}n\text{-}Me$ is summarized in Scheme 1 (Y = Me) for $n = 5$ and Scheme 2 for $n = 6$. Analytical and $^{31}P\{^1H\}$ NMR spectroscopic data for the new compounds are collected in Table 1.

The digold(I) precursors $[Au_2(\mu\text{-}C_6H_3\text{-}2\text{-}PPh_2\text{-}n\text{-}Me)_2]$ ($n = 6$, **1a**; $n = 5$, **1b**) are obtained similarly to $[Au_2(\mu\text{-}2\text{-}C_6H_4PPh_2)_2]$ in ca. 40−50% yield by reaction of the appropriate aryllithium reagents with $[AuBr(PEt_3)]$ in ether at −70 °C. The compounds are white solids that are stable to air and moisture. Their EI-mass spectra each show a parent-ion molecular peak at *m*/*z* 944, and their $^{31}P\{^1H\}$ NMR spectra contain the singlet expected for equivalent phosphorus atoms. Compound **1a** has also been characterized by single-crystal X-ray diffraction. The molecular structure, shown in Figure 2, is very similar to that of $[Au_2(\mu\text{-}2\text{-}C_6H_4PPh_2)_2]$, and the Au−Au distance, 2.861(2) Å, is equal, within experimental error, to that in the parent compound [2.8594(3) Å].[16] Other important bond lengths and angles in **1a** are listed in Table 2.

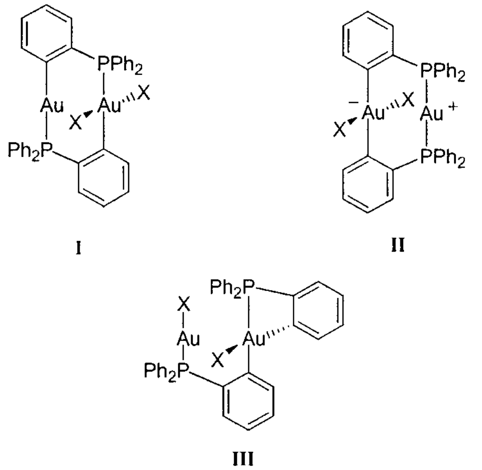
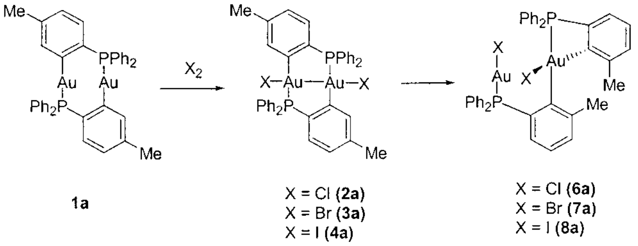


Figure 1. Suggested intermediates in the C−C coupling shown in Scheme 1.

Scheme 2



Treatment of **1a** or **1b** with 1 equiv of $PhICl_2$, Br_2, or I_2 in dichloromethane at ca. −70 °C gives yellow, orange, or red solutions containing the dihalodigold(II) complexes $[Au_2X_2(\mu\text{-}C_6H_3\text{-}2\text{-}PPh_2\text{-}n\text{-}Me)_2]$ [$n = 6$, X = Cl (**2a**), Br (**3a**), I (**4a**); $n = 5$, X = Cl (**2b**), Br (**3b**), I (**4b**)], which can be isolated by precipitation with hexane at low temperature. Complex **1b** also reacts with an excess of dibenzoyl peroxide over a period of days at room temperature to give the corresponding pale yellow bis(benzoato)digold(II) complex $[Au_2(O_2CPh)_2\{\mu\text{-}(C_6H_3\text{-}2\text{-}PPh_2\text{-}5\text{-}Me\}_2]$ (**5b**). The IR spectrum of **5b** shows typical carboxylate bands at 1632 and 1577 cm^{-1} due to ν(C=O) and at 1320 and 1298 cm^{-1} due to ν(C−O). In contrast, **1a** does not react with dibenzoyl peroxide even on heating; long reaction times cause decomposition to elemental gold. All these compounds show singlet $^{31}P\{^1H\}$ NMR resonances, the chemical shifts (Table 1) being very similar to those of their $C_6H_4PPh_2$ counterparts;[18] as found in the latter, the shielding decreases in the order I > Br > Cl > O_2CPh. The mass spectra do not show a parent ion, the highest mass peak corresponding to the loss of one halide ion. The formulation of the compounds as metal−metal bonded, digold(II) complexes ($5d^9−5d^9$) has been confirmed by X-ray-photoelectron and Mössbauer spectroscopies.[19,20]

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Table 1. Elemental Analyses and ^{31}P NMR Data for Gold Complexes Derived from C_6H_3-2-PPh_2-6-Me and C_6H_3-2-PPh_2-5-Me[a]

