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Dinuclear Cycloaurated Complexes Containing Bridging (2-Diphenylphosphino)phenylphosphine and (2-Diethylphosphino)phenylphosphine, $C_6H_4PR_2$ (R = Ph, Et). Carbon−Carbon Bond Formation by Reductive Elimination at a Gold(II)−Gold(II) Center

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Abstract: The digold(I) complexes $Au_2(\mu\text{-}C_6H_4PR_2)_2$ [R = Ph (**1a**), Et (**1b**)] obtained by treatment of $AuBr(PEt_3)$ with *o*-$LiC_6H_4PR_2$ undergo addition with halogens or benzoyl peroxide to give metal−metal bonded digold(II) complexes $Au_2X_2(\mu\text{-}C_6H_4PR_2)_2$ [R = Ph, Et; X = I (**2a**, **2b**), Br (**3a**, **3b**), Cl (**4a**, **4b**), O_2CPh (**5a**, **5b**)], which are structurally similar to the bis(ylide) complexes $Au_2X_2\{\mu\text{-}(CH_2)_2PR_2\}_2$. The benzoate ligands in **5b** are monodentate and the gold−gold bond length [2.5243(7) Å] is significantly less than that in the diiodide (**2a**) [2.5898(6) Å, 2.5960 (Å) for independent molecules], reflecting the trans influences of the axial anionic ligands. The corresponding complexes $Au_2X_2(\mu\text{-}C_6H_4PR_2)_2$ [R = Ph, Et; X = O_2CMe (**6a**, **6b**), ONO_2 (**7a**, **7b**)] are made from **2**−**4** and the appropriate silver salt. The axial anionic ligands undergo immediate scrambling when solutions of $Au_2X_2(\mu\text{-}C_6H_4PR_2)_2$ and $Au_2Y_2(\mu\text{-}C_6H_4PR_2)_2$ are mixed. The bridging $C_6H_4PR_2$ units also scramble rapidly on mixing solutions of $Au_2X_2(\mu\text{-}C_6H_4PPh_2)_2$ [X = I (**2a**), Br (**3a**)] and $Au_2X_2(\mu\text{-}C_6H_4PEt_2)_2$ [X = I (**2b**), Br (**3b**)], but this occurs only slowly for X = Cl and not at all for X = O_2CPh, O_2CMe, or ONO_2. Solutions of the diiodo complexes **2a**, **2b** and the dibromo complexes **3a**, **3b** isomerize cleanly to the digold(I) complexes $Au_2X_2(\mu\text{-}R_2PC_6H_4C_6H_4PR_2)$ [R = Ph, Et; X = I (**8a**, **8b**), Br (**9a**, **9b**)] containing 2,2′-biphenylyl(diphenylphosphine) or 2,2′-biphenylyl(diethylphosphine), respectively, as a consequence of a reductive elimination in which a C−C bond is formed at the expense of two Au−C bonds. In **8b** the Au−Au separation is 3.167(1) Å and the phenyl rings of the biphenyl unit are almost orthogonal. Qualitatively, the rates of isomerization of $Au_2X_2(\mu\text{-}C_6H_4PR_2)_2$ to $Au_2X_2(\mu\text{-}R_2PC_6H_4C_6H_4PR_2)$ are in the order R = Ph > Et; X = I > Br >> Cl; isomerization does not occur for X = O_2CPh, O_2CMe, or ONO_2. The rates of thermal isomerization of **2a** and **3a** are first order in complex, only slightly sensitive to solvent polarity, and, for **2a**, inhibited by iodide ion. It is suggested that reversible loss of halide ion initiates aryl group transfer between the gold atoms, thus allowing reductive elimination of Au−C bonds to take place at one center. Treatment of **2a** or **3a** with an excess of iodine or bromine gives initially digold(III) complexes *cis,trans*-$Au_2X_4(\mu\text{-}C_6H_4PPh_2)_2$ [X = I (**14**), Br (**15**)], which are in equilibrium with monomers $\overline{AuX_2(C_6H_4P}Ph_2)$ [X = I (**16**), Br (**17**)], as shown by ^{31}P NMR spectroscopy. These species isomerize at room temperature by internal electrophilic cleavage of their Au−C bonds to give stable gold(I) complexes of (2-halogenophenyl)diphenylphosphine, $AuX(o\text{-}XC_6H_4PPh_2)$ [X = I (**12**), Br (**11**)].

Introduction

An extensive family of binuclear complexes containing the framework $Au_2(LL')$ is known in which two linearly coordinated gold(I) atoms are held in close contact by a pair of 1,3-bifunctional ligands (LL′) such as dithiocarbamate, $[R_2NCS_2]^-$, dithiophosphate, $[S_2P(OR)_2]^-$, methylenethiophosphinate, $[R_2P(S)CH_2]^-$, bis(diphenylphosphino)methane, $Ph_2PCH_2PPh_2$, bis(diphenylphosphino)amines, $Ph_2PN(R)PPh_2$ (R = H, Me), bis(diphenylphosphino) methanide, $[Ph_2PCHPPh_2]^-$, and phosphorus bis(ylides) $[R_2P(CH_2)_2]^-$.[2−6] The Au−Au separations in the complexes depend on the geometry and electronic nature of the ligands, but are usually in the range 2.80−3.10 Å indicative of a weak attractive interaction between the gold atoms, *cf.* the interatomic distance of 2.88 Å in gold metal. Many of these compounds undergo oxidative addition with an equivalent of halogen, pseudo-halogen, or alkyl halide (XY) to give either binuclear gold(II)−gold(II) ($5d^9$−$5d^9$) complexes containing a conventional electron-pair metal−metal bond or mixed-valent gold(I)−gold(III) ($5d^{10}$−$5d^8$) complexes; in some cases, both isomers can be isolated (Schemes 1−3).[7−17] The gold(II)−gold(II) complexes can also be oxidized further

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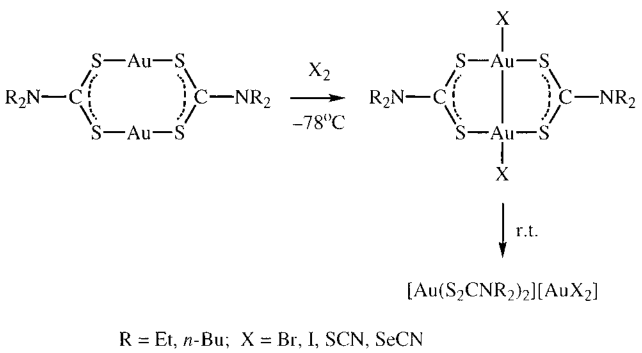
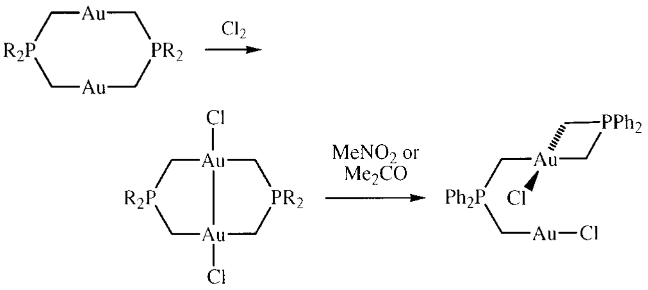
S0002-7863(96)01511-9 CCC: $12.00

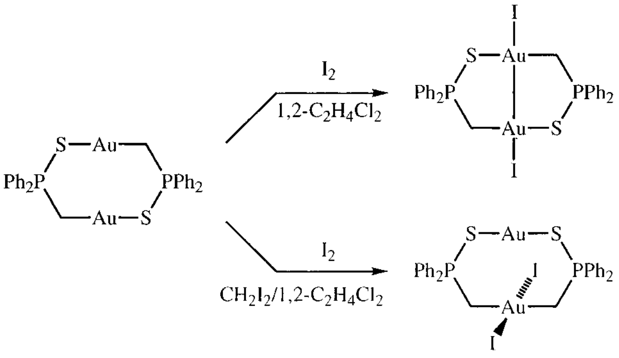
Scheme 1



Scheme 2



Scheme 3



by halogens to give dinuclear gold(III)−gold(III) complexes.[7,10,13,18−23]

Apart from the methylenethiophosphinate and ylide complexes, in which the metal−carbon bonds are probably stabilized by the presence of the formally positively charged phosphorus atoms, there are only a few examples of dinuclear gold complexes containing carbanionic ligands. The digold(I) complexes $Au_2(\mu\text{-}C_6H_4CH_2PPh_2\text{-}o)_2$[24] and $Au_2\{\mu\text{-}C(SiMe_3)_2C_5H_4N\}_2$[25] have been made from the reaction of gold(I) chloro complexes with (*o*-lithio)benzyldiphenylphosphine and lithiated 2-bis(trimethylsilyl)methylpyridine, respectively; treatment of $Au_2(\mu\text{-}C_6H_4CH_2PPh_2\text{-}o)_2$ with an excess of bromine gives the digold(III) derivative $Au_2Br_4(\mu\text{-}C_6H_4CH_2PPh_2\text{-}o)_2$.[24] We have reported in preliminary communications[26,27] that the carbanions (*o*-diphenylphosphino)phenyl and (*o*-diethylphosphino)phenyl, *o*-$C_6H_4PR_2$(R = Ph, Et), give dinuclear cycloaurated compounds $Au^I_2(\mu\text{-}C_6H_4PR_2)_2$ and $Au^{II}_2X_2(\mu\text{-}C_6H_4PR_2)_2$ (X = Cl, Br, I) and that the cyclometalated units in the latter readily undergo C−C coupling. We now provide a detailed account of our studies on these systems.

