Journal of Organometallic Chemistry, 122 (1976) 429—446

SYNTHESIS OF CATIONIC DIALKYLGOLD(III) COMPLEXES: NATURE OF THE FACILE REDUCTIVE ELIMINATION OF ALKANE

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(Received June 8th, 1976)

Summary

A series of gold(III) cations of the type *cis*-$[(CH_3)_2AuL_2]^+ X^-$ where L = PPh_3, $PMePh_2$, PMe_2Ph, PMe_3, $AsPh_3$, $SbPh_3$, $\frac{1}{2}$ $H_2NCH_2CH_2NH_2$, $\frac{1}{2}$ $Ph_2PCH_2CH_2PPh_2$, $\frac{1}{2}$ $Ph_2AsCH_2CH_2AsPh_2$, and $\frac{1}{2}$ *o*-$C_6H_4(AsMe_2)_2$ and X = BF_4^-, PF_6^-, ClO_4^-, and $F_3CSO_3^-$ has been prepared. In addition, the *cis* complexes $[(CH_3)(CD_3)Au(PPh_3)_2]F_3CSO_3$, $[(C_2H_5)_2Au(PPh_3)_2]F_3CSO_3$ and $[(n\text{-}C_4H_9)_2Au(PPh_3)_2]F_3CSO_3$ have been synthesized. All have been characterized by PMR, Raman and infrared spectroscopy. These $[R_2AuL_2]X$ compounds yield only ethane, butane, or octane via reductive elimination, and no disproportionation is observed. The alkane eliminations have been studied in $CHCl_3$, CH_2Cl_2, and CH_3COCH_3 solution as a function of temperature, concentration of the complex, and concentration of added ligand L. Elimination is fastest when L is bulky ($PPh_3 > PMePh_2 > PMe_2Ph > PMe_3$), decreases in the sequence $SbPh_3 > AsPh_3 > PPh_3$, is slow with chelating ligands, is inhibited by excess ligand, and there is a small anion effect as X is varied. As R is varied, the rate of elimination decreases Bu $\simeq$ Et > Me. An intramolecular dissociative mechanism is proposed which involves rapid elimination of alkane from an electron deficient dialkylgold(III) complex with nonequivalent gold—carbon bonds and produces the corresponding $[AuL_2]X$ complex.

Introduction

The recent syntheses of thermally stable tetramethylaurate(III) [1,2] and hexamethylplatinate(IV) [3] compounds require a reassessment of the factors contributing to the stability of organogold(III) and organoplatinium(IV) compounds. In general, decomposition of compounds of this type appears to occur by reductive elimination. It is essential during synthesis to prevent the occurrence of conditions which increase the rate of the elimination reaction. On the other hand, in cross coupling of alkyl halides with alkyl—Grignard or alkyl-lithium reagents catalyzed by transition metals, conditions must be such that elimination is a fast reaction.

Previously it was noted that certain cationic dimethylgold(III) compounds, e.g. $[(CH_3)_2Au(PPh_3)_2]ClO_4$ underwent an unusually rapid reductive elimination of ethane at room temperature in $CHCl_3$ solution [4] (eq. 1). On the basis of PMR spectra of chloroform solutions of $[(CH_3)_2Au(AsPh_3)_2]ClO_4$ and $[(CH_3)_2Au(SbPh_3)_2]ClO_4$ [5], it also was suggested [4] that these compounds underwent an even faster reductive elimination of ethane in solution. This was of interest because the isoelectronic $[R_2Pt(PR'_3)_2]$ complexes are considered to be among the most stable organo-σ-transition metal complexes known in terms of thermal stability [6].

$$[(CH_3)_2Au(PPh_3)_2]ClO_4 \xrightarrow{CHCl_3} CH_3CH_3 + [Au(PPh_3)_2]ClO_4 \qquad (1)$$

It now is clear that a number of types of alkylgold(III) compounds undergo reductive elimination of alkane. Long ago, it was noted by Gibson and coworkers that the compounds $[R_2AuL][R_2AuX_2]$ (R = Me, Et, n-Pr; X = Br, I, CN; L = ethylenediamine (en), 1, 10-phenanthroline, dipyridyl) eliminated alkane [7,8] from the anion in boiling chloroform, benzene, or ethanol. At temperatures above 100° C, butane was evolved from $[(C_2H_5)_2Auen]Br$ [9]. It was assumed that radical processes took place throughout.

There was little note of these reactions until Tamaki and Kochi [10] demonstrated that the reaction between CH_3AuPPh_3 and CH_3I which, at room temperature, yields ethane [11] proceeds via oxidative addition of CH_3I and reductive elimination of ethane. In this reaction, oxidative addition yields $(CH_3)_2AuIPPh_3$ which is alkylated by more CH_3AuPPh_3 to give $(CH_3)_3AuPPh_3$, and the trimethylgold(III) complex gives ethane rapidly in methyl iodide solution (eq. 2). In pure form, $(CH_3)_3AuPPh_3$ yields ethane only when heated to ca. 120° C, either as the pure solid, in xylene solution, or at 175° C in a biphenyl melt [12]. It also is reported to decompose smoothly, eliminating ethane, at 80° C in t-butylbenzene [13]. The exact manner in which the CH_3I increases the rate of reductive elimination is not clear.