	color	Anal. [calcd (found)] % C	% H	% other	$\delta_P(J_{PP})$[b]
$[Au^I_2\{(C_6H_3\text{-6-Me})PPh_2\}_2]$ (**1a**)	white	48.32 (47.99)	3.41 (3.13)	6.56 (6.32) (P)	36.2[c]
$[Au^I_2\{(C_6H_3\text{-5-Me})PPh_2\}_2]$ (**1b**)	white	48.32 (48.43)	3.41 (3.48)	6.56 (6.16) (P)	35.9[c]
$[Au^{II}_2Cl_2\{(C_6H_3\text{-6-Me})PPh_2\}_2]$ (**2a**)	yellow	nm	nm	nm	−0.5[d]
$[Au^{II}_2Cl_2\{(C_6H_3\text{-5-Me})PPh_2\}_2]$ (**2b**)	yellow	44.95 (44.72)	3.18 (3.10)	6.10 (6.24) (P)	1.3
$[Au^{II}_2Br_2\{(C_6H_3\text{-6-Me})PPh_2\}_2]$ (**3a**)	orange	41.33 (41.57)	2.92 (3.08)	14.47 (14.38) (Br)	−5.3[d]
$[Au^{II}_2Br_2\{(C_6H_3\text{-5-Me})PPh_2\}_2]$ (**3b**)	orange	41.33 (40.89)	2.92 (3.08)	5.61 (5.61) (P)	−3.9
$[Au^{II}_2I_2\{(C_6H_3\text{-6-Me})PPh_2\}_2]$ (**4a**)	rust-red	38.09 (37.53)	2.69 (3.18)	5.17 (4.93) (P)	−13.1[d]
$[Au^{II}_2I_2\{(C_6H_3\text{-5-Me})PPh_2\}_2]$ (**4b**)	rust-red	38.09 (37.74)	2.69 (2.87)	5.17 (4.62) (P)	−12.5
$[Au^{II}_2(O_2CPh)_2\{(C_6H_3\text{-5-Me})PPh_2\}_2]$ (**5b**)	pale yellow	52.63 (51.48)	3.57 (3.75)	5.22 (4.91) (P)	4.3
$[Au^{I,III}_2Cl_2\{(C_6H_3\text{-6-Me})PPh_2\}_2]$ (**6a**)	white	44.95 (45.14)	3.18 (2.86)	6.10 (6.32) (P)	34.3, −58.4 (13)
$[Au^{I,III}_2Br_2\{(C_6H_3\text{-6-Me})PPh_2\}_2]$ (**7a**)	cream	41.33 (41.41)	2.92 (3.12)	14.47 (14.31) (Br)	33.9, −65.2 (13)
$[Au^{I,III}_2I_2\{(C_6H_3\text{-6-Me})PPh_2\}_2]$ (**8a**)	pale pink	38.09 (37.47)	2.69 (3.12)	5.17 (4.86) (P)	37.5, −78.2 (13)
$[Au^I_2I_2\{2,2'\text{-}PPh_2(5,5'\text{-}Me_2C_6H_3C_6H_3)PPh_2\}]$ (**8b**)	white	38.09 (37.87)	2.69 (2.84)	21.18 (21.54) (I)	31.6[e]
$[Au^{III}_2Cl_4\{(C_6H_3\text{-6-Me})PPh_2\}_2]0.2CH_2Cl_2$ (**9a**)	yellow	38.24 (37.93)	2.89 (2.97)	4.93 (4.59) (P) 22.58 (22.14) (Cl)	49.8, −65.3 (19)[c]
$[AuBr\{Ph_2P(C_6H_3\text{-2-Br-3-Me})\}]$ (**10a**)	white	36.10 (36.24)	2.55 (2.20)	4.90 (5.13) (P)	35.9
$[AuI\{Ph_2P(C_6H_3\text{-2-I-3-Me})\}]$ (**11a**)	white	31.43 (31.37)	2.22 (2.42)	4.27 (4.01) (P)	48.2

[a] Abbreviation: nm = not measured. [b] In CD_2Cl_2 at 23 °C, except where stated. [c] In $CDCl_3$ at 23 °C. [d] In $CDCl_3$ at −40 °C. [e] δ_P values for corresponding dichloro and dibromo compounds, **6b** and **7b**, are 27.3 and 29.0, respectively.

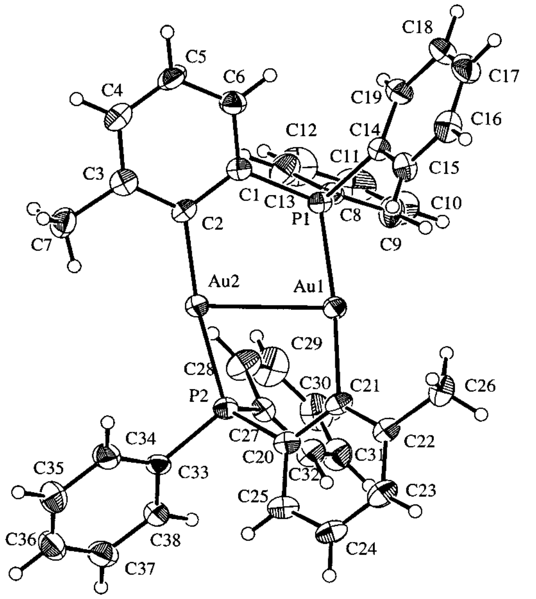

Figure 2. Molecular structure of $[Au_2(\mu\text{-}C_6H_3\text{-2-}PPh_2\text{-6-}Me)_2]$ (**1a**) with atom labeling; ellipsoids show 30% probability levels, and hydrogen atoms are drawn as circles with small radii.

Table 2. Selected Bond Distances (Å) and Angles (deg) in $[Au_2(\mu\text{-}C_6H_3\text{-2-}PPh_2\text{-6-}Me)_2]$ (1a)

Au(1)···Au(2)	2.861(2)	P−C	1.819(8)−1.829(8)
Au(1)−P(1)	2.302(2)	Au(2)−P(2)	2.295(2)
Au(1)−C(21)	2.061(7)	Au(2)−C(2)	2.042(7)
Au(2)−Au(1)−P(1)	78.87(5)	Au(2)−Au(1)−C(21)	95.6(2)
P(1)−Au(1)−C(21)	174.3(2)	Au(1)−Au(2)−P(2)	77.18(6)
Au(1)−Au(2)−C(2)	96.3(2)	P(2)−Au(2)−C(2)	171.8(2)
Au(1)−P(1)−C(1)	116.0(3)	Au(2)−P(2)−C(20)	114.3(3)
Au(2)−C(2)−C(1)	119.2(6)	Au(1)−C(21)−C(20)	118.6(6)

The solutions of the digold(II) complexes **2a**−**4a** containing C_6H_3-2-PPh_2-6-Me decolorize within minutes above −20 °C, and almost colorless solids of the same empirical formula [X = Cl (**6a**), Br (**7a**), I (**8a**)] can be isolated in good yield by adding hexane to the resulting solutions. Qualitatively, the rate of isomerization decreases in the order I > Br > Cl. The half-life for the disappearance of **2a** was estimated as ca. 70 s at 308 K by UV−visible spectroscopy. The highest mass peak in the FAB-mass spectra of the isolated solids corresponds to the loss of one halide ion. The $^{31}P\{^1H\}$ NMR spectra contain a pair of doublets ($^2J_{PP} = 13$ Hz) in the regions of δ 35 and −60 to −80, the highly shielded resonance being characteristic of a phosphorus atom in a four-membered metallacycle;[21] the ^{1}H NMR spectra show two singlets arising from inequivalent methyl groups. These data are consistent with the formulation of compounds **6a**−**8a** as heterovalent gold(I)−gold(III) complexes containing one bidentate C_6H_3-2-PPh_2-6-Me group bound to gold(III) and one C_6H_3-2-PPh_2-6-Me group bridging gold(I) and gold(III), i.e., $[XAu^I\{\mu\text{-2-}Ph_2P(C_6H_3\text{-6-Me})\}\text{-}Au^{III}X\{\eta^2\text{-}(C_6H_3\text{-2-}PPh_2\text{-6-Me})\}]$ (Scheme 2). This conclusion has been confirmed by a single-crystal X-ray diffraction study of **8a** (X = I) (see below).