Results

Synthesis, Structure, and Reactions of Cycloaurated Complexes. The digold(I) complexes $Au_2(\mu\text{-}C_6H_4PR_2)_2$ [R = Ph (**1a**), Et (**1b**)] can be prepared as colorless, air-stable solids in *ca.* 60% yield by the action of the organolithium reagents *o*-$LiC_6H_4PR_2$ on $AuBr(PEt_3)$ at −50 °C in ether. The more labile precursor AuCl(tht) (tht = 2,2,5,5-tetrahydrothiophene) cannot be used because it is rapidly reduced to gold under these conditions. All attempts to prepare cycloaurated complexes directly from triphenylphosphine, e.g. by heating $Au(O_2CMe)(PPh_3)$ or $AuMe(PPh_3)$ with or without added Ph_3P, led only to decomposition. Complex **1a** is soluble only in dichloromethane and chloroform, whereas **1b** is soluble also in toluene and THF. Both complexes show parent ions in their EI-mass spectra and singlets in their $^{31}P\{^1H\}$ NMR spectra. The IR spectrum of **1a** contains bands at 1563 (w), 1420 (w), and 723 (m) cm^{-1} that are characteristic of *o*-metalated triphenylphosphine complexes.[28−30] These data are consistent with a dinuclear structure containing linearly coordinated gold(I), which has been confirmed by an X-ray structural analysis of **1a**.[26] The Au−Au separation [2.8594(3) Å] is in the expected range and is significantly greater than the value of 2.776(1) Å found in the isosteric cation $[Au_2(\mu\text{-}NC_5H_4PMe_2\text{-}o)_2]^{2+}$ derived from 2-pyridyldimethylphosphine.[31]

The digold(I) compounds react with 1 equiv of halogen at low temperature or of benzoyl peroxide at room temperature to give the corresponding digold(II) complexes $Au_2X_2(C_6H_4PR_2)_2$ [R = Ph, Et; X = I (**2a**, **2b**), Br (**3a**, **3b**), Cl (**4a**, **4b**), O_2CPh (**5a**, **5b**)] as air-stable solids in 60−80% yields (Scheme 4). The iodides are red, the bromides are orange, and the chlorides and benzoates are yellow. The chloro compounds can also be made conveniently by use of $PhICl_2$ in place of Cl_2. All the compounds show singlets in their $^{31}P\{^1H\}$ NMR spectra that are at higher frequency than those of the digold(I) complexes (Table 1); the shielding increases in the order I > Br > Cl > O_2CPh. In the ^1H NMR spectra of **2b**−**5b** the diastereotopic methylene protons of the $C_6H_4PEt_2$ fragment appear as a pair of multiplets in C_6D_6, whereas in CD_2Cl_2 the chemical shift

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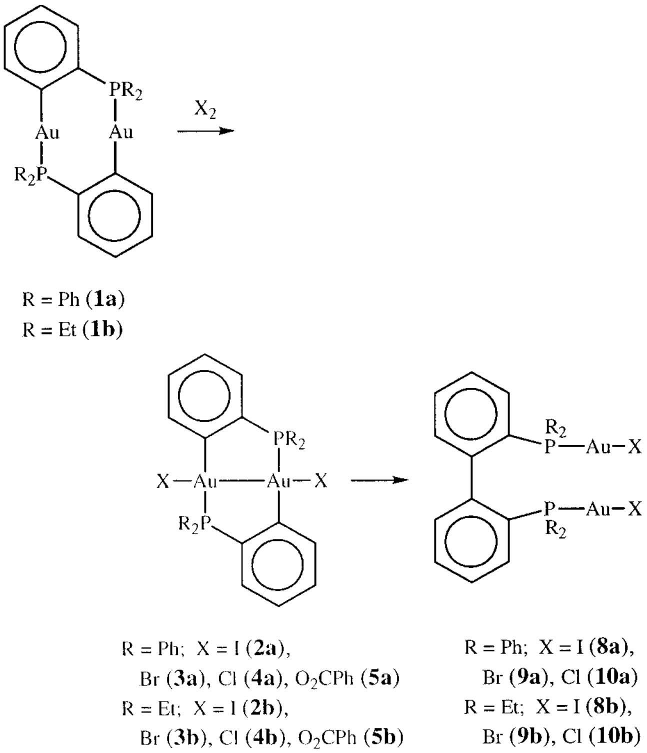
Scheme 4



R = Ph (**1a**)
R = Et (**1b**)

R = Ph; X = I (**2a**), Br (**3a**), Cl (**4a**), O$_2$CPh (**5a**)
R = Et; X = I (**2b**), Br (**3b**), Cl (**4b**), O$_2$CPh (**5b**)

R = Ph; X = I (**8a**), Br (**9a**), Cl (**10a**)
R = Et; X = I (**8b**), Br (**9b**), Cl (**10b**)

difference is not resolved. The ^{197}Au Mössbauer spectra of **2a**, **2b**, and **3a** are in agreement with a gold(II)−gold(II) formulation for these compounds,[32] and this is confirmed by the X-ray structures of $Au_2I_2(\mu\text{-}C_6H_4PPh_2)_2$ (**2a**)[27] and $Au_2(O_2CPh)_2(\mu\text{-}C_6H_4PEt_2)_2$ (**5b**).

The molecular structure of **5b** is shown in Figure 1; selected bond distances and angles are in Table 2. The monodentate benzoate groups are located along the Au−Au axis and the eight-membered $\overline{\text{Au}-\text{P}-\text{C}-\text{C}-\text{Au}-\text{P}-\text{C}-\text{C}}$ ring is puckered, as shown by the torsion angles P−Au−Au−P (−143.5°), C−Au−Au−C (−142.5°), P−Au−Au−C (38.9°), and P−Au−Au−C (35.0°). A similar though smaller puckering occurs in **2a**, whereas in **1a** the Au_2P_2 unit is flat and the ring has a twist "recliner" conformation in which the carbon atoms are displaced by 0.40 and 0.25 Å from the Au_2P_2 plane.[26] The Au−Au separation in **5b** [2.5243(7) Å] appears to be one of the shortest so far reported for digold(II) complexes. It is significantly less than that in **2a** [2.5898(6), 2.5960(7) Å for independent molecules],[27] in the monodentate benzoato bis(ylide) complex $Au_2(O_2CPh)_2\{\mu\text{-}(CH_2)_2PPh_2\}_2$ [2.587(1), 2.560(2) Å for independent molecules],[33] and in the dibromo bis(ylide) complex $Au_2Br_2\{\mu\text{-}(CH_2)_2PPh_2\}_2$ [2.614(1) Å].[34] The trends reflect the relative *trans* influences of benzoate and iodide or bromide ($O_2CPh^- < I^-, Br^-$) and suggest that, for a given axial ligand, the gold(II)−gold(II) distance in the μ-bis(organophosphino)phenyl complexes is slightly less than that in the μ-bis(ylide) complexes. The operation of a *trans* influence on a Au−Au bond is evident from a comparison of the Au−Au distances in $Au_2(Br)(CH_3)\{(CH_2)_2PPh_2\}_2$ [2.674(1)Å][16] with that in $Au_2Br_2\{(\mu\text{-}(CH_2)_2PPh_2\}_2$, and there is also evidence for the transmission of the high *trans* influence of methyl through the gold−gold bond to an axial gold−halide bond.[12,16]

The anionic ligands in the digold(II) complexes are readily interchanged. The benzoato complexes **5a** and **5b** react with lithium halides at room temperature to give the halide complexes **2a**−**4a** and **2b**−**4b**, respectively. Conversely, treatment of the halide complexes with a large excess of silver benzoate, acetate, or nitrate forms the corresponding pale yellow digold(II) complexes $Au_2Y_2(\mu\text{-}C_6H_4PR_2)_2$ [R = Ph, Et; Y = O_2CPh (**5a**, **5b**), O_2CMe (**6a**, **6b**), ONO_2 (**7a**, **7b**)], all of which show singlets in their $^{31}P\{^1H\}$ NMR spectra. Similar reactions occur in the binuclear ylide series.[34] The IR spectra of the acetato complexes **6a** and **6b** show intense bands at *ca.* 1625 and 1590 cm^{-1} due to ν(C=O) and at 1290−1300 cm^{-1} due to ν(C−O), the large separation between the two frequencies being typical of monodentate acetate ligands.[35] Although assignment of the mode of coordination of nitrate from IR spectroscopy is not so clear-cut, the IR spectra of **7a** and **7b** exhibit strong N−O stretching bands at 1485−1500 and 1270−1255 cm^{-1}, which are close to the values reported for typical monodentate nitrato complexes such as $Re(CO)_5NO_3$ and $[Co(NH_3)_5NO_3]^{2+}$.[36,37] In **4a** and **3a** the bands due to gold−halogen stretching appear at 278 vs/261 s and 190 cm^{-1}, respectively; those in **4b** and **3b** could not be located owing to strong ligand absorption. The values for **4a** and **3a** are significantly less than the corresponding values in the bis(ylide) complexes $Au_2X_2\{\mu\text{-}(CH_2)_2PPh_2\}_2$ (X = Cl, Br) (293 and 220 cm^{-1}, respectively),[38] indicative of weaker gold−halogen bonds in the cyclometalated complexes.