$$(CH_3)_3AuPPh_3 \xrightarrow{CH_3I} CH_3CH_3 + CH_3AuPPh_3 \qquad (2)$$

In this work we have synthesized a number of new cationic dialkylgold(III) complexes to study their reductive elimination. It also was of particular interest to compare the decomposition of the gold cations with the isoelectronic dialkylplatinium(II) molecules. When the platinum(II) compounds contain alkyls which have β hydrogens, they decompose by β elimination of alkane and alkene [14]. The platinum(II) compounds generally appear to be more stable than the gold(III) analogues, although no precise comparisons have been made. Pyrolysis of $(C_6H_5)_2Pt(PPh_3)_2$ has been reported to yield biphenyl via a conserted intramolecular process which was promoted by neutral nucleophiles [15]. This is the opposite of the behavior reported for the elimination from $[RR'_2Au(PPh_3)]$ compounds [13].

Experimental section

All of the solvents used were dried thoroughly, degassed, and stored under nitrogen. Diethyl ether, tetrahydrofuran, and petroleum ether (b.p. 30—60° C) were distilled from $LiAlH_4$ under nitrogen. Benzene was shaken with concentrated H_2SO_4 and distilled under nitrogen. Acetone was dried with 4 Å molecular sieves and distilled from $KMnO_4$. All, with the exception of the petroleum ether, were Mallinckrodt Spectrophotometric Grade. Chloroform was shaken with concentrated H_2SO_4 and distilled. Methylene chloride was distilled from BaO and P_4O_{10}. The $CDCl_3$ was obtained from Merck and Co. and was degassed before use. Acetone-d_6 was obtained from Norell Chemical Co. The solvents were stored in vessels equipped with stopcocks and rubber septums, so transfers could be made with syringes. Gold, magnesium, and lithium metals were obtained from Matthey Bishop, Mallinckrodt, and Lithcoa, respectively. The silver salts AgF_3CSO_3, $AgPF_6$, $AgBF_4$, and $AgClO_4$ were from Alfa—Ventron. The phosphine, arsine, and stibine ligands as well as pyridine, ethylenediamine and thallous acetylacetonate were obtained from Eastman, K and K Laboratories, and Baker. Methyl iodide, perdeuteromethyl iodide, and n-butyl bromide were obtained from Columbia Organic Chemicals, Stohler Isotope Co., and Matheson, Coleman and Bell, respectively. Hexane solutions of n-butyllithium were obtained from Foote Mineral Co. Trifluoromethane sulfonic-acid was obtained from the Aldrich Chemical Co. Styrene and di-t-butyl nitroxide were supplied by Eastman Organic Chemicals.

Microanalyses were performed by the Departmental Microanalytical Laboratory and by Schwarzkopf Microanalytical Laboratory. Melting points were obtained either with a Mel-Temp apparatus or during pyrolysis studies using a paraffin oil bath. Dimethylgold iodide was prepared by the method of Brain and Gibson [16] and diethylgold bromide by the procedure by Pope and Gibson [17]. They were stored in the dark and recrystallized prior to use from petroleum ether

Note: These compounds as is the case for all organogold(III) compounds can decompose violently [18], especially when very dry, and should be handled accordingly.

The $[(CH_3)_2AuL_2]X$ compounds were prepared using Schlenk techniques under dry N_2 or Ar atmospheres except where aqueous solutions were used.

Preparation of $[(CH_3)_2Au[P(C_6H_5)_3]_2]X$ *(X =* BF_4^-, PF_6^-, $F_3CSO_3^-$, ClO_4^-*).* To a solution of 0.502 g (7.09×10^{-4} mol) $[(CH_3)_2AuI]_2$ in 20 ml petroleum ether was added a solution of 0.276 g (1.42×10^{-3} mol) $AgBF_4$ in THF. A precipitate of AgI began to form at once, and stirring was continued for one hour. The AgI was removed by filtration and 0.744 g (2.84×10^{-3} mol) PPh_3 dissolved in diethyl ether was added to the filtrate. A white solid formed immediately, it was collected on a frit, excess solvent was removed under vacuum, and the product was washed with 3 × 10 ml aliquots of Et_2O and dried. The PF_6^-, $CF_3SO_3^-$, and ClO_4^- salts were prepared similarly, and the analyses for all four compounds are given in Table 1.

Preparation of $[(CH_3)_2AuL_2][F_3CSO_3]$ *(L =* $AsPh_3$, $SbPh_3$, $PMePh_2$, PMe_2Ph, PMe_3*).* These compounds were synthesized by the general procedure described above for $[(CH_3)_2Au(PPh_3)]_2F_3CSO_3$. The arsine and stibine complexes were isolated at 0°C because of their lower thermal stability. The $PMePh_2$ complexes were obtained initially as oils. These were washed with diethyl ether, and upon removal of the excess solvent under vacuum white crystalline solids were ob-