The far IR spectrum of **6a** shows a strong band due to ν(AuCl) at 328 cm^{-1}, which is replaced in the spectrum of **7a** by a band due to ν(AuBr) at 233 cm^{-1}. Bands at similar positions are observed in the spectra of tertiary phosphine−gold(I) complexes $[AuX(PR_3)]$ (X = Cl, Br, respectively).[22−24] A band at 291 cm^{-1} in the spectrum of **6a** is assigned tentatively to ν(AuCl) for Cl trans to aryl carbon on gold(III); the corresponding band due to ν(AuBr) appears at 207 cm^{-1} in the spectrum of **6b**.

The molecular structure of **8a** is shown in Figure 3, together with atom numbering. Selected bond lengths and angles are listed in Table 3. The trivalent gold atom, Au(1), is coordinated in a planar array by the four-membered chelate C_6H_3-2-PPh_2-6-Me group, the carbon atom of the bridging C_6H_3-2-PPh_2-6-Me group, and iodide; the iodide is trans to the carbon atom of the four-membered ring. The univalent gold atom, Au(2), is

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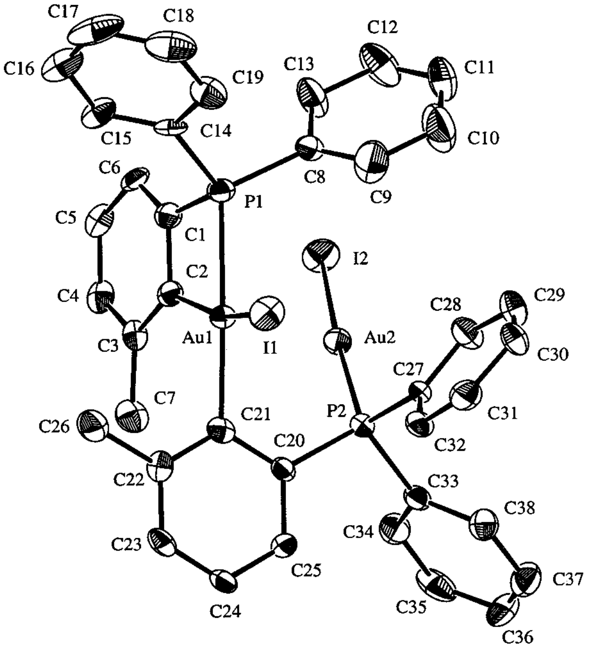

Figure 3. Molecular structure of [IAu^{I}(μ-2-$Ph_2PC_6H_3$-6-Me)Au^{III}I{η^2-C_6H_3-2-PPh_2-6-Me)}] (**8a**) with atom labeling; ellipsoids show 30% probability levels, and hydrogen atoms are drawn as circles with small radii.

Table 3. Selected Bond Distances (Å) and Angles (deg) in [IAu^{I}(μ-2-$Ph_2PC_6H_3$-6-Me)Au^{III}-I{η^2-(C_6H_3-2-PPh_2-6-Me)}] (8a)

Au(1)···Au(2)	3.4692(7)		
Au(1)−I(1)	2.645(1)	Au(1)−P(1)	2.347(3)
Au(1)−C(2)	2.092(11)	Au(1)−C(21)	2.079(11)
Au(2)−I(2)	2.545(1)	Au(2)−P(2)	2.252(3)
I(1)−Au(1)−P(1)	99.02(8)	I(1)−Au(1)−C(2)	163.7(3)
I(1)−Au(1)−C(21)	90.4(3)	P(1)−Au(1)−C(2)	68.6(3)
P(1)−Au(1)−C(21)	170.4(3)	C(2)−Au(1)−C(21)	102.4(4)
I(2)−Au(2)−P(2)	172.50(8)	Au(1)−P(1)−C(1)	84.4(4)
Au(2)−P(2)−C(20)	116.1(3)	P(1)−C(1)−C(2)	101.9(9)
P(1)−C(1)−C(6)	136(1)	Au(1)−C(2)−C(1)	104.7(8)
Au(1)−C(2)−C(3)	134.1(9)		

linearly coordinated by iodide and the phosphorus atom of the bridging C_6H_3-2-PPh_2-6-Me group. The angle subtended at Au(1) by the chelate four-membered ring is only 69°, typical of that observed in η^2-$C_6H_4PPh_2$, or substituted derivatives thereof, in planar platinum(II) complexes[25−27] and in complexes of iridium(III),[28,29] rhodium(III),[29] platinum(IV),[30] osmium(II),[31] and manganese(I).[32] The gold(III)−carbon bond lengths [Au(1)−C(2) = 2.092(11) Å; Au(1)−C(21) = 2.079(11) Å] are significantly greater than those in gold(III) complexes containing cyclometalated N-donors such as $C_6H_4(CH_2NMe_2)$-2 or C_6H_4(N=NPh)-2, which generally fall in the range 2.01−2.03 Å.[33,34] The gold atoms are separated by 3.47 Å, indicative of little or no interaction. Other bond lengths are unexceptional.

