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

$C_{18}H_{15}AsAuCl_3$: C, 35.46; H, 2.49. Found: C, 35.67; H, 2.44. The electronic spectrum, recorded in THF, exhibited a maximum at 345.8 nm (ϵ 4150).

Disodium Maleonitriledithiolate (Na_2mnt). This compound was prepared by the method of Bahr and Schleitzer.[11] The pale yellow product was dried for 12 hr at 1 mm and 100° before use.

Bis(triphenylphosphine)gold(I) Bis(maleonitriledithiolato)aurate(III) from Trichlorotriphenylphosphinegold(III). Trichlorotriphenylphosphinegold(III), 0.62 g, 0.0011 mol, was dissolved in 20 ml of 1:1 acetone–THF. To the resulting yellow solution was added a solution of Na_2mnt, 0.20 g, 0.0011 mol, in 20 ml of ethanol. A light brown solution formed. Triphenylphosphine, 0.29 g, 0.0011 mol, in 15 ml of ethanol, was added. The color of the solution immediately turned to orange-brown and a solid began to separate. The mixture was warmed on a water bath and the brown solid redissolved. The solution was immediately filtered and the filtrate was allowed to cool. Brown crystals separated from the solution. The product was filtered off and air-dried. An analytical sample was prepared by recrystallizing the product two times from hot THF. The complex melted at a temperature greater than 250°. Anal. Calcd for $C_{22}H_{15}PN_2S_2Au$: C, 44.07; H, 2.52; N, 4.67; S, 10.68. Found: C, 44.10; H, 2.56; N, 4.76; S, 10.77. The visible spectrum, recorded in DMF, exhibited a maximum at 383 nm (ϵ 3375). The conductivity of the complex, measured in DMF at 25°, was 42 $cm^2/(mol\ ohm)$.

Bis(triphenylarsine)gold(I) Bis(maleonitriledithiolato)aurate(III) from Trichlorotriphenylarsinegold(III). This complex was prepared by a method similar to that used for the triphenylphosphine analog. An analytical sample was prepared by recrystallization from THF. The sample decomposed at 175°. Anal. Calcd for $C_{22}H_{15}AsN_2S_2Au$: C, 41.06; H, 2.35; N, 4.35; As, 11.64. Found: C, 41.27; H, 2.42; N, 4.45; As, 11.90. The visible spectrum, recorded in DMF, exhibited a maximum at 380 nm (ϵ 4600). The conductivity of the complex, measured in DMF at 25°, was 42 $cm^2/(mol\ ohm)$.

Tetra-*n*-butylammonium Bis(maleonitriledithiolato)aurate(III). This compound was prepared by a method similar to that reported for the tetraethylammonium salt.[12] An analytical sample was prepared by recrystallization from a 1:1 acetone–ethanol mixture. The complex melted at 174°. Anal. Calcd for $C_{24}H_{36}N_5S_4Au$: C, 40.04; H, 5.05. Found: C, 40.11; H, 5.20. The visible spectrum, recorded in DMF, exhibited a maximum at 465 nm (ϵ 100).

Bis(triphenylphosphine)gold(I) Bis(maleonitriledithiolato)aurate(III) from Gold(I) and Gold(III) Reactants. Chlorotriphenylphosphinegold(I), 0.32 g, 0.00065 mol, and triphenylphosphine, 0.17 g, 0.00065 mol, were dissolved in 30 ml of acetone and 10 ml of THF. A colorless solution, which contained $[(C_6H_5)_3P]_2Au^+Cl^-$,[13] resulted. To this solution was added a solution consisting of 0.47 g, 0.00065 mol, of tetra-*n*-butylammonium bis(maleonitriledithiolato)aurate(III) in 20 ml of acetone. The resulting brown solution was rapidly stirred and 20 ml of ethanol was added. A brown crystalline precipitate slowly formed. After 24 hr the product was filtered off. The brown complex was washed with 20 ml of ethanol and air-dried. The mass of the buff product was 1.45 g. About one-third of the buff product was extracted with 75 ml of hot THF, filtered, and allowed to crystallize at room temperature. The brown crystals were filtered off, washed with 50 ml of ethanol, and air-dried. Anal. Calcd for $C_{44}H_{30}N_4P_2S_4Au_2$: C, 44.07; H, 2.52. Found: C, 44.04; H, 2.65. The physical properties of this complex were identical with those of the bis(triphenylphosphine)gold(I) bis(maleonitriledithiolato)aurate(III) system described previously.