TABLE 1

ANALYTICAL DATA (found (calcd.)) FOR THE DIALKYLGOLD(III) COMPOUNDS

Complex	Carbon (%)	Hydrogen (%)	Phosphorus (%)	Gold (%)	Nitrogen (%)
$[(CH_3)_2Au(PPh_3)_2]BF_4$	54.6	4.07	7.61		
	(54.4)	(4.33)	(7.39)		
$[(CH_3)_2Au(PPh_3)_2]PF_6$	50.9	4.08	10.6		
	(50.9)	(4.05)	(10.4)		
$[(CH_3)_2Au(PPh_3)_2]F_3CSO_3$	51.8	4.02	7.00		
	(52.0)	(4.03)	(6.88)		
$[(CD_3)(CH_3)Au(PPh_3)_2]F_3CSO_3$	51.8	4.13		22.0	
	(51.8)	(4.34)		(21.8)	
$[(CH_3)_2Au(PPh_3)_2]ClO_4$	53.5	4.24	7.56		
	(53.6)	(4.26)	(7.28)		
$[(C_2H_5)_2Au(PPh_3)_2]F_3CSO_3$	53.2	4.25	6.91		
	(53.0	(4.34)	(6.67)		
$[(n\text{-}C_4H_9)_2Au(PPh_3)_2]F_3CSO_3$	54.2	3.93		21.7	
	(54.9)	(4.91)		(20.0)	
$[(CH_3)_2Au(AsPh_3)_2]F_3CSO_3$	47.6	3.84		19.8	
	(47.4)	(3.67)		(19.9)	
$[(CH_3)_2Au(SbPh_3)_2]F_3CSO_3$	43.1	3.18		18.4	
	(43.3)	(3.35)		(18.2)	
$[(CH_3)_2Au(PMePh_2)_2]F_3CSO_3$	44.0	3.99	8.24		
	(44.8)	(4.15)	(7.98)		
$[(CH_3)_2Au(PMe_2Ph)_2]F_3CSO_3$	34.8	4.20	9.71		
	(35.0)	(4.33)	(9.49)		
$[(CH_3)_2Au(PMe_3)_2]F_3CSO_3$	20.7	4.63	11.65		
	(20.5)	(4.58)	(11.73)		
$[(CH_3)_2Au(PPh_2CH_2)_2]F_3CSO_3$	45.1	3.95	8.30		
	(45.0)	(3.90)	(8.00)		
$[(CH_3)_2Au(AsPh_2CH_2)_2]F_3CSO_3$	40.4	3.63			
	(40.4)	(3.51)			
$[(CH_3)_2Au(Me_2As)_2C_6H_4]F_3CSO_3$	23.6	3.53		29.8	
	(23.6)	(3.35)		(29.7)	
$[(CH_3)_2Au(H_2NCH_2)_2]F_3CSO_3$	13.8	3.18			6.68
	(13.8)	(3.24)			(6.42)

tained. Analyses are given in Table 1.

Preparation of $[(CH_3)_2AuL][F_3CSO_3]$ *(L = 1,2-bis(diphenylphosphino)ethane-(diphos), 1,2-bis(diphenylarsino)ethane, o-phenylenebis(dimethylarsine) (diars), ethylenediamine (en)).* The syntheses again were similar to the preparation of $[(CH_3)_2Au(PPh_3)_2]F_3CSO_3$. The diphos complex separated as an oil which crystallized under vacuum at 0°C. The diars complex precipitated as a white solid. The en complex was an oil initially, but treatment with diethyl ether induced crystallization. Analyses are given in Table 1.

Alternate preparations of $[(CH_3)_2Au(PPh_3)_2]X$ *($X = F_3CSO_3^-$, PF_6^-) using an aqueous medium.* In a typical synthesis, 0.25 g (3.5×10^{-4} mol) $[(CH_3)_2AuI]_2$ was dissolved in 20 ml petroleum ether, and to this solution was added 0.18 g (7.0×10^{-4} mol) AgF_3CSO_3 in 25 ml H_2O. The mixture was stirred for two hours, and the organic layer was evaporated with a stream of nitrogen. The AgI was removed by filtration, and a solution of 0.185 g (7.01×10^{-4} mol) PPh_3 in 20 ml diethyl ether was added to the filtrate. A white solid formed, this was collected on a frit and dried over P_4O_{10} under vacuum. Anal. Found: C, 51.8;

H, 4.02; P, 7.00. $C_{39}H_{36}P_2F_3SO_3Au$ calcd.: C, 52.0; H, 4.03; P, 6.88%. Found: C, 51.0; H, 3.91; P, 10.6. $C_{38}H_{36}P_3F_6Au$ calcd.: C, 50.9; H, 4.05; P. 10.4%.

Alternate preparation of $[(CH_3)_2Au(PPh_3)_2]ClO_4$ *from* $(CH_3)_2Au(acac)$ *(Hacac = 1,4-pentanedione).* A sample of 2,4-pentanedionatodimethylgold(III) was prepared as described by Brain and Gibson [16]; m.p.: Found 81—83°C, lit. 84°C. This was dissolved in THF, an equivalent of $HClO_4$ was added, and then two equivalents of PPh_3 in THF were used to precipitate the white product. Anal. Found: C, 53.5; H, 4.24; P. 7.56. $C_{38}H_{36}P_2ClO_4Au$ calcd.: C, 53.6; H, 4.26; P. 7.28%.

Preparation of $[(CH_3)_2Au(AsPh_2CH_2)_2]F_3CSO_3$. This compound was synthesized as described above by adding F_3CSO_3H to $(CH_3)_2Au(acac)$ in THF followed by 1,2-bis(diphenylarsino)ethane which yielded an oil, which crystallized under diethyl ether after 2 days at 0°C, the white solid was dried over P_4O_{10} under vacuum. The analysis is given in Table 1.

