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Redistribution Processes in Mixed Halodisilanes. Reaction of Silicon Difluoride with Hydrogen Bromide

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The mixed halodisilane 1-bromo-1,1,2,2-tetrafluorodisilane, SiF_2BrSiF_2H (I), has been obtained as the primary product of the low-temperature reaction of silicon difluoride with hydrogen bromide. The compound shows a marked tendency toward decomposition at 25° involving redistribution of fluorine and bromine. The redistribution process generates the known compound Si_2F_5H and the new species $SiF_3SiFHBr$, SiF_3SiHBr_2, $SiF_2BrSiFHBr$, and $SiF_2BrSiHBr_2$. The relative abundance of the various decomposition products varies as a function of the extent of decomposition; the system is eventually composed almost exclusively of the three disilanes which contain the SiF_3 group—SiF_3SiF_2H, $SiF_3SiFHBr$, and SiF_3SiHBr_2. The latter compounds exhibit much greater thermal stabilities than I. The redistribution is accounted for by a mechanism involving both intra- and intermolecular pairwise exchange of fluorine and bromine atoms with no participation by hydrogen. Silicon–bromine bonds in $SiF_3SiFHBr$ and SiF_3SiHBr_2 can be fluorinated with SbF_3. Product structures were assigned primarily on the basis of both proton and fluorine NMR spectrometry; further characterization of several of the compounds was afforded by vapor density molecular weights and infrared spectra.

Introduction

Many of the known halodisilanes have been generated from reactions of disilane itself with such halogenating agents as HX^2 (X = Cl, Br, or I with AlX_3 serving as a catalyst), $AgCl$,[3] or BX_3[4] (X = Cl, Br). The monohalodisilanes were long thought[5] to be incapable of isolation due to redistribution reactions of the type $2Si_2H_5X = Si_2H_6 + Si_2H_4X_2$. Such reactions have been shown, however, to be highly susceptible to catalysis by such acids as AlX_3[2] and to amine bases as well. The monohalodisilanes are now believed to be reasonably stable thermally if impurities with catalytic activity are rigorously excluded.

The list of known polyhalodisilanes remains rather short despite the recent contributions of Drake and Goddard,[4] Feher and coworkers,[6] and Brinckman and Coyle.[7] Drake and Goddard[4] have demonstrated the utility of BCl_3 and BBr_3 as halogenating agents for Si–H bonds in disilanes

$$Si_2H_6 + BBr_3 \xrightarrow{0^\circ} Si_2H_5Br,\ Si_2H_4Br_2 \text{ (mainly the 1,2 isomer)},\ Si_2H_3Br_3 \text{ (1,1,2 isomer only), and } Si_2H_2Br_4 \text{ (1,1,2,2 isomer only)}$$

Feher[6] has reported direct bromination and chlorination of disilane without rupture of the silicon–silicon bond by working at −80° with dilute solutions of the halogens in CF_2Cl_2 or $CFCl_3$.

More recently, Brinckman and Coyle[7] have reported a variety of halogen-exchange reactions on perhalo mono- and disilane systems and in addition have generated several new monosubstituted derivatives of Si_2F_6 via metathetical reactions of various trimethylsilyl derivatives with Si_2F_6.

Two classes of halodisilanes about which little is known are mixed halodisilanes of the forms $Si_2X_nY_{6-n}$ and $Si_2X_mY_nH_{6-m-n}$. The scarcity of such compounds can be largely ascribed to a lack of appropriate synthetic techniques. These mixed halodisilanes would present a potentially rich chemistry with respect to exchange of halogen and/or hydrogen via both intra- and intermolecular routes. We report here the synthesis of a bromotetrafluorodisilane, SiF_2BrSiF_2H (I), and its decomposition involving novel redistribution of fluorine and bromine.