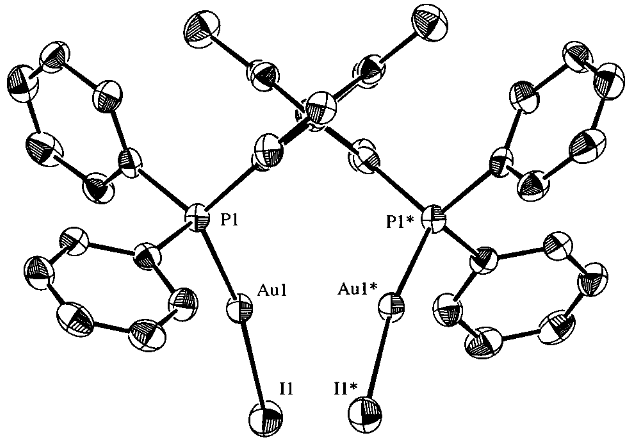

Figure 4. Molecular structure of [Au_2I_2{μ-2,2′-Ph_2P(5,5′-$Me_2C_6H_3C_6H_3$)PPh_2}] (**8b**) with selected atom labeling viewed along the C−C axis of the biphenyl backbone. Asterisks indicate atoms generated by crystallographic symmetry. Ellipsoids show 50% probability levels, and hydrogen atoms have been omitted. Distances: Au(1)···Au(1)* 2.9789(3) Å, Au(1)−P(1) 2.256(1) Å, Au(1)−I(1) 2.5498(4) Å; angle I(1)−Au(1)−P(1) 170.58(3)°.

Solutions of the digold(II) complexes **2b**−**4b** having the 5-methyl substituent also decolorize at room temperature over a period of hours. The $^{31}P\{^1H\}$ NMR spectra of these solutions show singlets in the region of δ 30, similar to those reported for the (2,2′-biphenylyl)bis(diphenylphosphine) complexes [Au_2X_2(μ-2,2′-$Ph_2PC_6H_4C_6H_4PPh_2$)];[17,18] no intermediates could be detected. From the solutions, the colorless digold(I) complexes [Au_2X_2{μ-2,2′-Ph_2P(5,5′-$Me_2C_6H_3C_6H_3$)PPh_2}] [X = Cl (**6b**), Br (**7b**), I (**8b**)] can be isolated as colorless solids in good yield (Scheme 1; Y = Me). As in the case of the parent series, the bis(benzoato)digold(II) complex **5b** does not rearrange, even on heating. The structural formulation of **8b** has been established by single-crystal X-ray diffraction. The molecular structure is shown in Figure 4, together with atom numbering. As in the cases of [Au_2Br_2(μ-2,2′-$Ph_2PC_6H_4C_6H_4PPh_2$)] and [Au_2I_2(μ-2,2′-$Et_2PC_6H_4C_6H_4PEt_2$)], the aromatic rings of the biphenyl backbone are approximately perpendicular to each other, the dihedral angle being 101°; the Au···Au separation of 2.98 Å is suggestive of a weak aurophilic interaction.[35] The ligand 2,2′-Ph_2P(5,5′-$Me_2C_6H_3C_6H_3$)PPh_2 (**12b**) is liberated from **8b** by treatment with NaCN.

The 5-methyl-substituted gold complexes thus behave very similarly to their unsubstituted analogues (Scheme 1). The only difference that we have observed is that, qualitatively, the rate of isomerization is in the order X = Cl (**2b**) > I (**4b**) > Br (**3b**), the position for X = Cl being the reverse of that found in the parent series. The half-lives $t_{1/2}$ for these rearrangements determined by ^{31}P NMR spectroscopy at 310 K were 3.8 min (**2b**), 22.5

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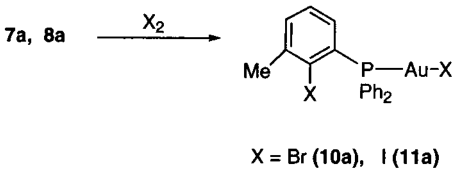
Scheme 3



min (**3b**), and 17.0 min (**4b**). The half-life for **4b** is very similar to that for the iodo compound in the parent series (18 min, 311 K), whereas the half-life for the bromo compound **3b** is much less than for its analogue in the parent series (165 min, 311 K).[18]

Although complexes **6a**–**8a** are structurally analogous to one of the intermediates, III, suggested to be a precursor to the C–C coupled product in the unsubstituted series (Scheme 1), attempts to induce C–C coupling in complex **8a** have failed. The main product identified by ^{31}P NMR spectroscopy after heating **8a** in toluene for 6 days was the digold(I) complex formed by loss of iodine. There was also a small amount of the product of iodine oxidation of **8a** (see below) and other unidentified species. Heating **6a** in toluene for the same period of time led to decomposition to elemental gold and several other unidentified species.

Complexes **6a**–**8a** react with an additional equivalent of halogen, but the products depend on the halogen used. Treatment of **7a** with bromine or of **8a** with iodine gives colorless halogold(I) complexes of the appropriate (2-halogeno-3-methylphenyl)diphenylphosphine, [AuX{$Ph_2P(C_6H_3$-2-X-3-Me)}] [X = Br (**10a**), I (**11a**)], arising from electrophilic cleavage of the gold(III)–carbon bonds (Scheme 3). The same compounds are obtained by treatment of **1a** with 2 equiv of bromine or iodine. They show singlets in their $^{31}P\{^1H\}$ NMR spectra whose chemical shifts are close to those of [AuBr(2-$BrC_6H_4PPh_2$)] and [AuI(2-$IC_6H_4PPh_2$)], respectively.[18] The identity of **11a** has been confirmed by single-crystal X-ray diffraction, and **10a** has been synthesized independently from K[$AuBr_4$] and (2-bromo-3-methylphenyl)diphenylphosphine. The structure of **11a** (Figure 5) shows the expected linear coordination about gold(I).