Preparation of $[(CD_3)(CH_3)Au(PPh_3)_2]F_3CSO_3$. *trans*-$CD_3(CH_3)_2AuPPh_3$ was synthesized by the oxidative addition of CD_3I to $Li[(CH_3)_2Au]$ in the presence of an equivalent of PPh_3 by the procedure of Tamaki and Kochi [19]. Under a nitrogen atmosphere, 1.70 g (3.37×10^{-3} mol) *trans*-$CD_3(CH_3)_2AuPPh_3$ was dissolved in 30 ml acetone, and a solution of 1.22 g (3.5×10^{-3} mol) $HgBr_2$ in 30 ml acetone was added. After two hours at 0°C, the acetone was removed under reduced pressure and the white residue was extracted with several portions of methanol to remove all CH_3HgBr. The $(CD_3)(CH_3)AuBrPPh_3$ produced was dissolved in 25 ml benzene, reprecipitated with 75 ml petroleum ether, collected on a frit, and dried over P_4O_{10} under vacuum. This product, 0.50 g, (8.8×10^{-4} mol) was dissolved in 25 ml benzene, and 0.225 g (8.76×10^{-4} mol) AgF_3CSO_3 in 25 ml H_2O was added. The organic layer was removed in a stream of nitrogen, and the solution was filtered to remove AgBr. To the clear solution was added a solution of 0.230 g (8.76×10^{-4} mol) PPh_3 in diethyl ether, a white solid precipitated, this was collected on a frit, washed with diethyl ether, and dried over P_4O_{10} under vacuum.

Preparation of $[(C_2H_5)_2Au(PPh_3)_2]F_3CSO_3$. To a solution of 0.46 g (6.8×10^{-4} mol) $[(C_2H_5)_2AuBr]_2$, in petroleum ether was added 0.352 g (1.37×10^{-3} mol) AgF_3CSO_3 in THF. After stirring for 1 h, the AgBr was removed by filtration, 0.718 g (1.37×10^{-3} mol) PPh_3 in diethyl ether was added, the white solid which precipitated was collected on a frit, washed with diethyl ether and dried.

Preparation of $[(n\text{-}C_4H_9)_2Au(PPh_3)_2]F_3CSO_3$. 0.39 g ($8.6 \times 10^{-4}$ mol) di-n-butyl(ethylenediamine)gold(III) bromide, prepared by the method of Gibson and Colles [20], was dissolved in 50 ml ice water, the solution was acidified with 2 *M* HBr to give pH 1—3, and the system was extracted with 4 × 75 ml petroleum ether. A solution of 0.227 g (8.65×10^{-4} mol) PPh_3 in petroleum ether was added to the solution of $[(CH_3)_2 AuBr]_2$, and the solvent was removed under vacuum to give $(n\text{-}C_4H_9)_2AuBrPPh_3$. This product, 0.460 g (7.04×10^{-4} mol), was dissolved in 10 ml benzene, 0.181 g (7.04×10^{-4} mol) AgF_3CSO_3 in THF was added, the AgBr was removed by filtration, and 0.185 g (7.04×10^{-4} mol) PPh_3 in diethyl ether was added to precipitate the solid white product.

Spectroscopic measurements

Infrared spectra were recorded with a Beckman IR-12 spectrometer. Nujol and halocarbon mulls between CsI plates were used for solid samples, and a KBr liquid cell was employed for solutions. The instrument was calibrated with polystyrene film or indene. The frequencies of sharp bands should be accurate to ±2 cm^{-1}, while those for broad bands should be within ±5 cm^{-1}.

Raman spectra of solid samples were measured with a Jarrell—Ash 25—300 Spectrophotometer using 632.8 nm excitation from a spectra Physics 125 He—Ne laser. The trans-illumination technique using capillaries was employed. Both the laser plasma lines and K_2CrO_4 were used for calibration, and sharp lines are accurate to ±2 cm^{-1}. Solution spectra were determined with an intrument described elsewhere [21], and the spectra were excited with 514.5 nm radiation from a Coherent Radiation Model 52G Ar^+ laser.

Proton magnetic resonance spectra were determined using Varian A60 and A60A spectrometers, probe temperature 40°C, as well as a Perkin—Elmer R-32 (90 MHz) spectrometer with a probe temperature of 35°C. Solvent peaks or TMS were used as internal references, and chemical shifts are believed to be accurate to ±0.02 ppm, coupling constants to ±1 Hz. The coupling constants for the $[(CH_3)_2Au(PR_3)_2]X$ compounds were calculated by the method of Harris [22], since this has been found to give values very similar to the best set obtained by computer simulation of the spectra [4].

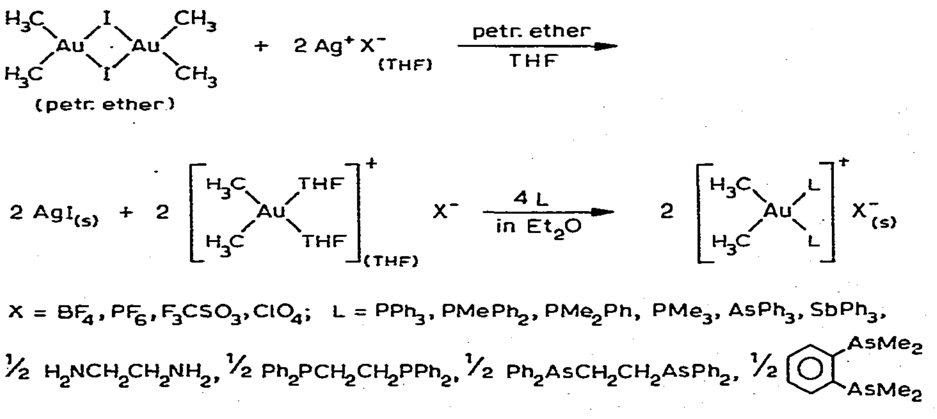
Mass spectra were recorded with a Hitachi RMU-6A spectrometer operating with an ion current between 5×10^{-13} and 1×10^{-11} A, ion voltage 75 eV. Low boiling (ca. 90°C) perfluorokerosene was used as the standard.