Reaction of Silicon Difluoride with Hydrogen Bromide. It has been claimed[8] that the principal product of the reaction of the high-temperature molecule silicon difluoride with HX (X = Cl, Br, or I) is pentafluorodisilane. We have shown, however, that I is the primary product of the reaction of SiF_2 with HBr and that Si_2F_5H is one of several products resulting from the thermal decomposition of I.

Table I. Infrared Spectral Frequencies (cm^{-1}) of Polyhalodisilanes

$SiF_2HSiF_2Br^a$	2230 m,^{c} 960 vs, 912 s, 860 s, 816 s, 565 w, 540 m, 430 w
$SiF_3SiHBr_2{}^a$	2220 m, 970 vs, 868 s, 752 s, 735 s, 520 w, 475 m
$SiF_3SiF_2H^b$	2233 m, 973 vs, 918 w, 848 m, 812 s, 807 s, 515 m, 369 m, 334 m, 306 w

^{a} Spectra taken in gas cells with 5-cm path length and KBr windows. ^{b} Data taken from ref 11. ^{c} Intensities.

Experimental Section

General Data. All materials were manipulated in a high-vacuum system constructed from borosilicate glass and greaseless (fluorocarbon polymer) high-vacuum stopcocks. SiF_4 and HBr were obtained from commercial sources and were outgassed at −196° prior to use. ^1H and ^{19}F NMR spectra were obtained on a Varian Associates T-60 (^{19}F at 56.4 MHz); infrared spectra, on a Beckman IR-20A or Perkin-Elmer 337, using glass cells with a 10-cm path length and equipped with KBr windows. Molecular weights were obtained by vapor density measurements (Dumas method).

Reaction of SiF_2 with HBr. Silicon difluoride was generated in the customary manner[9] from the reaction of SiF_4 with lump Si at 1200°. Product mixtures (which also contained unreacted SiF_4 and HBr) were distilled through a series of cold traps, with the species retained in each trap as follows: −196°, SiF_4, HBr, SiF_2HBr (low abundance), SiF_3Br (trace); −118°, Si_2F_6 (a side product in virtually all SiF_2 reactions) + Si_2F_5H if present; −84°, I; −63°, small amounts of various polysilanes. Due to its limited thermal stability, I could be obtained in high purity only if multiple fractionations were avoided and care was taken to prevent the compound from warming to room temperature in the course of purification. The samples used for NMR investigations of the decomposition of I were generally contaminated with a few percent of Si_2F_5H. Attempts to remove the last traces of Si_2F_5H from the system resulted in partial decomposition of I to give, among others, its isomer $SiF_3SiFHBr$, from which it is not readily separated.

Product Characterization. In addition to NMR spectral data cited below, the compounds I, SiF_3SiF_2H (II), and SiF_3SiHBr_2 (IV) were characterized via infrared spectra (Table I) and vapor density molecular weights: SiF_2BrSiF_2H calcd 213.1, found 210.8; Si_2F_5H calcd 152.2, found 153.6; SiF_3SiHBr_2 calcd 274.0, found 272.7. Low-temperature column distillation[10] was found to be the most effective means for isolation of compounds I and IV from mixtures resulting from total decomposition of I; however, due to a surprising similarity in volatility between II and $SiF_3SiFHBr$ (III), the latter could not be obtained uncontaminated with II.

Reactions of Si–Br and Si–H Bonds. Fluorination of Si–Br bonds was effected by condensing the disilanes into a bulb containing an excess of SbF_3 and shaking the bulb contents on warm-up from liquid nitrogen temperature. The major portion of samples rich in III or