On mixing solutions of digold(II) complexes containing different anionic ligands, i.e. $Au_2X_2(\mu\text{-}C_6H_4PPh_2)_2$ and $Au_2Y_2(\mu\text{-}C_6H_4PPh_2)_2$ or $Au_2X_2(\mu\text{-}C_6H_4PEt_2)_2$ and $Au_2Y_2(\mu\text{-}C_6H_4PEt_2)_2$, at room temperature, an approximately statistical mixture of $Au_2X_2(\mu\text{-}C_6H_4PR_2)_2$, $Au_2Y_2(\mu\text{-}C_6H_4PR_2)_2$, and $Au_2(X)(Y)(\mu\text{-}C_6H_4PR_2)_2$ is formed as a consequence of rapid exchange of the anionic ligands. The presence of the mixed species is evident from the observation of an AB quartet (J_{AB} *ca.* 75 Hz) in the $^{31}P\{^1H\}$ NMR spectrum whose chemical shift usually lies between those of the symmetrical precursors (Table 3). More surprisingly, when dichloromethane solutions of $Au_2I_2(\mu\text{-}C_6H_4PPh_2)_2$ (**2a**) and $Au_2I_2(\mu\text{-}C_6H_4PEt_2)_2$ (**2b**) are mixed at room temperature, a new species having a ^{31}P AB quartet (J_{AB} *ca.* 73 Hz) is formed immediately; this is presumably $Au_2I_2(\mu\text{-}C_6H_4PPh_2)(\mu\text{-}C_6H_4PEt_2)$ resulting from transfer of the $C_6H_4PR_2$ ligands between the gold(II) centers. The exchange is completely suppressed by addition of an excess of $[Et_4N]I$. A similar exchange occurs within 1 h for the bromo complexes **3a** and **3b** and over a period of 2 weeks for the dichloro complexes **4a** and **4b**, but it is accompanied by isomerization of the precursors (see below). The closest analogy to the scrambling of which we are aware is the transfer of bis(ylide) groups between gold(I) centers, which has been used to prepare heterobridged digold(I) complexes such as $Au_2\{\mu\text{-}(CH_2)_2PPh_2\}(\mu\text{-}S_2CX)]$ [X = NMe_2, NEt_2, $N(CH_2Ph)_2$, OMe, OEt, O-*i*-Pr].[39] These can be oxidized with halogens to the corresponding digold(II) complexes $Au_2X_2\{\mu\text{-}(CH_2)_2PPh_2)_2\}(\mu\text{-}S_2CX)$,[40,41] which apparently retain their identity in solution. In contrast to the behavior of

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Table 1. Elemental Analyses and ^{31}P NMR Data for Digold(I) and Digold(II) Complexes of $C_6H_4PR_2$

complex	color	Anal. [calcd (found)] % C	% H	% other	δ_P[a]
$Au_2(C_6H_4PPh_2)_2$ (**1a**)	white	47.18 (46.87)	3.08 (3.12)	6.76 (6.52) (P)	36.4
$Au_2(C_6H_4PEt_2)_2$ (**1b**)	white	33.16 (33.10)	3.90 (3.84)	8.55 (8.67) (P)	34.6
$Au_2I_2(C_6H_4PPh_2)_2$ (**2a**)	purple-red	36.95 (37.75)	2.41 (2.56)	5.29 (5.46) (P)	−12.7[b]
$Au_2Br_2(C_6H_4PPh_2)_2$ (**3a**)	orange	40.17 (39.73)	2.62 (2.50)	14.85 (14.78) (Br)	−4.6[c]
$Au_2Cl_2(C_6H_4PPh_2)_2$ (**4a**)	pale yellow	43.79 (43.48)	2.86 (2.78)	7.18 (7.49) (Cl)	1.3[d]
$Au_2(O_2CPh)_2(C_6H_4PPh_2)_2$ (**5a**)	yellow	51.83 (51.74)	3.31 (3.18)		4.3
$Au_2(O_2CMe)_2(C_6H_4PPh_2)_2$ (**6a**)	pale yellow	46.44 (45.15)	3.31 (3.21)		4.1
$Au_2(ONO_2)_2(C_6H_4PPh_2)_2$ (**7a**)	yellow	41.56 (41.38)	2.71 (2.44)	2.69 (2.10) (N)	5.4
$Au_2I_2(C_6H_4PEt_2)_2$ (**2b**)	rust red	24.56 (24.77)	2.89 (3.04)	25.95 (26.17) (I)	−11.6
$Au_2Br_2(C_6H_4PEt_2)_2$ (**3b**)	orange	27.17 (26.47)	3.19 (3.20)	18.08 (18.12) (Br)	−2.6
$Au_2Cl_2(C_6H_4PEt_2)_2$ (**4b**)	yellow	30.21 (30.36)	3.55 (3.68)	8.92 (9.06) (Cl)	3.0
$Au_2(O_2CPh)_2(C_6H_4PEt_2)_2$ (**5b**)	pale yellow	42.25 (42.02)	3.96 (3.91)		8.2
$Au_2(O_2CMe)_2(C_6H_4PEt_2)_2$ (**6b**)	pale yellow	34.22 (34.55)	4.07 (4.07)		7.5
$Au_2(ONO_2)_2(C_6H_4PEt_2)_2$ (**7b**)	pale yellow	28.32 (28.96)	3.33 (2.82)	3.30 (2.56) (N)	10.5

[a] In CD_2Cl_2. [b] −12.6 (d_8-toluene). [c] −3.9 (d_8-toluene). [d] 1.5 (d_8-toluene).

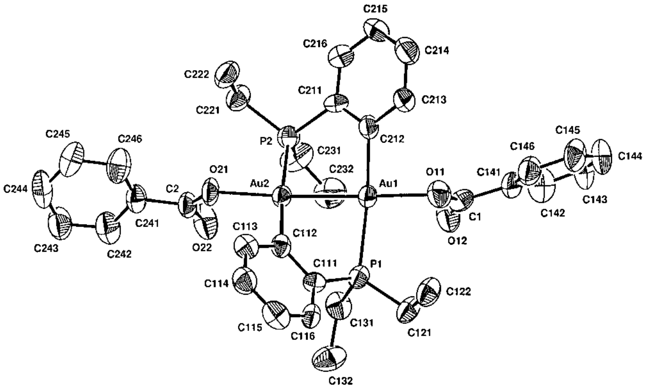

Figure 1. Molecular structure of $Au_2(O_2CPh)_2$ $(C_6H_4PEt_2)_2$ (**5b**) with atom labeling (hydrogen atoms omitted); ellipsoids show 30% probability levels.

Table 2. Selected Bond Distances (Å) and Angles (deg) in $Au_2(O_2CPh)_2(\mu\text{-}C_6H_4PEt_2)_2$ (**5b**)

Au(1)−Au(2)	2.5243(7)		
Au(1)−P(1)	2.336(4)	Au(2)−P(2)	2.333(4)
Au(1)−C(212)	2.01(1)	Au(2)−C(112)	2.04(1)
Au(1)−O(11)	2.126(9)	Au(2)−O(21)	2.088(8)
Au(1)···O(12)	2.97(1)	Au(2)···O(22)	3.02(1)
O(11)−C(1)	1.24(2)	O(21)−C(2)	1.24(2)
O(12)−C(1)	1.18(2)	O(22)−C(2)	1.24(2)
Au(2)−Au(1)−P(1)	84.11(8)	Au(1)−Au(2)−P(2)	86.48(8)
Au(2)−Au(1)−O(11)	171.9(3)	Au(1)−Au(2)−O(21)	174.8(3)
Au(2)−Au(1)−C(212)	90.2(3)	Au(1)−Au(2)−C(112)	89.2(3)
P(1)−Au(1)−O(11)	96.6(3)	P(2)−Au(2)−O(21)	93.5(3)
P(1)−Au(1)−C(212)	174.2(4)	P(2)−Au(2)−C(112)	175.1(3)
O(11)−Au(1)−C(212)	89.2(5)	C(112)−Au(2)−O(21)	90.5(4)

Table 3. ^{31}P NMR Parameters of Digold(II) Complexes Containing Different Anions

R	X, Y	δ_A	δ_B	J_{AB}(Hz)
Ph	I (**2a**), Br (**3a**)	−5.5	−11.9	77
Ph	I (**2a**), O_2CPh (**6a**)	0.3	−10.8	74
Ph	Br (**3a**), Cl (**4a**)	0.5	−3.4	79
Et	I (**2b**), Br (**3b**)	−4.8	−9.6	75
Et	I (**2b**), Cl (**4b**)	−0.8	−8.8	75
Et	I (**2b**), O_2CMe (**6b**)	3.1	−7.9	73
Et	I (**2b**), O_2CPh (**5b**)	3.6	−8.0	73
Et	Br (**3b**), Cl (**4b**)	1.7	−1.6	77

the bis(ylides), we observe no scrambling between the digold(I) complexes **1a** and **1b**.

Complex **1a** in dichloromethane reacts slowly with methyl iodide at room temperature. In addition to a singlet at δ 36.0 due to starting material, the $^{31}P\{^1H\}$NMR spectrum of the resulting solution shows singlets at δ −12.7 and 31.9 due to the diiodide **2a** and its rearrangement product (see below); there is also an AB quartet centered at δ 9.05 and 6.07 (J_{AB} *ca.* 54 Hz), which may be due to the oxidative addition product $Au_2(I)(Me)(\mu\text{-}C_6H_4PPh_2)_2$. The latter compound was obtained in a fairly pure state by repeated fractional crystallization, but the small amount and apparent sensitivity to decomposition prevented complete characterization. The initial addition of methyl iodide to **1a**, like the corresponding reactions with the bis(ylide) complexes $Au_2\{\mu\text{-}(CH_2)_2PR_2\}_2$ (R = Ph, Me), is probably reversible;[7,12,14,16] the methyl iodide adducts of the bis(ylide) complexes are reported to undergo photochemical decomposition to the diiodo complexes and starting material.[12,14] Attempted addition of ethyl iodide to **1a** gave only **2a**.