Bis(triphenylarsine)gold(I) Bis(maleonitriledithiolato)aurate(III) from Gold(I) and Gold(III) Reactants. This complex was prepared by a method similar to that for the bis(triphenylphosphine)gold(I) bis(maleonitriledithiolato)aurate(III) system. Anal. Calcd for $C_{44}H_{30}N_4As_2S_4Au_2$: C, 41.06; H, 2.35. Found: C, 40.81; H, 2.35. The physical properties of this complex were identical with those of the bis(triphenylarsine)gold(I) bis(maleonitriledithiolato)aurate(III) system described previously.

Spectrophotometric Studies of $(n\text{-}C_4H_9)_4NAu(mnt)_2$, $(C_6H_5)_3PAu(mnt)$, and $(C_6H_5)_3AsAu(mnt)$. Several solutions containing analytically pure $(n\text{-}C_4H_9)_4NAu(mnt)_2$, in DMF, were prepared. Absorbance data were collected at 465 nm. A plot of absorbance vs. concentration resulted in a typical Beer–Lambert tracing which obeyed the equation $A = 6 \times 10^{-4} + 100F$, where A is absorbance and F is formality.

Exactly 0.0072 g of the complex having the empirical formula $(C_6H_5)_3PAu(mnt)$ was weighed into a 10-ml volumetric flask, dissolved in the minimum amount of DMF, and diluted to the mark with this solvent. The absorbance of the complex, measured at 465 nm, was 0.0569, which corresponds to 0.557×10^{-5} mol of $Au(mnt)_2^-$, 0.00266 g, per 10 ml of solution. A comparison of this mass to the initial sample mass leaves 0.0045 g not accounted for. This mass corresponds to 0.62×10^{-5} mol of $[(C_6H_5)_3P]_2Au^+$. A similar result was obtained for $(C_6H_5)_3AsAu(mnt)$.

ESR Measurements. Solutions to be examined with ESR were prepared on a vacuum line to which two reactant vessels were attached. One of the vessels contained an ESR tube. The standard for ESR measurements was 1,1-diphenylpicrylhydrazyl.

A solution of the gold-containing reactant was placed in one reactant vessel along with a small stirring bar. A solution containing the Na_2mnt ligand was placed in the other vessel. Both solutions were degassed three times before they were allowed to interact. The pressure in the apparatus was maintained at 1 μ. After the reactants were allowed to mix, the resulting solution was stirred for 5 min. The ESR tube was filled and sealed with a propane torch. ESR spectra were recorded 21 min after the reactants were allowed to interact.

Electron Spin Resonance Study of Bis(triphenylphosphine)gold(I) Bis(maleonitriledithiolato)aurate(III) in the Presence of Excess Disodium Maleonitriledithiolate. Bis(triphenylphosphine)gold(I) bis(maleonitriledithiolato)aurate(III), 0.0147 g, 1.23×10^{-5} mol, was placed into the reaction chamber on the vacuum line which contained the ESR tube. Exactly 1.00 ml of DMF was added along with a small stirring bar. Disodium maleonitriledithiolate, 0.0456 g, 2.45×10^{-4} mol, was placed into a 10-ml volumetric flask along with 1.00 ml of methanol. The resulting solution was diluted to the 10.00-ml mark with peroxide-free THF. The yellow solution was transferred to a reactant pod on the vacuum line. The two solutions were degassed and allowed to interact with rapid stirring. A yellow solution resulted. The ESR tube was filled and sealed. The tube contained a paramagnetic material which produced a four-line ESR pattern. The g value was 2.005 and $A_{av}(^{197}Au)$ was 43.05 G. The signal level was 1000, the modulation amplitude 3200, and the attenuation 1.00. The scan was 3400 ± 250 G. The intensity of the spectrum was arbitrarily assigned a value of 1.00.