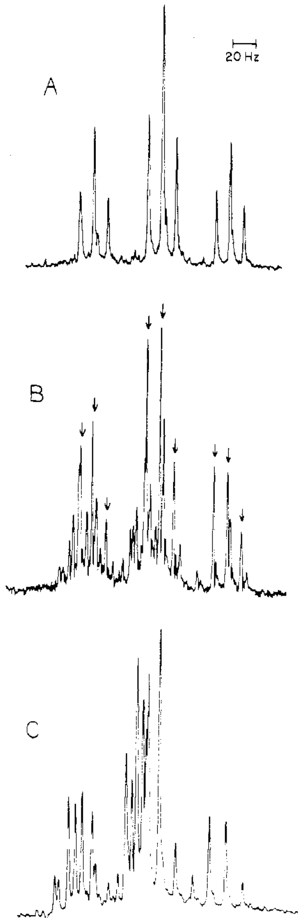


Figure 1. Proton NMR spectra of I at various stages of decomposition. Spectrum A is of a sample <10% decomposed; in spectrum B, I (denoted by arrows) is ca. 67% decomposed; in spectrum C, I is completely consumed.

IV was converted to Si_2F_5H in this manner. However, as is typical with such fluorinations of polyhalodisilanes, some scission of the Si–Si bond to form SiF_4 and SiF_3H was observed.

Bromination of the Si–H bond in IV was attempted by distilling approximately 2.5 mmol of IV and 4 mmol of anhydrous BBr_3 into an NMR tube and monitoring NMR spectra after the tube had been allowed to stand at 25° and then at 60°. No changes were observed in the original spectra even after prolonged heating at 60°.

Decomposition of I. Samples of I (ca. 95% pure, with Si_2F_5H being the principal impurity) were allowed to stand at 25° in NMR tubes, with spectra being taken intermittently. Figure 1 is a representation of the decomposition process as monitored by proton NMR. The decomposition may be viewed as proceeding in three stages, corresponding to parital, extensive, or total decomposition of I, respectively.

A. Partial Decomposition. Samples in which the extent of decomposition of I is less than approximately 40% exhibit three major decomposition products: Si_2F_5H (II), $SiF_3SiFHBr$ (III), and $SiF_2BrSiFHBr$ (V).

B. Extensive Decomposition. At the stage at which ca. 75% of the starting material has decomposed, the concentrations of II and III continue to increase, but the concentration of V is decreasing and two new products—SiF_3SiHBr_2 (IV) and $SiF_2BrSiHBr_2$ (VI)—have appeared.

C. "Total" Decomposition. When 99% of I has been consumed, II, III, and IV constitute >90% of the sample, with the concentrations of V and VI being ca. 4% and 3%, respectively. Heating this "totally decomposed" sample at 70° or prolonged standing at 25° results in the slow conversion of V to its isomer IV.

Relative abundances of the species present during the above stages were determined by NMR integration techniques and are listed for a typical system in Table II.

The time required to attain a particular stage varied somewhat from sample to sample, but typical values are about 1 hr for stage A, 1 day for stage B, and several days for stage C. The variation in reaction rate may be due to trace impurities with catalytic activity, since all samples displayed the same qualitative behavior.

Table II. Sample[a] Composition at Various States of Decomposition of SiF_2BrSiF_2H

Compd	A. Slight decomposition	B. Extensive decomposition	C. "Total" decomposition[b]
I	75[c]	16	<1
II	13	31	38
III	5	30	33
IV	<1	5	23
V	6	17	2
VI	<1	1	3

[a] The initial composition of the sample is estimated as 93% I, 6% II, and 1% bromine-containing impurities. [b] The composition of such a "totally" decomposed sample changes over long periods at 25° or on heating at 75° in such a way as to increase the concentration of IV and to reduce that of V. [c] Concentrations are expressed as mole percent of the total sample. The data are believed to be accurate to within one percentage unit.