Methyl iodide shows no reaction with the digold(II) complex $Au_2Br_2(\mu\text{-}C_6H_4PPh_2)_2$ (**3a**) at room temperature in dichloromethane, but the presence of a catalytic amount of $Au_2(C_6H_4PPh_2)_2$ (**1a**) induces rapid halide exchange to give a mixture of $Au_2(I)(Br)(\mu\text{-}C_6H_4PPh_2)_2$ and $Au_2I_2(\mu\text{-}C_6H_4PPh_2)_2$ (**2a**). A similar though somewhat slower exchange occurs on addition of **1a** to a mixture of **2a** and benzyl bromide. These processes may occur by an S_N2-type of oxidative addition of methyl iodide or benzyl bromide to **1a**; this releases the halide ion that exchanges with the labile halide groups of **2a** or **2b**. Similar observations have been made in the bis(ylide) series.[42]

Isomerization of the Digold(II) Complexes. On heating to *ca.* 50 °C for 4−6 h, toluene solutions of the digold(II) complexes **2a**, **2b**; **3a**, **3b**; and **4a**, **4b** become colorless and addition of hexane precipitates colorless compounds $Au_2X_2(\mu\text{-}R_2PC_6H_4C_6H_4PR_2)$ [R = Ph, Et; X = I (**8a**, **8b**), Br (**9a**, **9b**), and Cl (**10a**, **10b**)] (Scheme 4). Analytical, molecular weight, and ^{31}P NMR data are given in Table 4. X-ray studies of **8b** and **9a**[27] have shown that these complexes contain 2,2′-biphenylyl(diphenylphosphine) and 2,2′-biphenylyl(diethylphosphine), respectively, bridging gold(I) halide centers. The molecular structure of **8b** is shown in Figure 2. The ligands are formed by coupling of the chelating σ-aryl units at the dimetal centers (Scheme 4). Each gold atom is, as usual, linearly coordinated; the dihedral angles of the biphenyl units are 88.6° (**9a**) and 101.5° (**8b**), and the gold atoms are separated by 3.3013(5) (**9a**) and 3.167(1) Å (**8b**). Other features of the structures are unexceptional. Complexes **8**−**10** show singlet ^{31}P NMR resonances that are markedly deshielded relative to those of their precursors **2**−**4**; the shielding increases in the order Cl > Br > I, the reverse of that found for **2**−**4**. The ^{1}H NMR spectrum of **8b** provides clear evidence of coordination

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[42] Fackler, J. P., Jr.; Murray, H. H.; Basil, J. D. *Organometallics* **1984**, *3*, 821.

Table 4. Elemental Analyses, Molecular Weights, and ^{31}P NMR Data for Digold(I) Complexes of $R_2PC_6H_4C_6H_4PR_2$

		Anal. [calcd (found)]				
complex	mp (°C)	% C	% H	% X	MW	δ_P[a]
$Au_2I_2(Ph_2PC_6H_4C_6H_4PPh_2)$ (**8a**)	260 dec	36.95 (37.41)	2.41 (2.41)	21.69 (21.79)	1170 (1194)	31.5 (32.3)
$Au_2Br_2(Ph_2PC_6H_4C_6H_4PPh_2)$ (**9a**)[b]	218 dec	40.17 (40.72)	2.62 (2.78)	14.85 (15.78)	1076 (1051)	29.3 (29.4)
$Au_2Cl_2(Ph_2PC_6H_4C_6H_4PPh_2)$ (**10a**)	202 dec	43.70 (44.72)	3.06 (3.42)	7.17 (7.64)	987 (976)	27.0 (27.8)
$Au_2I_2(Et_2PC_6H_4C_6H_4PEt_2)$ (**8b**)[c,d]	nm	24.56 (24.73)	2.89 (2.93)	25.95 (25.71)	*e*	27.0

[a] In CD_2Cl_2; values in parentheses in d_8-toluene. [b] % P calcd, 5.76; found, 5.66. [c] $\delta_P[Au_2Br_2(Et_2PC_6H_4C_6H_4PEt_2)$(**9b**)] 23.6 ($CD_2Cl_2$). [d] $\delta_P[Au_2Cl_2(Et_2PC_6H_4C_6H_4PEt_2)$ (**10b**)] 21.0 (CD_2Cl_2). [e] Not measured.

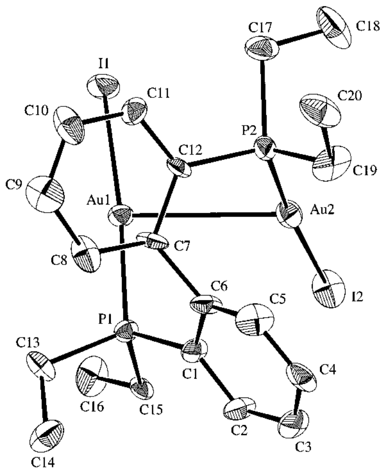

Figure 2. Molecular structure of $Au_2I_2(2,2'-Et_2PC_6H_4C_6H_4PEt_2)$ (**8b**) with atom labeling (hydrogen atoms omitted); ellipsoids show 20% probability levels. Distances: Au(1)−P(1) 2.234(6) Å, Au(2)−P(2) 2.275(6) Å, Au(1)−Au(2) 3.167(1) Å.

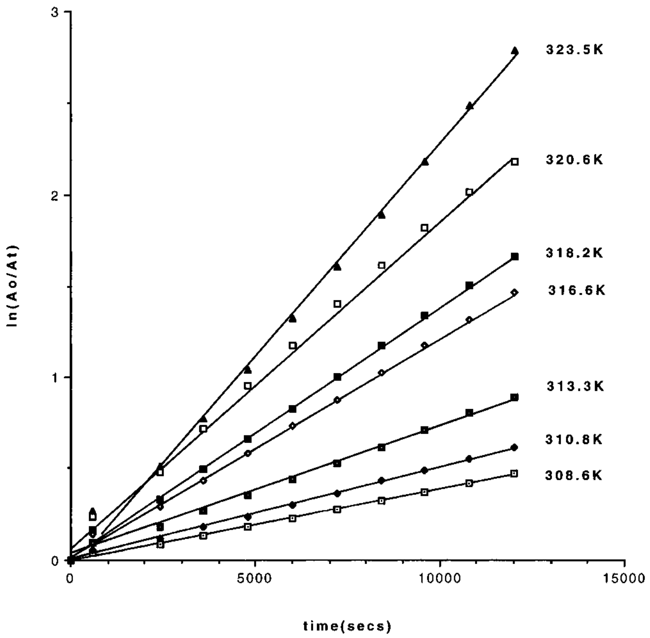

Figure 3. First-order rate plots from UV−visible spectroscopy for the isomerization of $Au_2I_2(o-C_6H_4PPh_2)_2$ (**2a**) to $Au_2I_2(2,2'-Ph_2PC_6H_4C_6H_4-PPh_2)$ (**8a**).

of an axially dissymmetric ligand: there are two sets of resonances due to the diastereotopic methyl groups and four multiplets arising from two pairs of diastereotopic methylene protons.

The biphenylyl ligands can be isolated almost quantitatively from the reaction of the digold(I) complexes with aqueous ethanolic NaCN. Although $o-Et_2PC_6H_4C_6H_4PEt_2-o$ has been synthesized previously from 2,2′-lithiobiphenyl and Et_2PCl,[43] the corresponding reaction with Ph_2PCl does not give $o-Ph_2PC_6H_4C_6H_4PPh_2-o$.[44−46] This compound has recently been made independently by Ullmann coupling of (2-iodophenyl)diphenylphosphine oxide and subsequent reduction with trichlorosilane.[45]

The isomerizations of the digold(II) complexes **2**−**4** to the digold(I) complexes **8**−**10** occur slowly in solution, even at room temperature, and are accelerated by UV light. Solutions of the digold(II) complexes **5**−**7** containing benzoate, acetate, and nitrate, respectively, as the axial ligand are either unchanged or undergo irreversible decomposition on heating or irradiation; there is no evidence for coupling of the σ-aryl units in these compounds or in the precursor complexes **1a** and **1b**. Qualitatively, the rates of isomerization are in the order **2a** > **3a** >> **4a** and **2a** > **2b**. Monitoring of the thermal isomerization of **2a** to **8a**, **3a** to **9a**, and **4a** to **10a** by ^{31}P NMR spectroscopy in various solvents showed no detectable intermediate, although in the first case a small amount (*ca.* 5%) of the digold(I) complex **1a** is formed by loss of iodine. In the first two cases, the kinetics of thermal isomerization could be determined conveniently either by UV−visible spectroscopy or, less precisely, by ^{31}P NMR spectroscopy in the temperature range 35−60 °C. Figure 3 shows typical first-order rate plots for the isomerization of **2a**, at seven temperatures, and Figure 4 shows the Eyring plot derived from such measurements. The thermal isomerizations of **2a** and **3a** are clearly first order in digold(II) complex, the activation parameters derived from UV−visible spectroscopic measurements being $\Delta H^{\ddagger} = 81.9 \pm 0.2$ kJ mol^{-1}, $\Delta S^{\ddagger} = 5.8 \pm 0.5$ J mol^{-1} K^{-1}, $E_{act} = 84.6 \pm 0.2$ kJ mol^{-1} for **2a** and $\Delta H^{\ddagger} = 122.2 \pm 0.3$ kJ mol^{-1}, $\Delta S^{\ddagger} = 41.5 \pm 0.9$ J mol^{-1} K^{-1}, and $E_{act} = 124.9 \pm 0.3$ kJ mol^{-1} for **3a**. Although reasonable first-order plots for the much slower isomerization of **4a** were obtained in the temperature range 58−66 °C, the rates did not vary sufficiently to allow accurate activation parameters to be derived. The first-order rate constants for the isomerization of **2a** increase slightly with increasing solvent polarity (see Experimental Section), indicative of relatively little charge separation in the intermediate or transition state for the process.[47] The rate constants are also unaffected by the radical inhibitor benzoquinone, are slightly increased by the radical initiator azobis(isobutyronitrile) (AIBN), and are strongly reduced, though not completely suppressed, by $[Et_4N]I$ (1−3 mol per mol of **2a**).

Reaction of Digold(II) Complexes with Halogen. Treatment of **3a** with 1 equiv of bromine at −78 °C gives a thermally unstable yellow solid of empirical formula $AuBr_2(C_6H_4PPh_2)$.

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(43) Allen, D. W.; Mann, F. G.; Millar, I. T. *J. Chem. Soc. C* **1967**, 1869.

(44) Miyamoto, T. K.; Matsuura, Y.; Okude, K.; Ichida, H.; Sasaki, Y. *J. Organomet. Chem.* **1989**, *373*, C8.