Treatment of **6a** with 1 equiv of $PhICl_2$ or of **1a** with 2 equiv of $PhICl_2$ gives a yellow solution, which, on standing, deposits a yellow solid, **9a**, that is insoluble in common organic solvents. However, the $^{31}P\{^1H\}$ NMR spectrum could be measured in situ as a suspension in $CDCl_3$. It shows a pair of doublets at δ 49.8 and −65.3 (J_{PP} = 19 Hz), similar in pattern to those of **6a** but differing in chemical shift. The matrix-assisted laser desorption ionization (MALDI) mass spectrum shows peaks at *m*/*z* 979 and 943 corresponding to the loss of three and four chlorine atoms, respectively. The IR spectrum shows strong bands at 366, 340, and 312 cm^{-1}, which are almost identical with the ν(AuCl) frequencies reported for [$AuCl_3(PPh_3)$].[36] These observations suggest that **9a** is derived from **6a** by addition of Cl_2 to the gold(I) atom (Scheme 4), and, in agreement, treatment of a suspension of **9a** in CH_2Cl_2 with zinc powder re-forms **6a** quantitatively, as shown by $^{31}P\{^1H\}$ NMR spectroscopy. Measurements of X-ray photoelectron[19] and Mössbauer spectra[20] have also confirmed that **9a** contains a pair of inequivalent gold(III) centers.

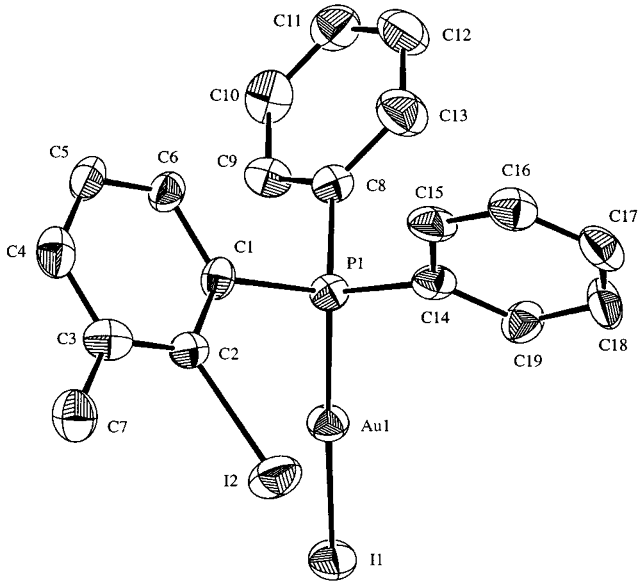
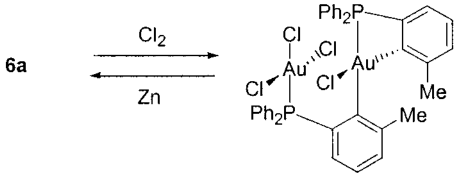


Figure 5. Molecular structure of [AuI{$Ph_2P(C_6H_3$-2-I-3-Me)}] (**11a**) with atom labeling; ellipsoids show 30% probability levels, and hydrogen atoms have been omitted. Distances: Au(1)–P(1) 2.251(4) Å, Au(1)–I(1) 2.550(1) Å; angle I(1)–Au–P(1) 174.0(1)°.

Scheme 4



9a

Discussion

The marked differences in the behavior of the digold complexes containing the C_6H_3-2-PPh_2-6-Me group compared with that of the corresponding complexes containing C_6H_3-2-PPh_2-5-Me or 2-$C_6H_4PPh_2$ can be attributed to steric repulsion between the 6-methyl substituents and ligands in the axial positions. This must be sufficient to prevent the addition of dibenzoyl peroxide to the digold(I) complex **1a** and to destabilize the symmetrical dihalodigold(II) complexes **2a**–**4a** in favor of their unsymmetrical gold(I)–gold(III) isomers **6a**–**8a**. The fact that complexes **2a**–**4a** can be isolated and characterized at low temperature clearly shows that they are the kinetic products of oxidative addition. This process must, therefore, involve both metal centers, in agreement with conclusions drawn about the oxidative addition of alkyl halides to the corresponding bis(ylide) complexes.[8]

Although the digold(II) complexes of C_6H_3-2-PPh_2-5-Me and 2-$C_6H_4PPh_2$ undergo similar C–C coupling reactions, the introduction of the methyl group para to phosphorus has the surprising effect of causing the chloro complex to become the most prone to isomerization rather than the least. There can be no doubt that the C–C coupling reaction is a multistep process involv-

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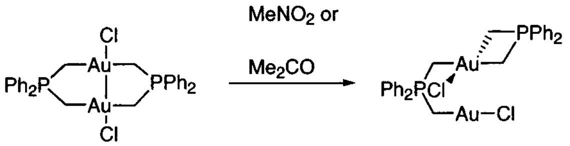
Scheme 5



ing several undetected intermediates; hence, the net effect of changing axial halide and aromatic ring substituents on the rates of the intervening steps is not easy to predict. Clearly, the kinetics of the process require more detailed study.

Complexes **6a**−**8a** represent the first fully characterized examples of complexes that contain a four-membered ring derived from a cyclometalated triarylphosphine attached to gold(III). In earlier work,[18] it was shown that bromination or iodination of [$Au^{II}_2X_2(\mu$-2-$C_6H_4PPh_2)_2$] to give as the final products [$Au^IX(Ph_2$-PC_6H_4-2-X)] (X = Br, I) proceeds through a number of cycloaurated intermediates, some of which were formulated as monomers, [AuX_2(2-$C_6H_4PPh_2$)], on the basis of their highly shielded ^{31}P resonances.

The formation of **6a**−**8a** from **2a**−**4a** requires migration of one of the metal−carbon σ-bonds from a gold atom to its neighbor; a similar process may occur also in the closely related isomerization in the bis(ylide) series shown in Scheme 5.[10] As noted above, the structure of **6a**−**8a** is very similar to that of one of the proposed intermediates, III, in the C−C coupling reaction (Scheme 1), and, in agreement, we have recently detected, though not isolated, intermediates in the corresponding rearrangements of [$Au_2X_2(\mu$-2-C_6H_4-$PPh_2)_2$] (X = SCN, C_6F_5), whose $^{31}P\{^1H\}$ NMR spectra closely resemble those of **6a**−**8a**.[37] It may be that reductive elimination of the two metal−carbon σ-bonds from the gold(III) centers of **6a**−**8a** is sterically hindered by the ortho-methyl groups.