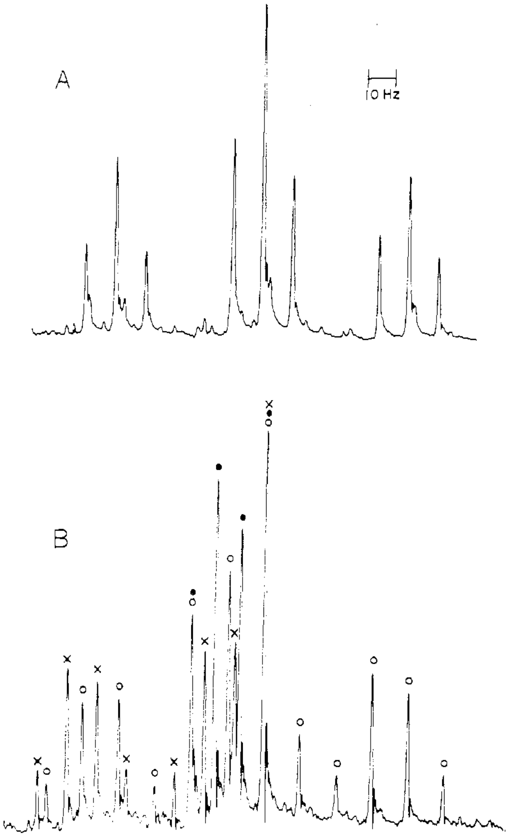


Figure 2. Expanded proton NMR spectra of (A) I <10% decomposed and (B) a mixture of the three most stable decomposition products [○ = SiF_3SiF_2H, × = $SiF_3SiFHBr$, ● = SiF_3SiHBr_2].

Figure 2 is an expansion of the ^1H NMR spectra of I and the decomposition products from a total decomposition which has been allowed to proceed at 25° until no further changes in composition are apparent. Molecular assignments are provided for the latter. Figure 3 displays ^{19}F spectra for the various compounds present in the system. Proton and fluorine NMR spectral parameters are listed in Table III. Chemical shifts and coupling constants are all consistent with those observed for related halosilanes.

Results and Discussion

The low-temperature reaction of SiF_2 with HBr affords a convenient synthesis of the new compound SiF_2BrSiF_2H (I), the product which formally corresponds to addition of HBr to an SiF_2 dimer. The compound previously ascribed[8] to be the principal product of the SiF_2–HBr reaction, Si_2F_5H (II),

Table III. NMR Parameters for Polyhalodisilanes

	δ(H)[a]	$\delta(SiF_3)$[b]	$\delta(SiF_2)$	δ(SiF)	J_{FF}[d]	J_{FSiH}	J_{FSiSiH}
SiF_2BrSiF_2H	−4.77		142.8 (SiF_2H) 110.8 (SiF_2Br)		10.1	54.3	11.0
SiF_3SiF_2H	−5.06	125.3	142.3		12.7	53.7	12.8
$SiF_3SiFHBr$	−5.45	127.3		161.9	9.5	51.1	11.0
SiF_3SiHBr_2	−4.96	129.0					9.2
$SiF_2BrSiFHBr$	−5.43		111.8	160.4	7.2	52.0	9.2
$SiF_2BrSiHBr_2$	*c*		112.7				7.4

[a] ^1H spectra reported in ppm from external TMS. [b] ^{19}F spectra reported in ppm from external $CFCl_3$. [c] ^1H resonance obscured by larger peaks. [d] Absolute magnitude of coupling constants in Hz.