(45) Desponds, A.; Schlosser, M. *J. Organomet. Chem.* **1996**, *507*, 257.

(46) In contrast, axially dissymmetric bis(phosphines) containing additional *ortho* substituents, such as (6,6′-dimethylbiphenyl-2,2′-diyl)bis(diphenylphosphine), can be made from the appropriate lithium reagent and Ph_2PCl: Schmid, R.; Cereghetti, M.; Heiser, B.; Schönholzer, P.; Hansen, H-J. *Helv. Chim. Acta* **1988**, *71*, 897.

(47) Carey, F. A.; Sundberg, R. J. *Advanced Organic Chemistry: Part A, Structure and Mechanism*, 3rd ed.; Plenum: New York, 1990; p 235.

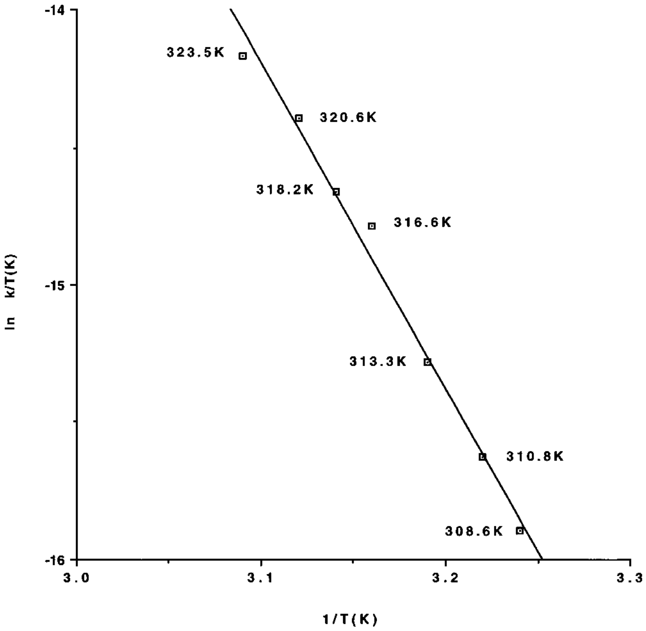


Figure 4. Eyring plot for the isomerization of $Au_2I_2(C_6H_4PPh_2)_2$ (**2a**) to $Au_2I_2(2,2'\text{-}Ph_2PC_6H_4C_6H_4PPh_2)$ (**8a**).

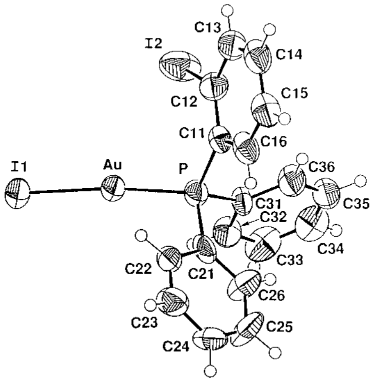
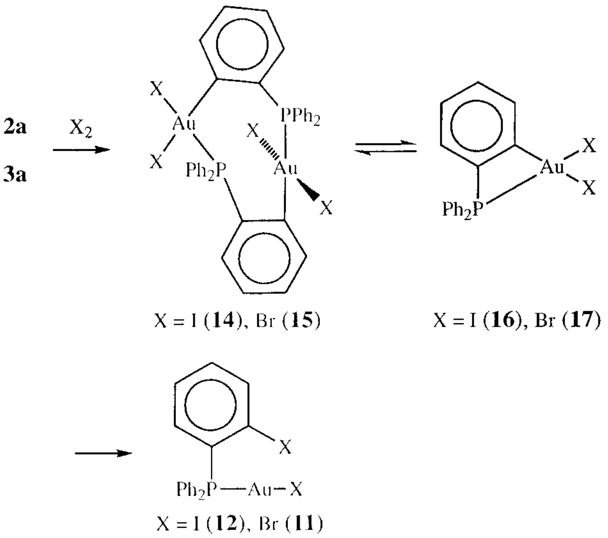


Figure 5. Molecular structure of AuI(o-$IC_6H_4PPh_2$) (**12**) with atom labeling (hydrogen atoms omitted); ellipsoids show 50% probability levels. Distances: Au−P1 2.253(4) Å, Au−I 2.552(1) Å, Au−I(2) 3.628(2) Å, angle P−Au−I(1) 173.4°.

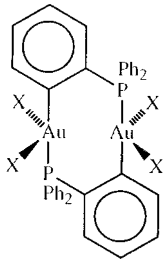
In CH_2Cl_2 at room temperature this rapidly becomes colorless and the solution shows ^{31}P NMR singlets at δ −75.5 and 35.1. Over a period of days the first peak disappears at the expense of the latter. The final product isolated is the gold(I) bromide complex AuBr(o-$BrC_6H_4PPh_2$) (**11**), which was identified by comparison with a sample prepared independently from (2-bromophenyl)diphenylphosphine.

To obtain further information, the halogenation reactions have been studied in situ by ^{31}P NMR spectroscopy in CH_2Cl_2. There is no reaction between **2a** and 1 equiv of iodine at −55 °C, but after 20 min at −15 °C there are a pair of doublets at δ 37.4 and 24.4 (J_{AB} = 4 Hz) and singlets at δ −94.5 and 47.6, in addition to the singlet at δ −11.7 due to unchanged **2a**. As the temperature is raised to 25 °C, the peak due to **2a** and the AB quartet disappear and the intensities of the remaining singlets increase. At 25 °C the singlet at δ −94.5 disappears leaving only the singlet at δ 47.6. The colorless compound responsible for this peak has been identified by X-ray crystallography as the gold(I) iodide complex of (2-iodophenyl)diphenylphosphine, AuI(o-$IC_6H_4PPh_2$) (**12**), whose structure is shown in Figure 5; it contains the expected linear P−Au−I framework, there being no interaction between the aromatic iodine atom and the metal. The reaction of **3a** with bromine (1 equiv) is generally similar to that of **2a** with iodine. At −10 °C one observes a pair of doublets (δ 33.2, 23.3; J_{AB} = 12.8 Hz) and singlets at δ −75.5 and 4.6, in addition to a singlet at δ −4.2 due to unchanged **3a**. At 25 °C the only peaks observed are those at δ −75.5 and 35.7, and after 2 days only the latter remains.

Scheme 5



These results are interpreted as shown in Scheme 5. The compound formed initially is presumably a dimer $Au_2X_4(\mu\text{-}C_6H_4PPh_2)_2$ (X = I, Br), characterized by a ^{31}P AB quartet with a small P−P coupling constant. This compound is clearly not the expected symmetrical species (**13**) arising from *trans* addition of halogen to each gold atom of **2a** or **3a**, although this species may be responsible for the singlet at δ 4.6 in the bromination reaction. The spectra are, however, consistent with structures **14** (X = I) and **15** (X = Br), in which the halides are mutually cis on one gold atom and mutually trans on the other. In the bis(ylide) series, both *trans*,*trans*- and *cis*,*trans*-digold(III) complexes can be isolated, the latter being the more stable.[7,18,20] The compounds responsible for the resonances at δ −94.5 and −75.5, which are in equilibrium with **14** or **15**, are probably cycloaurated monomers, $\overline{\text{AuX}_2(o\text{-C}_6\text{H}_4\text{PPh}_2)}$ [X = I (**16**), Br (**17**)], the remarkably high shielding being characteristic of the cyclometalated four-membered ring,[48] *cf.* Pt(o-$C_6H_4PPh_2$)$_2$, δ_p −52.2.[49] These compounds finally isomerize spontaneously to **12** or **11** by transfer of X^- from gold to carbon and cleavage of the gold(III)−carbon bond.



13

The reaction of **4a** with an excess of $PhICl_2$ at room temperature gives, after 30 min, small amounts of the chloro analogues of **14**−**17**, as shown by ^{31}P NMR spectroscopy, but after 2 h considerable decomposition has occurred and there is no evidence for the formation of AuCl(o-$ClC_6H_4PPh_2$).

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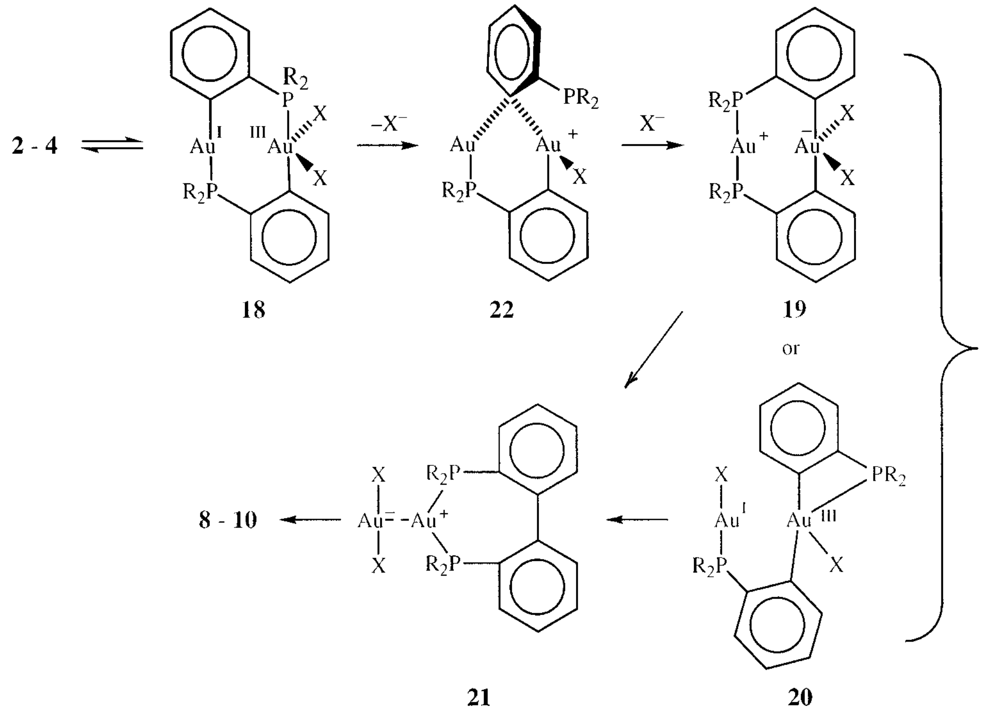
(48) Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229.