Electron paramagnetic resonance spectra were measured with an Alpha AL-X-10 spectrometer operating at 9 GHz. Samples were run as methylene chloride solutions in 3 mm tubes.

X-ray photoelectron spectra were obtained with a Hewlett—Packard 5950 A ESCA spectrometer. The aluminium $K_{\alpha 1,2}$ line (1486.6 eV) was used as the X-ray excitation source, and the powdered samples were dispersed on copper- or iridium-plated copper surfaces.

Data and results

Syntheses of $[(CH_3)_2AuL_2]X$ compounds. Since reductive elimination of alkane is rapid under certain conditions in solution, it is necessary to use proce-



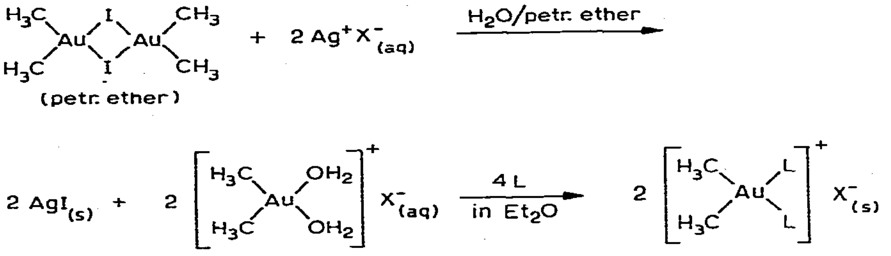
(3)

X = BF_4, PF_6, F_3CSO_3, ClO_4; L = PPh_3, $PMePh_2$, PMe_2Ph, PMe_3, $AsPh_3$, $SbPh_3$,

½ $H_2NCH_2CH_2NH_2$, ½ $Ph_2PCH_2CH_2PPh_2$, ½ $Ph_2AsCH_2CH_2AsPh_2$, ½ dures which minimize this reaction. The best synthetic method for preparation of the cationic complexes is summarized in eq. 3.

The solution of $[(CH_3)_2Au(THF)_2]X$ in THF is stable at 25° C, and the bis-L complexes precipitate at once upon addition of the ligand. In a variation of this reaction, the dimethylgold iodide was replaced by $[(C_2H_5)_2AuBr]_2$ in order to synthesize $[(C_2H_5)_2Au(PPh_3)_2]F_3CSO_3$.

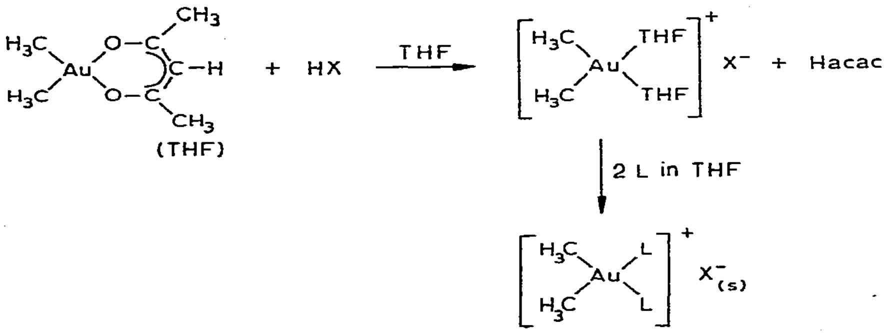
As an alternate route, the synthesis can proceed through the diaquo cation (eq. 4). This ion is stable in aqueous solution [23], and again the desired com-



(4)

plex precipitates immediately upon the addition of the solution containing the ligand L. In a very similar reaction, $[(n\text{-}C_4H_9)_2AuBr]_2$ was extracted into petroleum ether by addition of HBr to an aqueous solution of $[(n\text{-}C_4H_9)_2Auen]Br$. This was used in place of $[(CH_3)_2AuI]_2$ in reaction 4 to produce $[(n\text{-}C_4H_9)_2Au(PPh_3)_2]F_3CSO_3$.

A third route to the preparation of these complexes is via the acetylacetonate (eq. 5).