Experimental Section

General Procedures. Most syntheses were performed under dry argon with use of standard Schlenk techniques, although the solid gold complexes, once isolated, were air-stable. Solvents were dried by standard procedures, distilled, and stored under nitrogen. The following instruments were used for spectroscopic measurements: Varian XL-200E (^1H at 200 MHz, ^{31}P at 80.96 MHz), Varian Gemini 300 (^1H at 300 MHz), Bruker Aspect 2000 (^{31}P at 80.96 MHz), VG ZAB-2SEQ (high-resolution EI and FAB mass spectra), Perkin-Elmer PE 683 (infrared spectra as KBr disks in the range 4000−400 cm^{-1}), Perkin-Elmer FT 1800 (infrared spectra as polyethylene disks in the range 400−150 cm^{-1}). The NMR chemical shifts (δ) are given in ppm relative to TMS (^1H) and 85% H_3PO_4 (^{31}P), referenced either to residual solvent signals (^1H) or externally (^{31}P). Coupling constants (J) are given in hertz. The UV−vis kinetic experiments were performed with use of a Perkin-Elmer Lambda 12 spectrometer. Elemental analyses were carried out in the Microanalytical Laboratory of the Research School of Chemistry, Canberra.

Starting Materials. The compounds $PhICl_2$[38] and [AuBr-(PEt_3)][39] were prepared as described in the literature. By use of modified literature procedures, 2-bromo-3-iodotoluene was prepared in a three-step sequence from 2-methyl-6-nitroaniline (Aldrich)[40−42] and 3-bromo-4-iodotoluene in a two-step sequence from p-toluidine (BDH).[42,43] These compounds were converted into (2-bromo-3-methylphenyl)diphenylphosphine and (2-bromo-4-methylphenyl)diphenylphosphine by $PdCl_2$-$(NCMe)_2$-catalyzed reaction with diphenyl(trimethylsilyl)phosphine, Ph_2PSiMe_3, in yields of 76% and 80%, respectively.[42] $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −4.1 (s) and −5.5 (s), respectively.

Digold(I) Complexes, [$Au_2(\mu$-C_6H_3-2-PPh_2-n-$Me)_2$] (n = 6, 1a; n = 5, 1b). A solution of (C_6H_3-2-Br-3-Me)PPh_2 or (C_6H_3-2-Br-4-Me)PPh_2 (1.0 g, 2.8 mmol) in a mixture of ether (20 mL) and hexane (20 mL) treated with a 1.6 M solution of n-BuLi (2 mL) gave a white precipitate of the appropriate organolithium compound, (C_6H_3-2-PPh_2-6-Me)Li or (C_6H_3-2-PPh_2-5-Me)Li, which was washed with hexane and dried in vacuo. The yield in both cases was ca. 70%. A suspension of the solid in ether was added to a solution of [AuBr(PEt_3)] (1.27 g, 3.2 mmol) in ether at −70 °C. The mixture was stirred overnight at room temperature, and the resulting off-white solid was washed successively with ether (3 × 10 mL), methanol (15 mL), and hexane (2 × 20 mL). It was then extracted with hot dichloromethane (**1b** being particularly poorly soluble), and the solution was filtered through Celite. Evaporation and addition of hexane gave **1a** or **1b** as white, air-stable solids in yields of 0.83 g (50%) and 0.62 g (43%), respectively, which melted with decomposition at 280 °C (**1a**) and 260 °C (**1b**). **1a**: ^1H NMR ($CDCl_3$) δ 2.6 (s, CH_3), 6.8−7.7 (m, arom); EI-MS m/z 944 (M^+), 754, 471, 276, 197. **1b**: EI-MS m/z 745 (M^+), 471, 276, 197.

Dihalodigold(II) Complexes, [$Au_2X_2(\mu$-C_6H_3-2-PPh_2-n-$Me)_2$] [n = 6, X = Cl (2a), Br (3a), I (4a); n = 5, X = Cl (2b), Br (3b), I (4b)]. A stirred solution or suspension of **1a** or **1b** (100 mg, 0.106 mmol) in dichloromethane (10 mL) at −70 °C was treated dropwise with an equimolar amount of $PhICl_2$, bromine, or iodine in dichloromethane (5 mL), the temperature being kept below −65 °C. The mixture was stirred for 30 min, and an approximately equal volume of hexane was added. The solution was evaporated under reduced pressure at or below −20 °C until the product began to precipitate. The solid was separated by filtration, washed with hexane, and dried in vacuo. The complexes were obtained in yields of 60−70%.

Complexes **2b**−**4b** could also be prepared by treatment of the bis(benzoato) complex **5b** (see below) with a solution or suspension of the appropriate lithium halide in acetone. The suspension was filtered through Celite, and the product was precipitated by addition of hexane to the filtrate. Yields were >85%. **2a**: ^1H NMR (CD_2Cl_2, −40 °C) δ 2.5 (s, 2CH_3), 6.7−7.6 (m, arom). **2b**: ^1H NMR (CD_2Cl_2) δ 2.3 (s, 2CH_3), 6.6 (q, J = 7 Hz, 1 H), 7.0 (d, J = 7 Hz, 2 H), 7.2−7.8 (m, 19 H), 8.1 (d, J = 7 Hz, 4 H) (arom); FAB-MS m/z 1014 (M^+), 979, 943, 747, 471, 365. **3b**: ^1H NMR (CD_2Cl_2) δ 2.3 (s, 2CH_3), 6.5 (q, J = 7 Hz, 2 H), 7.0 (d, J = 7 Hz, 2 H), 7.2−7.6 (m, 20 H), 7.9 (t, J = 5 Hz, 2 H) (arom); FAB-MS m/z 1025 (M^+ − Br), 747, 473. **4b**: (CD_2Cl_2) δ 2.3 (s, 2CH_3), 6.3 (q, J = 7 Hz, 2 H), 6.9 (d, J = 7 Hz, 2 H), 7.1−7.6 (m, 20 H), 8.0 (m, 2 H) (arom); FAB-MS m/z 1071 (M^+ − I), 747, 589, 473, 365.