(49) Bennett, M. A.; Berry, D. E.; Bhargava, S. K.; Ditzel, E. J.; Robertson, G. B.; Willis, A. C. *J. Chem. Soc., Chem. Commun.* **1987**, 1613.

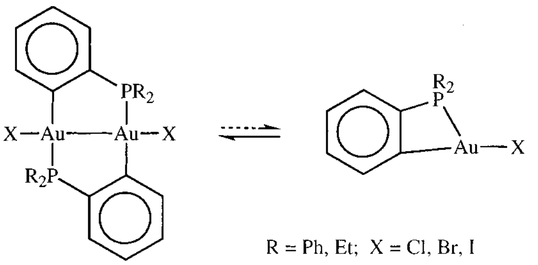
Scheme 6



Discussion

The oxidative addition chemistry of the digold(I) complexes of $C_6H_4PR_2$(R = Ph, Et) resembles in its general features that of the corresponding bis(ylide) complexes, but the digold(II) and digold(III) adducts of $C_6H_4PR_2$ are clearly more labile and more prone to rearrange to derivatives of gold(I). In the digold(II) complexes, this occurs by formation of a C−C bond at the expense of two Au−C bonds; in the digold(III) complexes the rearrangement can be described as the formation by reductive elimination of a C−X (X = Br, I) bond at the expense of a Au−C bond. The sequence depicted in Scheme 5 provides a model for the electrophilic cleavage of some metal−carbon σ-bonds by halogens, for which a commonly accepted mechanism involves one-electron oxidation and subsequent nucleophilic displacement of the metal atom by halide.[50−52]

Migration of the phosphorus atoms in the digold(II) and digold(III) complexes between adjacent metal centers occurs readily and is initiated by halide ion dissociation. In the case of the digold(III) complexes, the process is probably intramolecular. The corresponding process in the digold(II) complexes would generate three-coordinate, monomeric gold(II) species (eq 1), which would be expected to be paramagnetic. Since solutions of **2**−**4** show no ESR evidence for the existence of paramagnetic species, the concentration of monomers, if any, must be exceedingly low. It is also possible that phosphine scrambling in **2**−**4** occurs in a species formed by association between two digold(II) complexes. At present we cannot distinguish between these possibilities.



(1)

R = Ph, Et; X = Cl, Br, I

There are a number of examples of reductive elimination from digold ylide complexes, e.g. the irreversible loss of ethane from $Au_2Me_2\{\mu\text{-}(CH_2)_2PMe_2\}_2$,[7] the reversible loss of alkyl halides from $Au_2(R)(X)\{\mu\text{-}(CH_2)_2PPh_2\}_2$,[16] and the irreversible loss of propane from the μ-methylene complex $Au_2Me_2(\mu\text{-}CH_2)\{\mu\text{-}(CH_2)_2PPh_2\}_2$,[53] but the isomerization of the digold(II) complexes **2**−**4** to the digold(I) complexes **8**−**10** is, as noted previously,[27] an unusual case in which the product is retained in the coordination sphere. The reductive elimination of two σ-bonded organic ligands from a metal−metal bonded complex is forbidden by symmetry[54] and there are few well-established examples.[55] We suggest that dissociation of the anionic ligands in **2**−**4** initiates migration of the σ-aryl group between the gold atoms as shown in Scheme 6. In the light of the disproportionations shown in Schemes 1 and 2, the existence of small amounts of undetected heterovalent gold(I)−gold(III) species **18** formed from **2**−**4** by reversible dissociation of X^- is plausible.[56] Dissociation of X^- from **18** could then induce aryl group migration from gold(I) to gold(III) giving species such as **19** or **20** in which both metal−carbon σ-bonds are formed at the same atom. These are then presumed to undergo rate-determining reductive elimination from the gold(III) center to give complexes **8**−**10** containing the 2,2′-biphenylyl ligand, possibly via ionic interemediates $[Au(R_2PC_6H_4C_6H_4PR_2)][AuX_2]$ **(21)**. The analogous reductive elimination of alkanes from trialkylgold(III) complexes, such as $AuMe_2Et(PPh_3)$, is believed

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(50) Kochi, J. K. *Organometallic Mechanisms and Catalysis*; Academic: New York, 1978; pp 532−542.

(51) Halpern, J. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 274.

(52) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry,* 2nd ed.; University Science Books: Mill Valley, CA, 1987; pp 434−443.

(53) Schmidbaur, H.; Hartmann, C.; Riede, J.; Huber, B.; Müller, G. *Organometallics* **1986**, *5*, 1652.

(54) Trinquier, G.; Hoffmann, R. *Organometallics* **1984**, *3*, 370.

(55) Reference 52, pp 333−353.

(56) In contrast with the isomerizations of **2a** and **3a** to **8a** and **9a**, however, the processes shown in Schemes 1 and 2, and the disproportionation of $[Au_2X_2(i\text{-MNT})_2]$ to $[Au(i\text{-MNT})_2]^-$ and $[AuX_2]^-$ (i-MNT = 1,1-dicyanoethylene-2,2-dithiolate), are promoted by coordinating solvents and by added halide ion: Khan, M. N. I.; Wang, S.; Fackler, J. P., Jr. *Inorg. Chem.* **1989**, *28*, 3579.

to occur from a three-coordinate intermediate AuR_3 formed by dissociation of PPh_3.[57,58] The groups that are eliminated occupy *cis* positions and the elimination is a symmetry-allowed process from a Y-shaped AuR_3 molecule.[58] Since the $Au^{III}-C$ bonds in **19** or **20** are mutually trans, distortion is required before they can reach a geometry suitable for reductive elimination to occur; this process may represent one of the activation barriers to be surmounted. The formation in the rate-determining step of salt-like species such as **19** or $[Au^{III}(o\text{-}C_6H_4PPh_2)_2][Au^{I}X_2]$, appears to be ruled out by the fairly small dependence of isomerization rate on solvent polarity, although the cation in the latter case is isoelectronic with the stable platinum(II) complex $Pt(o\text{-}C_6H_4\text{-}PPh_2)_2$.[49]

Migration of the aryl group between the gold atoms in **2**−**4** may proceed via a two electron−three center intermediate or transition state such as **22** (Scheme 6). There are many structurally characterized examples of gold(I) compounds containing bridging aryl groups,[4,6] but none are known for gold(II) or gold(III). It is noteworthy that the isomerization is initiated by reversible loss of the more polarizable anions I^- and Br^-, less easily by Cl^-, and not at all by the excellent leaving groups $OCOCH_3^-$, $OCOPh^-$, or ONO_2^-. One possible explanation is that the heterovalent formulations **18**−**20** are disfavored by the presence of hard, strongly electron-withdrawing axial ligands. Conversely, they should be favored by good electron donors; in support of this idea, we have found that the dimethyl complexes $Au_2Me_2(C_6H_4PR_2)_2$ (R = Ph, Et) adopt structure **18** (X = Me) containing gold(I) and gold(III).[59] These compounds, however, do not isomerize to $Au_2Me_2(\mu\text{-}R_2\text{-}PC_6H_4C_6H_4PR_2)$, an observation that indicates the importance of an ionizable leaving group in promoting the C−C coupling. The longer Au−Au bond in $Au_2I_2(\mu\text{-}C_6H_4PPh_2)_2$ (**2a**) relative to that in $Au_2(O_2CPh)_2(\mu\text{-}C_6H_4PEt_2)_2$ (**5b**) may also be a significant factor, since the gold atoms have to be separated further in the coupled product.

Experimental Section

General Procedures. Most syntheses were performed under dry nitrogen with use of standard Schlenk techniques, although the solid complexes were air-stable. Reactions with gold complexes were carried out in vessels shielded from light. The following instruments were used for spectroscopic measurements: Varian XL-200E (^1H at 200 MHz, ^{31}P at 80.96 MHz), Varian Gemini-300 BB (^1H at 300 MHz, ^{31}P at 121.4 MHz), Varian VXR-300 (variable temperature, ^1H at 300 MHz, ^{31}P at 121.4 MHz), VGA Micromass 7070F (medium resolution EI mass spectra), VG ZAB−2SEQ (high resolution EI and FAB mass spectra), Perkin Elmer PE 683 and 1800 (infrared spectra as KBr disks or Nujol mulls in the ranges 4000−200 and 4000−150 cm^{-1}, respectively), and Hewlett Packard HP 8450 (UV and visible spectra). The NMR chemical shifts (δ) are given in ppm relative to TMS (^1H) and to 85% H_3PO_4 (^{31}P), both referenced to solvent. Coupling constants (J) are given in hertz. Elemental analyses and molecular weight determinations by osmometry in dichloromethane at 25 °C (Knauer) were performed in-house. These data together with the ^{31}P NMR chemical shifts are given in Tables 2 and 4.

Starting Materials. The compounds $o\text{-}BrC_6H_4PCl_2$,[60] $PhICl_2$,[61] and $AuBr(PEt_3)$[62] were prepared by the appropriate literature procedures. (2-Bromophenyl)diphenylphosphine, $o\text{-}BrC_6H_4PPh_2$, was made either from the $PdCl_2(NCMe)_2$-catalyzed reaction between *o*-bromoiodobenzene and diphenyl(trimethylsilyl)phosphine, Ph_2PSiMe_3 (yield 61%)[63] or, less conveniently, by treatment of $o\text{-}BrC_6H_4PCl_2$ with PhMgBr (2 equiv).[60] Mp 110−112 °C. $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ −5.2 (s).