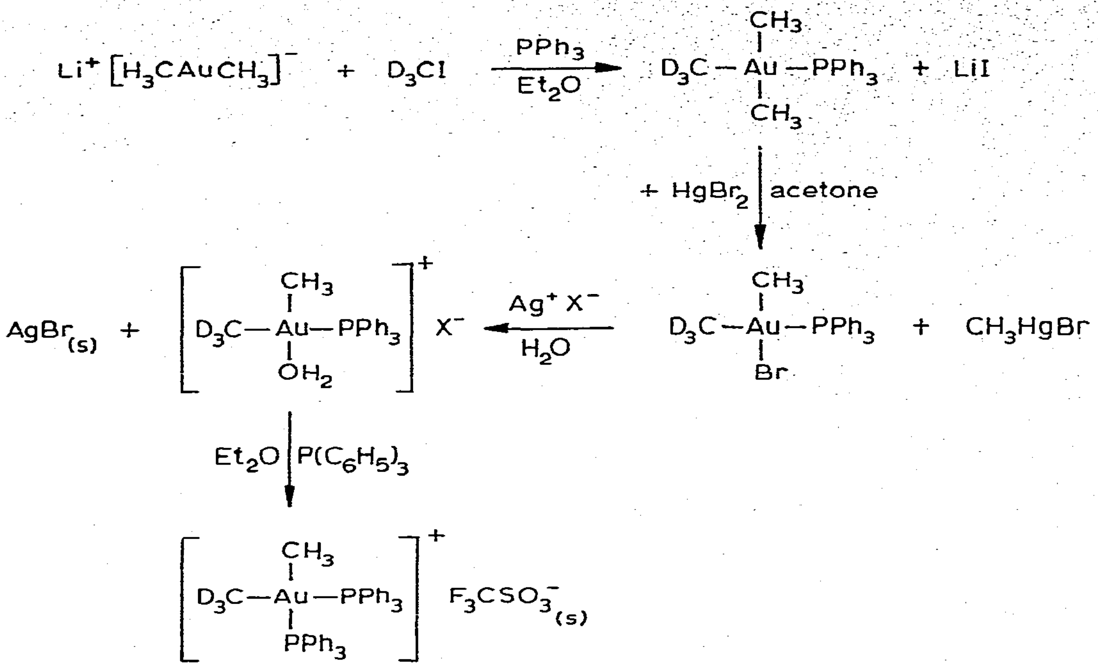
(5)

Synthesis of $[(CH_3)(CD_3)Au(PPh_3)_2]F_3CSO_3$. The sequence of reactions used to prepare the mixed methyl—perdeuteromethyl cation is outlined in eq. 6.

The reaction of lithium dimethylaurate(I) with alkyl halides is reported to yield the *trans*-isomer in a relatively high state of stereochemical purity [19]. The reaction with mercuric bromide is stereospecific, and one of the mutually *trans*-methyl groups is cleaved [24]. In this step, any *cis*-$[(CH_3)_2(CD_3)AuPPh_3]$ impurity should yield roughly equal amounts of the desired $(CH_3)(CD_3)AuBrPPh_3$ and $(CH_3)_2AuBrPPh_3$. Spectroscopic examinations of the purity are discussed below.

Spectra of dimethylgold(III) cations

Nuclear magnetic resonance spectra. The dimethylbis(phosphine)gold(III)



complexes exhibit $A_3XX'A'_3$ pseudotriplet spectra as discussed previously [4]. Chemical shifts and coupling constants are tabulated in Table 2 for all of the cations. From the data in Table 2 for $[(CH_3)_2Au(PPh_3)_2]X$, X = ClO_4, F_3CSO_3, BF_4, and PF_6, it can be seen that these noncoordinating anions have no significant effect either on the chemical shifts or the coupling constants of the cation in solution. Exchange of the phosphine is slow on the PMR time scale for all of these complexes.

To check the purity of the $[(CH_3)(CD_3)Au(PPh_3)_2]F_3CSO_3$, the methyl and phenyl resonances were integrated. The ratio Me/Ph should be 1/10; a value of 9.2 ± 0.5 was obtained, suggesting that there was a small amount of the nondeuterated compound present. Otherwise the spectrum was indistinguishable from that of $[(CH_3)_2Au(PPh_3)_2]F_3CSO_3$. Both $[Et_2Au(PPh_3)_2]F_3CSO_3$ and $[n\text{-}Bu_2Au(PPh_3)_2]F_3CSO_3$ decomposed so rapidly that spectra only could be obtained in the presence of excess PPh_3 to inhibit the decomposition, vide infra. Under these conditions, the diethyl cation at 90 MHz gave two complex resonances at $\tau \simeq 9.06$ and 8.05 ppm assigned to the methyl and methylene resonances, respectively. The di-n-butyl cation gave a very complex spectrum, and no attempt was made to analyze it.

Both $[(CH_3)_2Au(AsPh_3)_2]F_3CSO_3$ and $[(CH_3)_2Au(SbPh_3)_2]F_3CSO_3$ were more than 75% decomposed when PMR spectra were recorded immediately after solution preparation. Addition of 10% excess of the arsine or stibine ligand reduced the rate of decomposition, so the spectra could be obtained. The chemical shifts are listed in Table 2.