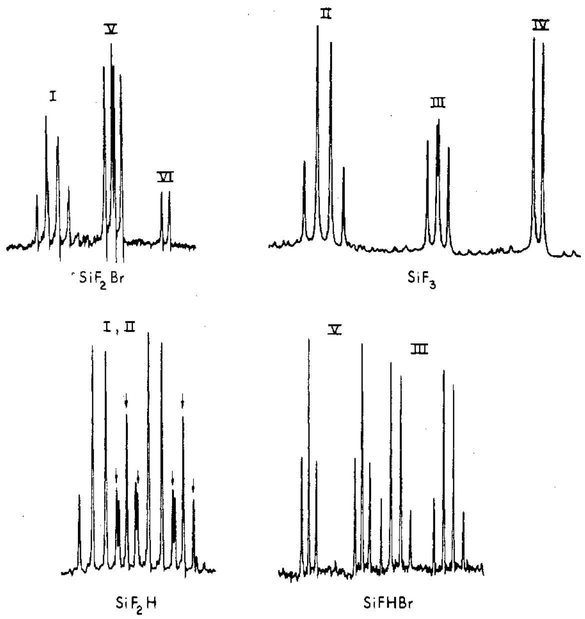


Figure 3. ^{19}F NMR spectra of the six compounds observed in this system. The four scans–each of a chemical shift region characteristic of the indicated functional group– were taken at various stages of the decomposition process. The arrows in the SiF_2H region denote the doublet of triplets due to I. The resemblance of the SiF_2Br resonance in I and the SiF_3 resonance in II to binomial quartets is due to the near-equivalence of J_{FSiSiF} and J_{FSiSiH} in these molecules.

is in fact a decomposition product of I.

The decomposition of I may conveniently be followed by NMR monitoring of samples of initially pure (or nearly so) I as a function of time.

The first stage of decomposition (up to ca. 40% decomposition) of the starting material generates three species: Si_2F_5H (II), $SiF_3SiFHBr$ (III), and $SiF_2BrSiFHBr$ (V). As the decomposition proceeds, the concentration of V begins to diminish and spectra attributable to two new species, SiF_3SiHBr_2 (IV) and $SiF_2BrSiHBr_2$ (VI), appear. In the final stage of decomposition—as the last 10% of I is being consumed—the abundances of II and III continue to increase slightly, IV grows rapidly, V decreases rapidly, and VI remains at a low concentration of ca. 3%. Compositional makeups typical of the three stages are listed in Table II.

Heating a "terminal" mixture at 70° results in the apparent slow conversion of V to its isomer IV, without appreciable change in the concentrations of the other materials present. No species other than the six compounds cited here were observable in concentrations exceeding 1% in either proton or fluorine NMR spectra.

Most striking in this system is the uniform preservation of the Si_2X_5H skeleton, where X = F or Br. No formation of monosilanes or disilanes containing other than one hydrogen was detected. It is of interest to note the ease with which I undergoes redistribution in comparison to other polyhalodisilanes. Thus, not only are compounds III and IV stable at 25° for extended periods of time but also halogen exchange between, for example, SiF_4 and Si_2Cl_6 requires heat (150°) and an Al_2Cl_6 catalyst.[7] Additionally, 1,2-dibromo- and 1,1,2-tribromodisilane are reported to resist isomerization in the presence of the acid BBr_3.[4]

Redistribution Mechanism. The nature and sequence of appearance of the products formed in the decomposition of I may be rationalized by eq 1–6 (the asterisks denote the F and Br atoms which undergo exchange).

$$SiF_2Br^*SiF^*_2H \rightarrow SiF_3SiFHBr \qquad (1)$$

$$SiF_2Br^*SiF_2H + SiF_2BrSiF^*_2H \rightarrow SiF_3SiF_2H + SiF_2BrSiFHBr \qquad (2)$$

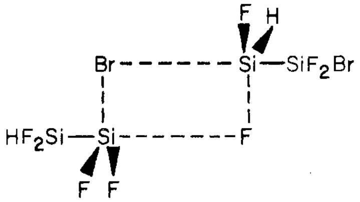
$$SiF_2Br^*SiFHBr + SiF_2BrSiF^*_2H \rightarrow SiF_3SiFHBr + SiF_2BrSiFHBr \qquad (3)$$

$$SiF_2BrSiF^*HBr + SiF_2Br^*SiF_2H \rightarrow SiF_2BrSiHBr_2 + SiF_3SiF_2H \qquad (4)$$

$$SiF_2Br^*SiFHBr + SiF_2BrSiF^*HBr \rightarrow SiF_3SiFHBr + SiF_2BrSiHBr_2 \qquad (5)$$

$$SiF_2Br^*SiF^*HBr \rightarrow SiF_3SiHBr_2 \qquad (6)$$

Reactions 2–5 are postulated to occur through pairwise F–Br exchange between an SiF_2Br function on one molecule and SiF_2H (reactions 2 and 3) or SiFHBr (reactions 4 and 5) on a second molecule. Such an exchange might occur via a four-center transition state involving pentacoordinate silicons. If so, reaction 2 would, for example, proceed through



We have, however, no direct evidence for the importance of such a transition state.