(2-Bromophenyl)diethylphosphine, $o\text{-}BrC_6H_4PEt_2$. To an ice-cooled solution of EtMgI (0.06 mol) in ether (50 mL) was added slowly $o\text{-}BrC_6H_4PCl_2$ (8 g, 0.03 mol) in ether (60 mL), the temperature being kept between 0 and 5 °C. After being stirred overnight at room temperature, the mixture was treated with a deoxygenated, saturated solution of NH_4Cl (95 mL). After addition of some water to give two layers, the ether layer was dried (Na_2SO_4), solvent was evaporated, and the residue was distilled in vacuo. The product was collected at 111−112 °C/0.8 mm (lit.[64] 90−91 °C/0.15 mm). The yield was 5.4 g (70%). $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 15.4 (s).

Bis(μ-(2-diphenylphosphino)phenyl)digold(I), $Au_2(\mu\text{-}C_6H_4PPh_2)_2$ (1a). A solution of $o\text{-}BrC_6H_4PPh_2$ (2.0 g, 5.9 mmol) in ether (40 mL) was treated with a 1.6 M solution of *n*-BuLi (3 mL) over 30 min to give a colorless precipitate of $o\text{-}LiC_6H_4PPh_2\cdot Et_2O$,[65,66] which was washed with hexane. The yield was 1.4 g (5.1 mmol, 87%). This solid, suspended in ether, was added via cannula to a suspension of $AuBr(PEt_3)$ (1.6 g, 4.1 mmol) in ether (25 mL), the temperature being kept below −65 °C. The temperature was then held at −40 °C for 2 h and at room temperature for 1.5 h. The off-white solid was separated by filtration and washed successively with ether (3 × 20 mL), methanol (15 mL), and hexane (3 × 20 mL). It was then extracted with hot dichloromethane (300 mL) and the extract was filtered through Celite. Evaporation gave **1a** as a colorless, air-stable solid (1.2 g, 63%), mp 216 °C dec.

Bis(μ-(2-diethylphosphino)phenyl)digold(I), $Au_2(\mu\text{-}C_6H_4PEt_2)_2$ (1b). The solution obtained by addition of *n*-BuLi to $o\text{-}BrC_6H_4PEt_2$ was added to a suspension of $AuBr(PEt_3)$ in ether. Workup as described above gave **1b** in *ca.* 60% yield, mp 228 °C; it is more soluble than **1a** in CH_2Cl_2, THF, and toluene. ^1H NMR (CD_2Cl_2) δ 1.5 (dt, $^3J_{PH}$ = 19, J_{HH} = 7, CH_3), 2.1 (m, CH_2), 7.1−7.8 (m, C_6H_4).

Dihalodigold(II) Complexes, $Au_2X_2(\mu\text{-}C_6H_4PR_2)_2$ [R = Ph, X = I (2a), Br (3a), Cl (4a); R = Et, X = I (2b), Br (3b), Cl (4b)]. A stirred suspension of **1a** or **1b** (0.138 mmol) in dichloromethane (20 mL) at −70 °C was treated dropwise with a solution of iodine, bromine, or $PhICl_2$ (0.142 mmol) in dichloromethane, the temperature being kept below −65 °C. In the case of iodine, toluene could also be used as the reaction medium. After addition was complete, the flask was shielded from light; the solution was then stirred at −70 °C for 1 h, at −40 °C for 30 min, and finally at room temperature for 1 h. The volume of the solution was reduced to about half under reduced pressure and hexane was added. Precipitation of the product was completed by cooling the solution to 0 °C. The solid was filtered, washed with hexane, and dried in vacuo. Yields were 60−80%. The chloro complexes **4a** and **4b** were also made by addition of chlorine in CCl_4 to **1a** or **1b**. **2b**−**8b**: ^1H NMR (CD_2Cl_2) δ 1.3 (dt, J_{HH} = 7.5, $J_{PH} + J_{P'H}$ = 19), 2.6 (m, CH_2), 6.9−8.3 (m, C_6H_4); **2b** $\{^{31}P\}(C_6D_6)$ δ 0.95 (t, J_{HH} = 7.5, CH_3), 1.75 (sxt, sepn = 7.5 Hz, CH*H*), 2.11 (sxt, sepn = 7.5 Hz, C*H*H).

Bis(benzoato)digold(II) Complexes, $Au_2(O_2CPh)_2(\mu\text{-}C_6H_4PR_2)_2$ [R = Ph (5a), Et (5b)]. A stirred suspension of **1a** or **1b** (0.163 mmol) in CH_2Cl_2 (40 mL) was treated with an excess of solid benzoyl peroxide (0.245 mmol). The mixture, shielded from light, was set aside at room temperature for 48 h, and solvent was removed under reduced pressure. The yellow residue was stirred with ether for 2 h to remove the excess of benzoyl peroxide and again pumped to dryness. The solid was dissolved in the minimum quantity of CH_2Cl_2, hexane was added, and the mixture was set aside at 0 °C. The solid products were separated by filtration and washed with hexane. Yields were 80−90%. Crystals of **5b** suitable for X-ray structural analysis were obtained from CH_2Cl_2/hexane.

Other $Au_2Y_2(\mu\text{-}C_6H_4PR_2)_2$ Complexes [R = Ph, Et; Y = OAc (6a, 6b), ONO_2 (7a, 7b)]. The dihalodigold(II) complexes **2a**−**4a** or

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Table 5. Crystal and Refinement Data for Compounds **5b**, **8b**, and **12**

compd	$Au_2(O_2CPh)_2(C_6H_4PEt_2)_2$ (**5b**)	$Au_2I_2(Et_2PC_6H_4C_6H_4PEt_2)$ (**8b**)	$AuI(Ph_2PC_6H_4I)$ (**12**)
(a) Crystal Data			
chem formula	$C_{34}H_{38}Au_2O_4P_2$	$C_{20}H_{28}Au_2I_2P_2$	$C_{18}H_{14}AuI_2P$
fw	966.55	978.13	712.06
cryst system	monoclinic	orthorhombic	orthorhombic
unit cell dimens			
a (Å)	10.607(2)	15.984(3)	15.131(3)
b (Å)	8.143(4)	9.064(4)	16.406(3)
c (Å)	38.890(6)	18.047(3)	15.683(4)
β (deg)	96.14(2)		
V (Å^3)	3340(2)	2614(1)	3893(1)
space group	$P2_1/c$	$Pna2_1$ (No. 33)	$Pbca$
D_c (g cm^{-3})	1.922	2.485	2.429
Z	4	4	8
$F(000)$	1847.5	1768.00	2575.5
color, habit	pale yellow needle	colorless prism	colorless prism
cryst dimens (mm)	0.05 × 0.33 × 0.02	0.19 × 0.08 × 0.06	0.16 × 0.21 × 0.26
μ (cm^{-1})	177.2 (Cu Kα)	136.4 (Mo Kα)	108.1 (Mo Kα)
(b) Data Collection and Processing			
diffractometer	Rigaku AFC 6R	Rigaku AFC 6S	Rigaku AFC 6S
X-radiation	Cu Kα	Mo Kα	Mo Kα
T	26(1)	23(1)	20(1)
scan mode	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$
ω-scan width	$1.0 + 0.3 \tan \theta$	$0.80 + 0.34 \tan \theta$	$1.4 + 0.3 \tan \theta$
2θ limits (deg)	4−120	4−50.1	4−50
min, max h, k, l	0, 11	0, 11	0, 18
	0, 9	0, 19	0, 19
	−43, 42	0, 22	0, 18
no. of reflcns			
unique	4945	2656	3445
obsd	3371	1625	1828
	$[I > 3\sigma(I)]$	$[I > 3\sigma(I)]$	$[I > 3\sigma(I)]$
abs corr (transm factors)	analytical (0.384−0.766)	analytical (0.447−0.507)	analytical (0.168−0.248)
(c) Structure Analysis and Refinement			
structure soln	Patterson methods[68]	Patterson methods[69]	Patterson methods[70]
refinement	full-matrix least-squares	full-matrix least-squares	full-matrix least-squares
no. of params	379	234	199
weighting scheme w	$[\sigma^2(F) + (0.0009)F^2]^{-1}$	$4F_o^2/[\sigma^2(E_o^2) + (0.001E_o^2)^2]$	$[\sigma^2(F) + (0.0004)F^2]^{-1}$
R(obsd data) (%)	4.3	3.4	3.4
R_w(obsd data) (%)	5.9	2.1	4.6
GOF	1.34	1.75	1.44

2b−**4b** were dissolved in CH_2Cl_2 and treated with a 50−200% molar excess of the appropriate silver salt AgX. The mixture was stirred for several hours; too short a reaction time occasionally gave some mixed species $Au_2(X)(Y)(\mu\text{-}C_6H_4PR_2)_2$ (see below). The insoluble silver salts were removed by centrifugation, the supernatant liquid was evaporated to dryness under reduced pressure, and the solid product was washed with hexane. Yields were quantitative. ^1H NMR (CD_2Cl_2): **6a**, δ 1.40 (s, O_2CMe); **6b**, δ 2.05 (s, O_2CMe).

Anion Exchange in Digold(II) Complexes. Equimolar amounts of $Au_2X_2(\mu\text{-}C_6H_4PR_2)_2$ and $Au_2Y_2(\mu\text{-}C_6H_4PR_2)_2$ (ca 0.005 mmol) were placed in an NMR tube, CD_2Cl_2 was added, and a $^{31}P\{^1H\}$ NMR spectrum was recorded at room temperature. The equilibria giving rise to $Au_2(X)(Y)(\mu\text{-}C_6H_4PR_2)_2$ were established within 1 h of mixing, as shown by the appearance of an AB quartet in addition to the singlets due to the starting compounds. The data are summarized in Table 3.