Vibrational spectra. The Raman and infrared spectra of the crystalline $[(CH_3)_2$-$Au(PPh_3)_2]X$ (X = ClO_4, F_3CSO_3, BF_4, and PF_6) compounds are a superposition

TABLE 2

NUCLEAR MAGNETIC RESONANCE[a] AND RAMAN[b] SPECTRA OF THE $[(CH_3)_2Au(PPh_3)_2]X$ COMPLEXES

Compound	Solvent	CH_3—Au		$\tau(C_6H_5)$[d] (ppm)	(H—C—P)[e]		Raman frequencies (cm^{-1})	
		τ(ppm)	$^3J(^{31}P-^1H)$[c] (Hz)		τ(ppm)	$^2J(^{31}P-H)$ (Hz)	$\nu(AuC_2)$	$\delta_s(CH_3)$
$[(CH_3)_2Au(PPh_3)_2]ClO_4$	$CDCl_3$	8.82	9.0, 7.2	2.62			536, 530 516	1222, 1188
$[(CH_3)_2Au(PPh_3)_2]ClO_4$	CH_2Cl_2	8.82	9.0, 7.2	2.62				
$[(CH_3)_2Au(PPh_3)_2]F_3CSO_3$	$CDCl_3$	8.81	8.4, 6.4	2.59			542, 528 516	1224, 1194
$[(CH_3)_2Au(PPh_3)_2]F_3CSO_3$	CH_2Cl_2	8.82	8.6, 6.6	2.62				
$[(CH_3)_2Au(PPh_3)_2]F_3CSO_3$	$(D_3C)_2CO$	8.81	8.3, 6.8	2.48				
$[(CH_3)(CD_3)Au(PPh_3)_2]F_3CSO_3$	CH_2Cl_2	8.82	8.4, 7.0	2.62			542, 492 520	1217, 928
$[(CH_3)_2Au(PPh_3)_2]BF_4$	$CDCl_3$	8.81	8.4, 6.6	2.59			534, 530 517	1222, 1188
$[(CH_3)_2Au(PPh_3)_2]BF_4$	CH_2Cl_2	8.82	8.5, 7.0	2.61				
$[(CH_3)_2Au(PPh_3)_2]PF_6$	CH_2Cl_2	8.82	7.8, 6.0	2.61			543, 534 516	1227, 1196
$[(CH_3)_2Au(PMePh_2)_2]F_3CSO_3$	$CDCl_3$	8.95	8.6, 6.8	2.54	8.02	10	534, 525	1222, 1187
$[(CH_3)_2Au(PMe_2Ph)_2]F_3CSO_3$	$CDCl_3$	8.82	8.2, 8.6	2.49	8.20	10	535, 522	1225, 1189
$[(CH_3)_2Au(PMe_3)_2]F_3CSO_3$	$CDCl_3$	8.98	8.0, 6.5		8.24	10.2	533, 522	1225, 1197
$[(CH_3)_2Au(PPh_2CH_2)_2]F_3CSO_3$	CH_2Cl_2	8.75	7.5	2.36	7.07[f]	17[f]	542, 535	1225, 1188
$[(CH_3)_2Au(AsPh_3)_2]F_3CSO_3$	CH_2Cl_2	8.58		2.68			542, 528	1222, 1190
$[(CH_3)_2Au(AsPh_2CH_2)_2]F_3CSO_3$	CH_2Cl_2	8.46		2.44	7.15[g]		538, 534	1227, 1187
$[(CH_3)_2Au(AsMe_2)_2C_6H_4]F_3CSO_3$	CH_2Cl_2	8.65		2.17[h]	8.09		542, 534	1228, 1182
$[(CH_3)_2Au(SbPh_3)_2]F_3CSO_3$	CH_2Cl_2	8.63		2.67				

[a] 0.1 *M* solutions, ^1H chemical shifts relative to TMS, τ 10 ppm. [b] Microcrystalline powders excited at 632.8 nm. [c] All $^2J(^{31}P-^{31}P)$ in the range 0 to 2 Hz. [d] Chemical shift of the maximum in the phenyl resonance. [e] Actually $^2J(^{31}P-H) + {}^4J(^{31}P-Au-P-C-H)$. [f] Methylene protons of the diphos ligand. [g] Methylene protons of the 1,2-bis(diphenylarsino)ethane. [h] Bisubstituted benzene ring of diars ligand.

of the cation spectra and the spectra of the uncoordinated anions as can be seen from the data in Table 2. Even when the neutral ligands are varied, the vibrations associated with the $(CH_3)_2Au^{III}$ moiety are very similar for all of the phosphine, arsine, and stibine complexes. The Au—C stretching and CH_3 symmetric deformation modes are most accurately measured in the Raman spectra, and these frequencies are tabulated in Table 2.

As discussed previously, the two Au—C coordinates couple with a ligand mode in the bis(triphenylphosphine) complexes [25]. This gives rise to three intense Raman and infrared bands in the 500—600 cm^{-1} region. This effect is not observed with the bis(trimethylphosphine) or bis(triphenylarsine) complexes. The effect can be seen in the Raman spectra, Fig. 1. Because of this coupling, it is meaningless to attempt to interpret the small frequency changes in this region in terms of varying *trans* influences of the neutral ligands. The influences, however, must be very similar for all the phosphine, arsine and stibine ligands, since the ν(Au—C) modes occur in a very narrow range.

The Raman spectrum of $[(CH_3)(CD_3)Au(PPh_3)_2]F_3CSO_3$ also indicates that it is relatively pure, although the analysis is complicated by the coupling of the Au—C coordinates with phosphine modes. The intensity of the 928 ($\delta_s(CD_3)$) and 492 cm^{-1} ($\nu(Au—CD_3)$) modes indicates extensive deuterium substitution, while the fact that only one band is observed in the $\delta_s(CD_3)$ region demonstrates the absence of $(CD_3)_2Au^{III}$. The absence of a band at 528 cm^{-1} indicates that any contamination by $(CH_3)_2Au^{III}$ must be slight. This is illustrated in Fig. 1.