Bis(benzoato)digold(II) Complex [$Au_2(O_2CPh)_2\{(\mu$-C_6H_3-2-PPh_2-5-$Me)_2\}$] (5b). A stirred suspension of **1b** (0.581 g, 0.615 mmol) in dichloromethane (25 mL) was treated with an excess of solid dibenzoyl peroxide (0.29 g, 1.20 mmol). The mixture was stirred at room temperature for 3 days and evaporated to dryness in vacuo. The yellow solid was stirred with ether for 2 h to remove the excess of peroxide, the ether was removed by decantation, and the solid was dried in vacuo. It was dissolved in a small volume of dichloromethane, and hexane was added. The solution was evaporated until the

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Table 4. Crystal and Refinement Data for Compounds 1a, 8a, 8b, and 11a

	1a	**8a**	**8b**	**11a**
(a) Crystal Data				
chem formula	$C_{38}H_{32}Au_2P_2$	$C_{38}H_{32}Au_2I_2P_2$	$C_{38}H_{32}Au_2I_2P_2$	$C_{19}H_{16}AuI_2P$
fw	944.55	1198.36	1198.36	726.08
cryst syst	triclinic	monoclinic	monoclinic	orthorhombic
unit cell dimens				
a (Å)	10.808(6)	14.749(2)	19.2078(3)	15.717(2)
b (Å)	12.795(5)	11.559(3)	10.7202(2)	15.217(3)
c (Å)	13.191(6)	21.691(2)	19.0440(3)	17.026(2)
α (deg)	98.63(4)			
β (deg)	112.59(4)	101.631(9)	112.823(1)	
γ (deg)	97.66(5)			
V (Å^3)	1628(2)	3622(1)	3614.4(1)	4072(2)
space group	*P*	$P2_1/c$ (# 14)	$C2/c$ (# 15)	*Pbca* (# 61)
D_c (g cm^{-3})	1.926	2.197	2.202	2.369
Z	2	4	4	8
F(000)	896.00	2216.00	2216.00	2640.00
color, habit	colorless, needle	pale yellow, blade	colorless, cuboid	colorless, block
cryst dimens (mm)	0.40 × 0.15 × 0.08	0.27 × 0.13 × 0.06	0.20 × 0.15 × 0.13	0.23 × 0.12 × 0.09
μ (cm^{-1})	90.93 (Mo Kα)	98.66 (Mo Kα)	99.60 (Mo Kα)	385.99 (Cu Kα)
(b) Data Collection and Processing				
diffractometer	Rigaku AFC6S	Rigaku AFC6S	Nonius Kappa CCD	Rigaku AFC6R
X-radiation	Mo Kα	Mo Kα	Mo Kα	Cu Kα
T (°C)	23(1)	23(1)	−73(1)	23(1)
scan mode	$\omega-2\theta$	$\omega-2\theta$		$\omega-2\theta$
ω-scan width	$1.20 + 0.34 \tan \theta$	$1.00 + 0.34 \tan \theta$		$1.10 + 0.30 \tan \theta$
$2\theta_{max}$ (deg)	55.1	55.1		120.0
no. of reflcns				
unique	7504	8768	4141[a]	3417
obsd	4807	4016	3456	2009
	[$I > 2.0\sigma(I)$]	[$I > 2.0\sigma(I)$]	[$I > 2.0\sigma(I$)	[$I > 2.0\sigma(I)$]
abs corr	analytical	numerical[b]	analytical	analytical
(transm factors)	(0.26−0.53)	(0.34−0.63)	(0.25−0.45)	(0.02−0.14)
(c) Structure Analysis and Refinement				
structure soln	Patterson methods	direct methods	direct methods	direct methods
refinement	full matrix least squares			
no. of params	379	397	199	208
weighting scheme w	$[\sigma^2(F) + (0.0001)F^2]^{-1}$			
R (obsd data) %	3.3	3.5	2.9	4.1
R_w (obsd data) %	3.1	3.3	2.9	5.0
GOF	1.52	1.13	1.11	1.61
ρ_{max}, ρ_{min} (e Å^{-3})	1.90, −1.51	0.84, −0.83	0.96, −1.49	1.44, −1.11

[a] Total reflections 33 991. [b] Correction for 1.7% decay also applied.

product began to separate and then set aside at 0 °C. The solid was separated by filtration, washed with hexane, and dried in vacuo. The yield was 0.40 g, 0.337 mmol, 55%: ^{1}H NMR (CD_2Cl_2) δ 2.3 (s, $2CH_3$), 6.7 (q, J = 7 Hz, 2 H), 6.9−7.1 (m, 2 H), 7.2−7.6 (m, 30 H), 7.7 (t, J = 7 Hz, 2 H) (arom); FAB-MS m/z 945 ($M^+ - 2$ OBz), 747, 473, 365.

Under the same conditions, complex **1a** did not react with dibenzoyl peroxide.

Gold(I)−Gold(III) Complexes, [XAu(μ-2-$Ph_2PC_6H_3$-6-Me)AuX{η^2-(C_6H_3-2-PPh_2-6-Me)}] [X = Cl (6a), Br (7a), I (8a)]. These were prepared from **1a** as described for **2a**−**4a** (see above), except that the solutions were kept at room temperature. Immediately after addition of the halogenating agent, the solutions were strongly colored, but they became colorless within a few minutes. Hexane was added, and the solutions were evaporated until the products began to precipitate; the solutions were then set aside at 0 °C. The yields of **6a**−**8a** were >60%. The compounds were also obtained quantitatively by allowing solutions of **2a**−**4a** to stand at room temperature for 20 min and then adding hexane to precipitate colorless solids. **6a**: ^{1}H NMR (CD_2Cl_2) δ 1.2 (s, CH_3), 2.6 (s, CH_3), 6.8−8.1 (m, arom); FAB-MS m/z 979 ($M^+ -$ Cl), 747, 472, 306. **7a**: ^{1}H NMR (CD_2Cl_2) δ 1.8 (s, CH_3) 2.5 (s, CH_3), 6.6−8.0 (m, arom); FAB-MS m/z 1025 ($M^+ -$ Br), 747, 471, 384. **8a**: ^{1}H NMR (CD_2Cl_2) δ 1.8 (s, CH_3), 2.4 (s, CH_3), 6.5−8.2 (m, arom); FAB-MS m/z 1198 (M^+), 1071, 943, 747, 471, 275.