Electron Spin Resonance Study of Bis(triphenylarsine)gold(I) Bis(maleonitriledithiolato)aurate(III) in the Presence of Excess Disodium Maleonitriledithiolate. Bis(triphenylarsine)gold(I) bis(maleonitriledithiolato)aurate(III), 0.0117 g, 9.09×10^{-6} mol, was placed into the reaction chamber on the vacuum line which contained the ESR tube. Exactly 1.00 ml of DMF was added along with a small stirring bar. Disodium maleonitriledithiolate, 0.0334 g, 1.79×10^{-4} mol, was placed into a 10-ml volumetric flask along with 1.00 ml of methanol. The resulting solution was diluted to the 10.00-ml mark with peroxide-free THF. The yellow solution was transferred to a reactant pod on the vacuum line. The two solutions were degassed and allowed to interact with rapid stirring. The tube contained a paramagnetic material which produced a four-line ESR pattern. The g value was 2.005 and $A_{av}(^{197}Au)$ was 43.05 G. The signal level was 800, the modulation amplitude 250, and the attenuation 2.0. The scan was 3400 ± 250 G. The intensity of the ESR spectrum, relative to that of bis(triphenylphosphine)gold(I) bis(maleonitriledithiolato)aurate(III) in the presence of excess Na_2mnt, was 1.28.

Results and Discussion

When trichlorotriphenylphosphinegold(III) is allowed to react with 1 molar equiv of Na_2mnt and 1 molar equiv of triphenylphosphine, in tetrahydrofuran, a product is obtained which has the stoichiometry $(C_6H_5)_3P{:}Au{:}mnt = 1{:}1{:}1$. The triphenylarsine analog is obtained when triphenylarsine and trichlorotriphenylarsinegold(III) are the gold-containing reactants. Such compounds have the correct stoichiometry for divalent gold.

An authentic gold(II) complex would have one unpaired electron due to a $5d^9$ configuration. Since naturally occurring gold consists of 100% $^{196.97}Au$, which has a nuclear spin of $^3/_2$, solutions of a complex of divalent gold would be expected to give rise to electron spin resonance spectra consisting of four equally spaced, equally intense lines. A solid gold(II) complex would also be expected to display paramagnetic behavior.

The compounds $(C_6H_5)_3ZAu(mnt)$, Z = P or As, in DMF or in the solid state, do not afford ESR spectra and are assumed to be diamagnetic. Both compounds are conductors of electricity with $\Lambda_{DMF} \doteq 41$ cm^2/(mol ohm). Such a value is consistent with a 1:1 electrolyte involving a gold complex.[14] In addition the electronic spectra of the complexes are nearly identical with that of $Au(mnt)_2^-$. The physical data allow the complexes to be formulated as mixed-valence systems consisting of equimolar portions of $Au(mnt)_2^-$ and $[(C_6H_5)_3Z]_2Au^+$, Z = P or As.

When preformed bis(triphenylphosphine)gold(I) chloride[15] was allowed to react with 1 molar equiv of tetra-*n*-butylammonium bis(maleonitriledithiolato)aurate(III), in tetrahydrofuran, a product of the composition $(C_6H_5)_3P$:Au:mnt = 1:1:1 was obtained. This complex was identical in all aspects with the one mentioned earlier in this paper. The same result was obtained in the case of the triphenylarsine complex when bis(triphenylarsine)gold(I) chloride was the gold(I) reactant.

The complex anion $Au(mnt)_2^-$ exhibits a maximum at 465 nm. A typical Beer–Lambert plot is obtained at this wavelength. The mixed-valence systems show a maximum wavelength very close to 465 nm. Since solutions containing $[(C_6H_5)_3Z]_2Au^+Cl^-$, Z = P or As, are colorless and transparent in the visible region of the electronic spectrum, it can be assumed that the transition observed near 465 nm for the mixed-valence systems is associated with $Au(mnt)_2^-$. By comparing absorption data obtained from solutions containing preweighed samples of the mixed-valence compounds to the Beer–Lambert plot for $Au(mnt)_2^-$ it is possible to determine the amount of $Au(mnt)_2^-$ present in the sample. In both cases the amount of $Au(mnt)_2^-$ present is less than the amount of sample present by an amount approximating $[(C_6H_5)_3Z]_2Au^+$, Z = P or As.[16]

The previous results are taken as further evidence for the formulation of the complexes as mixed-valence systems.