Exchanges between two SiF_2Br groups are contraindicated by absence of species containing $SiFBr_2$ functions. Reaction 3 is the bimolecular equivalent to the isomerization of I that constitutes reaction 1. Reaction 1 may well be important since at all times the concentration of III is similar to or greater than that of V. Investigation of the decomposition of pure V would be a highly desirable adjunct to the present experiment. The relative tendencies of V to isomerize to IV or to undergo bimolecular exchange to produce III + VI should be related to the relative importance of reactions 1 and 3 in the preceding scheme. Unfortunately, attempts to isolate V from decomposition mixtures by either distillation or chromatographic techniques have thus far been unsuccessful—perhaps because of the ease with which the molecule decomposes into other materials present in the mixture.

Reactions 1 and 2 (or 2 and 3) are sufficient to account formally for the products present in the early stages of the decomposition. Reactions 4–6 become important later, as the concentration of V builds. Reaction 6 appears to proceed with a higher energy of activation than the other reactions and requires several hours at 70° to go to completion. The importance of reaction 6 at 25° is, however, suggested by the concomitant increase in concentration of IV and decrease of V.

Other exchange processes such as

$$\mathrm{SiF_3SiF^*HBr + SiF_2Br^*SiHBr_2 \rightarrow 2SiF_3SiHBr_2}$$

are also feasible. The mechanistic scheme outlined in eq 1–6 is one which accounts simply and directly for the observed products and their sequential appearance.

The driving force in the above reactions is most probably the formation of an SiF_3 group, wherein the electronegative fluorines act synergistically to enhance p→d π bonding. A similar although less pronounced effect is seen in the metathesis of Si–Cl bonds in Si_2Cl_6 by SiF_4–$AlCl_3$ mixtures.[7] Here the trifluoro- and tetrafluorodisilanes preferentially exist as isomers containing the SiF_3 group.

Consistent with the assumption about the kinetic (and presumably thermodynamic) stability of the SiF_3 function in these systems is the fact that the three stable "end products"—II, III, and IV—all contain the SiF_3 group.

Fluorination of Si–Br and Attempted Bromination of Si–H Bonds. The Si–Br bonds in the two decomposition products III and IV are susceptible to fluorination with SbF_3. As expected, the major product in both instances is Si_2F_5H, although, as in the analogous fluorination of Si_2Cl_6,[7] some rupture of the Si–Si bond does occur.

Bromodisilane can easily be generated from the $AlBr_3$-catalyzed bromination of Si_2H_6 by HBr.[2] Although compounds I–IV were manipulated in the presence of HBr, no interaction with the HBr was apparent.

Drake and Goddard have recently employed BBr_3 as a brominating agent for the Si–H bonds in, for example, Si_2H_5Cl and Si_2H_5Br.[4] We find, however, that IV shows no sign of reaction with BBr_3 even under conditions more severe than those used by Drake and Goddard. In this respect, it is perhaps significant to note that, whereas 1,1,2-tribromodisilane can be brominated with BBr_3, only the 1,1,2,2-tetrabromo isomer is observed as a product. Presumably the loss of hydridic character of the hydrogen in a $SiBr_2H$ function renders the hydrogen less susceptible to electrophilic attack by the boron tribromide.