Gold(III)−Gold(III) Complex [Cl_3Au(μ-2-$Ph_2PC_6H_3$-6-Me)AuCl{η^2-(C_6H_3-2-PPh_2-6-Me)}][(9a). To a stirred solution of **6a** (250 mg, 0.265 mmol) in dichloromethane (20 mL) was added dropwise an equimolar solution of $PhICl_2$ in dichloromethane (10 mL) at room temperature. The mixture was set aside overnight. The resulting bright yellow solid was separated by filtration and washed with dichloromethane and hexane. The yield was 200 mg (70%). The compound was also obtained by treatment of **1a** with an excess of $PhICl_2$ under similar conditions. FAB-MS: m/z 979 ($M^+ - 3$ Cl), 943, 747, 471, 313, 289, 252.

Reactions of 7a or 8a with Halogen. A stirred solution of **7a** or **8a** (100 mg, 0.106 mmol) in dichloromethane (10 mL) was treated dropwise with a solution of bromine (for **7a**) or iodine (for **8a**) (0.11 mmol) in dichloromethane (5 mL) at room temperature. After 20 min, hexane was added to precipitate the colorless solids [AuX{$Ph_2P(C_6H_3$-2-X-3-Me)}] [X = Br (**10a**), I (**11a**)] in yields of 60−70%.

An authentic sample of **10a** was prepared by adding an ethanolic solution of (C_6H_3-2-Br-3-Me)PPh_2 (1.8 g, 5.1 mmol) to an ethanolic solution of K[$AuBr_4$] (1.39 g, 2.5 mmol). The resulting colorless solid was separated by filtration and washed with ethanol. Recrystallization from ethanol gave white needles of **10a** (0.7 g, 44%). **10a**: ^{1}H NMR (CD_2Cl_2) δ 2.5 (s, CH_3), 6.6 (t, J = 7 Hz, 1 H), 7.2 (dt, J = 7, 1 Hz, 1 H), 7.4 (d, J = 7 Hz, 1 H), 7.5−7.7 (m, 10 H) (arom); FAB-MS m/z 632 (M^+), 551, 471, 355, 275. **11a**: ^{1}H NMR (CD_2Cl_2) δ 2.5 (s, CH_3), 6.6 (t, J = 7 Hz, 1 H), 7.2 (dt, J = 7, 1 Hz. 1 H), 7.4 (d, J = 7 Hz, 1 H), 7.5−7.7 (m, 10 H) (arom); EI-MS m/z 726 (M^+), 599, 471, 401, 275, 197.

Digold(I) Complex [$Au_2I_2\{\mu$-2,2′-$Ph_2P(5,5'$-$Me_2C_6H_3C_6H_3)$-$PPh_2\}$] (8b). When heated at 50 °C for 2 h a solution of complex **4b** (45 mg, 0.038 mmol) in toluene (5 mL) became colorless. The solution was evaporated under reduced pressure, and the colorless compound **8b** was precipitated almost quantitatively by addition of hexane. Crystals suitable for X-ray crystallography were obtained from dichloromethane/hexane: ^{1}H NMR (CD_2Cl_2) δ 1.8 (s, 2CH_3), 6.1 (d, $J = 4$ Hz, 2 H), 7.0−7.2 (m, 4 H), 7.4−7.7 (m, 20 H), 7.8−8.0 (m, 4 H) (arom); FAB-MS m/z 1071 ($M^+ - I$), 747, 365.

5,5′-Dimethyl-2,2′-biphenylyl)bis(diphenylphosphine) (12b). A suspension of **8b** (30 mg, 0.025 mmol) in degassed ethanol (10 mL) was stirred for 24 h with an aqueous solution of NaCN. The white solid that had formed was filtered and washed with water. Recrystallization from hexane afforded 13 mg (0.024 mmol, 93%) of **12b** as colorless needles, mp 182−183 °C: ^{1}H NMR (CD_2Cl_2) δ 2.1 (s, 2CH_3), 6.6 (d, $J =$ 4 Hz, 2 H), 6.9−7.1 (m, 4 H), 7.1−7.5 (m, 20 H) (arom); ^{31}P-{^{1}H} NMR (CD_2Cl_2) δ −14.9 (s); EI-MS m/z 549 (M^+), 473, 365. Anal. Calcd for $C_{38}H_{32}P_2$: C, 82.89; H, 5.86; P, 11.25. Found: C, 82.52; H, 5.92; P, 10.93.

Kinetic Experiments. (1) A sample of the digold(II) complex was dissolved in $CDCl_3$ in an NMR tube and placed in the NMR spectrometer set to 310 K. The half-lives of the digold(II) compounds were determined from the increase in peak height of the product or from the decrease in peak height of the starting compound. (2) A small amount of **2a** was placed in a quartz cell of path length 1 cm. Toluene was added and the cell heated with a Peltier heating system. The half-life was determined from the decrease in absorbance at 354 nm. Half-lives for **3a** and **4a** could not be determined because of the very fast isomerization of these compounds.

X-ray Crystallography. The crystal and refinement data for compounds **1a**, **8a**, **8b**, and **11a** are summarized in Table 4. The structure of **1a** was solved by Patterson methods;[44] the others by direct methods (SIR 92).[45] They were expanded by use of Fourier techniques.[46] Hydrogen atoms were included at geometrically determined positions, which were periodically recalculated but not refined. Methyl hydrogen atoms were oriented to best-fit peaks in difference electron density maps. The neutral atom scattering factors were taken from ref 47; $\Delta f'$ and $\Delta f''$ values and mass attenuation coefficients were taken from ref 48. Anomalous dispersion effects were included in F_{calc}.[49] All calculations were performed with the teXsan crystallographic software package.[50]

Supporting Information Available: Full crystallographic data for **1a**, **8a**, **8b**, and **11a** including tables of atomic coordinates, anisotropic displacement parameters and bond lengths and angles is available free of charge via the Internet at http://pubs.acs.org.

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