Recently we reported a reaction in which the authentic gold(II) complex $[(n\text{-}C_4H_9)_4N]_2Au(mnt)_2$ was isolated pure from reactants which consisted of equimolar portions of gold(I) and gold(III).[6] The gold-containing reactants were the mixed-valence compounds $[(C_6H_5CH_2)_2SAuX_3]$-$[(C_6H_5CH_2)_2SAuX]$, X = Cl or Br, and the solvent was degassed 90% THF–10% methanol. When the diamagnetic complexes $[(C_6H_5)_3Z]_2Au^+Au(mnt)_2^-$, Z = P or As, are allowed to react with excess Na_2mnt, in carefully degassed DMF, ESR spectra consisting of four lines are observed. The ESR g and $\langle a \rangle$ values are identical with those initially reported for $[(n\text{-}C_4H_9)_4N]_2Au(mnt)_2$.[5] Two possible mechanisms can be postulated for the formation of the Au^{II}–mnt anion. The first is a process in which $Au(mnt)_2^-$ is reduced to $Au(mnt)_2^{2-}$ by excess mnt^{2-} ligand. This path is ruled out, however, since ESR spectra are not observed when $(n\text{-}C_4H_9)_4NAu(mnt)_2$ and Na_2mnt are allowed to interact in degassed DMF. The second path involves a one-electron transfer between $Au(mnt)_2^-$ and a gold(I) complex containing the mnt ligand. Such a reaction can be formulated as in eq 1–3, where Z = P or As.

$$[(C_6H_5)_3Z]_2Au^+Au(mnt)_2^-(s) \rightarrow [(C_6H_5)_3Z]_2Au^+(soln) + Au(mnt)_2^-(soln) \quad (1)$$

$$[(C_6H_5)_3Z]_2Au^+(soln) + 2mnt^{2-}(soln) \rightarrow 2(C_6H_5)_3Z(soln) + Au(mnt)_2^{3-}(soln) \quad (2)$$

$$Au(mnt)_2^-(soln) + Au(mnt)_2^{3-}(soln) \rightleftharpoons 2Au(mnt)_2^{2-}(soln) \quad (3)$$

In the present ESR experiments the molar ratio of $[(C_6H_5)_3P]_2Au^+$:excess mnt^{2-} was 0.502×10^{-1} and that of $[(C_6H_5)_3As]_2Au^+$:excess mnt^{2-} was 0.508×10^{-1}. In the former case the intensity of the ESR spectrum was assigned a value of 1.00 and the relative intensity of the latter was observed to be 1.28. The greater intensity of the ESR spectrum for the mixed-valence triphenylarsine complex can be attributed to (2) and (3). If the excess mnt^{2-} ligand in (2) displaces more triphenylarsine than triphenylphosphine from $[(C_6H_5)_3Z]_2Au^+$, more $Au(mnt)_2^{3-}$ will be generated for Z = As. Since the amount of $Au(mnt)_2^{2-}$ in (3) depends upon the amount of $Au(mnt)_2^{3-}$ produced in (2) a more intense ESR pattern would be expected for the Z = As system.

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Registry No. $(C_6H_5)_3PAuCl$, 14243-64-2; $(C_6H_5)_3AsAuCl$, 25749-29-5; $(C_6H_5)_3PAuCl_3$, 14243-66-4; $(C_6H_5)_3AsAuCl_3$, 17855-35-5; Na_2mnt, 18820-77-4; $[(C_6H_5)_3P]_2Au^+Au(mnt)_2^-$, 55925-82-1; $[(C_6H_5)_3As]_2Au^+Au(mnt)_2^-$, 55925-83-2; $(n\text{-}C_4H_9)_4NAu(mnt)_2$, 14710-21-5.

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Phosphorus(V) Chloride–Pyrazine Addition Compound

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It has been established that the compound of empirical formula PCl_5 exhibits three coordination numbers dependent upon the physical state and choice of solvent. Two competing equilibria have recently been reported[1] in ionizing solvents

$$2PCl_5 \rightleftharpoons PCl_4^+ + PCl_6^-$$

$$PCl_5 \rightleftharpoons PCl_4^+ + Cl^-$$

In the solid state, a metastable crystal modification has been found and proposed[2] to incorporate chloride ions into the crystal lattice which would normally contain only PCl_4^+ ions and PCl_6^- ions.

Likewise, addition compounds formed with organic bases have been reported[3] wherein the variable coordination number about phosphorus is again encountered. For example, pyridine forms a molecular, 1:1 addition complex with PCl_5.[4,8] The addition of 2 equiv of pyridine to an acetonitrile solution of $PCl_4^+SbCl_6^-$ yields the postulated *cis*-$PCl_4(py)_2^+$ complex ion in solution.[5] Addition of 1,10-phenanthroline to $PCl_4^+SbCl_6^-$ forms the crystalline salt $PCl_4(phen)^+SbCl_6^-$. The phen molecule presumably acts as a cis bidentate ligand to the PCl_4^+ species filling the two remaining octahedral positions around phosphorus.[5,9] The variable coordination number of phos-