Phosphine Exchange in Digold(II) Complexes. Equimolar amounts of $Au_2X_2(\mu\text{-}C_6H_4PPh_2)_2$ and $Au_2X_2(\mu\text{-}C_6H_4PEt_2)_2$ (*ca.* 0.005 mmol) were mixed in CD_2Cl_2 and the $^{31}P\{^1H\}$ NMR spectrum was recorded as described above. For X = I, equilibrium was established immediately, as shown by the appearance of an AB quartet at $\delta_A = -11.9$, $\delta_B = -13.3$, $J_{AB} = 73$ Hz. For X = Br, an AB quartet could be detected within 1 h of mixing: $\delta_A = -3.17$, $\delta_B = -4.31$, $J_{AB} = 77$ Hz. Over a longer period isomerization occurred to give a mixture of **9a** [δ_P 30.2] and **9b** [δ_P 23.7]; there was also a pair of doublets [δ 29.3, 23.7; $J = 5.9$ Hz] assigned to Au_2Br_2 (μ-2,2′-$Ph_2PC_6H_4C_6H_4PEt_2$). For X = Cl, an AB quartet [$\delta_A = 2.3$, $\delta_B = 1.0$, $J_{AB} = 78$ Hz] appeared over a period of 2 weeks accompanied by singlets due to the isomerization products **10a** and **10b**. In the case of X = I, addition of an excess of $[Et_4N]I$ completely suppressed scrambling.

Digold(I) Complexes $Au_2X_2(\mu\text{-}2,2'\text{-}R_2PC_6H_4C_6H_4PR_2)$ [R = Ph, X = I (8a), Br (9a), Cl (10a); R = Et, X = I (8b), Br (9b), Cl (10b)]. The digold(II) complexes $Au_2X_2(\mu\text{-}C_6H_4PR_2)_2$ (**2a**−**4a**, **2b**−**4b**) (*ca.* 0.1 mmol) were heated in toluene at 50 °C for 4−8 h, during which time the solutions became almost colorless. The same change occurred over a period of days at room temperature in CH_2Cl_2, especially when the solutions were exposed to sunlight or to a UV lamp. Addition of hexane precipitated the colorless, crystalline digold(I) complexes, which were recrystallized from toluene/hexane or dichloromethane/hexane. Yields were 80−90%. **8b**: ^1H NMR (CD_2Cl_2) δ 0.92 (dt, $J_{HH} = 7.5$, $J_{PH} = 17.7$, CH_3), 1.30 (dt, $J_{HH} = 7.5$, $J_{PH} = 20.8$, CH_3), 1.89 (qnt, sepn = 7.5, CH_2), 2.36 (8-line m, sepn *ca.* 7), 2.86 (m, CH_2). X-ray quality crystals of **8b** were obtained by diffusion of hexane into a dichloromethane solution.

Displacement of 2,2′-$Ph_2PC_6H_4C_6H_4PPh_2$ from Its Digold(I) Complexes. A suspension of **8a** (65 mg, 0.056 mmol) was suspended in ethanol (2 mL) and treated with a 5-fold excess of sodium cyanide in water (2 mL). The solution, which turned cloudy within 15 min, was stirred overnight. The white solid was separated by filtration, washed with water (2 × 2 mL), and recrystallized from hot hexane to give colorless crystals of 2,2′-$Ph_2PC_6H_4C_6H_4PPh_2$, mp 212 °C. The yield was 22 mg (75%). ^{31}P NMR (CD_2Cl_2) δ −15.0(s). Anal. Calcd for $C_{36}H_{28}P_2$: C, 82.74; H, 5.40; P, 11.85; *M*, 522. Found: C, 82.77; H, 5.69; P, 11.62; *M* (osmometry) 529.

Kinetics of Isomerization of 2a to 8a and 3a to 9a. (1) A sample of the digold(II) complex (0.005 mmol) was dissolved under nitrogen in toluene-d_8 in an NMR tube and placed in the NMR spectrometer set at the desired temperature. The rates of isomerization were determined from the increase in peak height of the product or from the decrease in peak height of the starting compound, or by measuring integrals; data were collected at 15-min intervals.

(2) Enough of the digold(II) complex to give an absorbance between 0.5 and 1.5 (*ca.* 1−4 × 10^{-3} M) was placed under nitrogen in a quartz cell of path length 1 cm containing a small stirrer bar. Toluene was added and the sealed cell placed in a thermostated sample holder. The solution was stirred at the desired temperature and the rates of isomerization were determined from the decrease in absorbance at 458 (**2a**) and 337 nm (**3a**).

Both methods gave good first-order rate plots over 80% of the reaction. Line-fitting and calculation of errors in the activation parameters were carried out with the IGOR PRO program.[67] The data are listed in the form k_1 (10^4 s^{-1}) [T (K)]: **2a** → **8a** (UV/vis) 0.39 (308.6), 0.51 (310.8), 0.72 (313.3), 1.20 (316.6), 1.37 (318.2), 1.88 (320.6), 2.37 (323.5), 3.69 (328.5). **2a** → **8a** (^{31}P NMR) 0.11 (299.5), 0.21 (302), 0.32 (304.5), 0.45 (309), 0.64 (311.5), 1.45 (316.5), 2.10 (319). **3a** → **9a** (UV/vis) 0.08 (317.7), 0.11 (320.6), 0.20 (323.7), 0.26 (326.5), 0.38 (328.5). **3a** → **9a** (^{31}P NMR) 0.07 (311.5), 0.10 (314), 0.12 (316.5), 0.21 (319), 0.23 (321.5), 0.34 (324). Addition of 1−3 mol of [Et_4N]I per mol of **2a** in toluene-d_8 reduced the value of k_1 at 323 K from 2.3 × 10^{-4} to 0.1−0.2 × 10^{-4} s^{-1}. The rate constants 10^4k_1 (s^{-1}) measured by ^{31}P NMR spectroscopy for the isomerization of **2a** to **8a** at 308 K in various solvent mixtures were 0.34 (toluene), 0.82 (1:1 toluene/acetone), 1.04 (CH_2Cl_2), 1.24 (1:1 toluene/MeOH), and 2.75 (CH_2Cl_2/MeOH). The similarly measured rate constants in toluene-d_8 containing, separately, AIBN and benzoquinone were 0.86 × 10^{-4} and 0.26 × 10^{-4} s^{-1}, respectively.

Reaction of $Au_2X_2(\mu\text{-}C_6H_4PPh_2)_2$ with an Excess of Halogen. (1) A stirred solution of $Au_2Br_2(C_6H_4PPh_2)_2$ (**3a**) (113 mg, 0.105 mmol) in dichloromethane (15 mL) contained in a flask shielded from light was cooled in dry ice and treated dropwise with a solution of bromine (16.7 mg, 0.105 mmol) in dichloromethane (5 mL). Stirring was continued for 1 h and the solution was allowed to warm to 0 °C. During this time, a yellow crystalline solid precipitated. It was separated by filtration at 0 °C while being shielded from light and was dried in vacuo. The yield of $[AuBr_2(C_6H_4PPh_2)]_n$ was 65 mg (53%). Anal. Calcd for $C_{18}H_{14}AuBr_2P$: C, 34.48; H, 2.41; Br, 25.49; Cl, 0.0; P, 4.94. Found: C, 34.12; H, 2.12; Br, 24.16; Cl, 0.57; P, 4.32. The $^{31}P\{^1H\}$ NMR spectrum measured immediately at room temperature showed singlets at δ −75.5 and 35.1; over a period of hours, the former disappeared at the expense of the latter, which was identified as being due to AuBr(o-$BrC_6H_4PPh_2$) (see below) (**11**).

(2) A stirred solution of $Au_2I_2(\mu\text{-}C_6H_4PPh_2)_2$ (**2a**) (25 mg, 0.027 mmol) in CH_2Cl_2 (2 mL) was treated with an excess of iodine (28 mg, 0.108 mmol) at room temperature. The clear red solution was stirred for 10 min and then zinc dust was added to remove the excess of iodine. After 2 h the solution was colorless. The precipitate was removed by centrifugation and the solvent was evaporated in vacuo to give an off-white foam (40 mg). A single crystal obtained by layering a C_6D_6 solution with hexane was identified as AuI(o-$IC_6H_4PPh_2$) (**12**) (see below). $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 47.6, (C_6D_6) 47.0.

The results of *in situ* ^{31}P NMR experiments are described in the text.

Bromo{(2-bromophenyl)diphenylphosphine}gold(I), AuBr(o-$BrC_6H_4PPh_2$). This compound was prepared following the literature method for AuBr(PEt_3).[62] Sulfur dioxide was bubbled through a solution of K[$AuBr_4$] (885 mg, 1.59 mmol) in ethanol (20 mL) until the color had changed from deep red to turbid yellow. The excess of SO_2 was displaced by nitrogen and to the stirred solution was added o-$BrC_6H_4PPh_2$ (542 mg, 1.59 mmol) suspended in ethanol (20 mL). After 15 min, the off-white product was separated by filtration, washed thoroughly with ethanol, and dried in vacuo. $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 35.3(s). Anal. Calcd for $C_{18}H_{14}AuBr_2P$: C, 34.98; H, 2.28. Found: C, 34.97; H, 1.93.

Crystallography. The crystal and refinement data for compounds **5b**, **8b**, and **12** are summarized in Table 5. All structures were solved by use of Patterson methods[68−70] and refined by use of full-matrix least-squares analysis. All non-hydrogen atoms were refined anisotropically; hydrogen atoms were included in calculated positions with C−H = 0.95 Å and U(C) = 1.2U_{eq} (C). The configuration for **8b** was set by refinement in each enantiomorph. Calculations for structures **5b** and **12** were carried out with the XTAL3.2 package;[71] those for **8b** were performed with teXsan.[72]

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Supporting Information Available: Crystallographic data, atomic coordinates, and equivalent isotropic displacement parameters, anisotropic displacement parameters, interatomic distances and angles for non-hydrogen atoms, torsion angles for non-hydrogen atoms, interatomic distances, angles, and torsion angles for hydrogen atoms, and selected least squares planes for **5b**, **8b**, and **12** (43 pages). See any current masthead page for ordering and Internet access instructions.

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