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Registry No. SiF_2, 13966-66-0; HBr, 10035-10-6; SiF_2BrSiF_2H, 51040-08-5; SiF_3SiF_2H, 24628-33-9; SiF_3SiHBr_2, 56144-86-6; $SiF_3SiFHBr$, 56144-87-7; $SiF_2BrSiFHBr$, 56144-88-8; $SiF_2BrSiHBr_2$, 56144-89-9.

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Notes

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Mixed-Valence Complexes of Gold Containing the Maleonitriledithiolato Ligand[1]

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The usual oxidation states of gold are +1 and +3. Authentic gold(II) complexes have been reported with the phthalocyanine ligand,[3] the maleonitriledithiolato ligand,[4-6] and the π-(3)-1,2-dicarbollyl ligand.[7] In addition to the authentic gold(II) complexes there are several examples of pseudo gold(II) systems. These compounds have the correct stoichiometry for divalent gold but consist of equimolar portions of gold(I) and gold(III). Classic examples are $(C_6H_5CH_2)_2SAuCl_2$,[8] $CsAuCl_3$,[9] and Au(dmg)Cl,[10] dmg = dimethylglyoximato.

We now wish to report the preparation and characterization of the pseudo gold(II) complexes $(C_6H_5)_3PAu(mnt)$ and $(C_6H_5)_3AsAu(mnt)$ and their relationship to the authentic Au^{II}-mnt anion $Au(mnt)_2^{2-}$.

Experimental Section

Reagents and Preparations. All chemicals were reagent grade and were used without further purification unless noted otherwise. Electronic spectra were recorded on either a Beckman DB-GT or a Cary 14 spectrophotometer. Electron spin resonance spectra were obtained with a Varian V-4502-13 instrument. Conductivity measurements were made with an Industrial Instruments bridge, Model RC16B2. Analytical work was performed by Robertson Laboratories.

Chlorotriphenylphosphinegold(I). Chloroauric acid, 1.44 g, 0.00366 mol, was dissolved in 5 ml of ethanol. To this solution was added a solution of triphenylphosphine, 1.88 g, 0.00717 mol, in 30 ml of ethanol. The color of the resulting solution rapidly faded and a white precipitate began to form. The precipitate was filtered and dried. An analytical sample was prepared by two recrystallizations from 1:1 acetone–THF. The complex decomposed at 243°. Anal. Calcd for $C_{18}H_{15}PAuCl$: C, 43.69; H, 3.06. Found: C, 44.03; H, 2.97. The ultraviolet spectrum, recorded in chloroform, exhibited a maximum at 252.3 nm (ε 8440).

Chlorotriphenylarsinegold(I). This complex was prepared by a method similar to that for the chlorotriphenylphosphinegold(I) complex. An analytical sample was prepared by recrystallization from 1:1 ethanol–THF. The complex decomposed at 115–117°. Anal. Calcd for $C_{18}H_{15}AsAuCl$: C, 40.13; H, 2.81. Found: C, 40.32; H, 3.11. No ultraviolet spectrum was obtained for this complex due to its insolubility in solvents appropriate for such a measurement.

Trichlorotriphenylphosphinegold(III). Chlorotriphenylphosphinegold(I), 1.17 g, 0.00236 mol, was suspended in 20 ml of 1:1 ethanol–THF. Chlorine gas was bubbled through the mixture until all of the gold(I) reactant dissolved, resulting in a yellow solution. The solution was filtered and concentrated. Yellow needles of trichlorotriphenylphosphinegold(III) were recovered. An analytical sample was prepared by recrystallization from 1:1 ethanol–THF. The compound decomposed at 178°. Anal. Calcd for $C_{18}H_{15}PAuCl_3$: C, 38.21; H, 2.67. Found: C, 38.50; H, 2.80. The electronic spectrum, recorded in acetone, exhibited a maximum at 342.5 nm (ε 9600).

Trichlorotriphenylarsinegold(III). This complex was prepared by a method similar to that for the trichlorotriphenylphosphinegold(III) system. The complex decomposed at 106–108°. Anal. Calcd for