There is no indication from the frequencies or widths of bands arising from degenerate vibrations of ClO_4^-, $F_3CSO_3^-$, BF_4^-,or PF_6^- for any significant lowering of the anion symmetry. In the Raman spectrum of the ClO_4^- salt which has been discussed previously [5], only ν_1 of ClO_4^- is observed at 931 cm^{-1}, while ν_3 and ν_4 appear in the infrared at 1092 and 625 cm^{-1}, respectively. The vibrational spectrum of the $F_3CSO_3^-$ anion has been discussed by Miles et al. [26] on the basis of a normal coordinate analysis. The CF_3 and SO_3 coordinates are highly mixed in the normal modes. Only the totally symmetric mode at ca. 1038 cm^{-1} is sufficiently intense to be observed with the normal signal amplitude used in recording Raman survey spectra of the microcrystalline powders (Fig. 1). It is obscured by a triphenylphosphine mode in the spectrum of $[(CH_3)_2Au(PPh_3)_2]F_3CSO_3$. In the infrared spectrum strong absorption bands are observed at 1261, 1225, 1148, and 1032 cm^{-1}, similar to the strong absorptions at 1280, 1232, 1168, and 1036 cm^{-1} reported for NaF_3CSO_3 [25]. The BF_4^- compound has ν_3 at 1056 cm^{-1} in the infrared, while ν_4 is obscured by the phosphine. For the PF_6^- complex, ν_3 and ν_4 occur as strong infrared absorptions at 838 and 558 cm^{-1}, respectively. These values are typical for BF_4^- or PF_6^- in ionic lattices with weak fields [27].

Both $[Et_2Au(PPh_3)_2]F_3CSO_3$ and $[n\text{-}Bu_2Au(PPh_3)_2]F_3CSO_3$ gave Raman spectra essentially characteristic of $[Au(PPh_3)_2]F_3CSO_3$. The spectra of the parent compounds can be predicted with some accuracy by analogy with spectra of stable compounds such as $Hg(C_2H_5)_2$ and $Hg(n\text{-}C_4H_9)_2$ [28] or $C_2H_5HgN_3$ and $n\text{-}C_4H_9HgN_3$ [29]. These have intense modes assigned to metal—carbon stretching, and it is apparent that the gold compounds eliminated alkane in the laser beam.

Thermal decomposition products. All of the $[(CH_3)_2AuL_2]X$ compounds

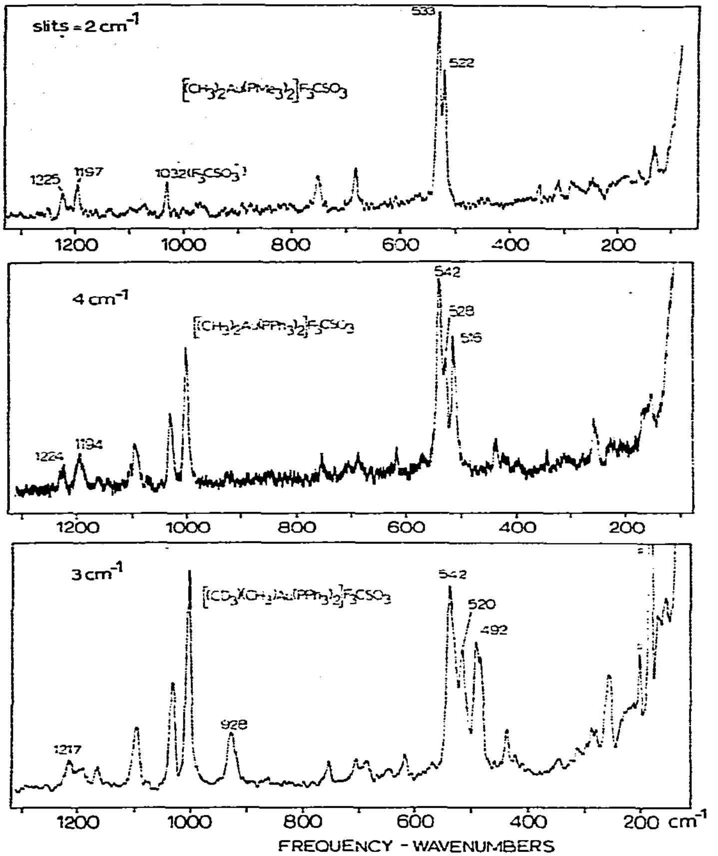


Fig. 1. Raman spectra of microcrystalline $[(CH_3)_2AuL_2]F_3CSO_3$ compounds excited by 632.8 n.m. Top, $[(CH_3)_2Au(PMe_3)_2]F_3CSO_3$; middle $[(CH_3)_2Au(PPh_3)_2]F_3CSO_3$; bottom $[(CD_3)(CH_3)Au(PPh_3)_2]F_3CSO_3$.

yield ethane as they decompose, although with widely differing rates. These reactions were followed using the proton magnetic resonance spectrum and, in some cases the Raman spectrum, of CH_2Cl_2 and $CHCl_3$ solutions. In both types of spectrum, there was no detectable amount of any organogold compound besides the reactant. This is illustrated in Fig. 2 and 3. The production of ethane is signaled by the growth of the PMR signal at 9.14 ppm, as observed earlier with $[(CH_3)_2Au(PPh_3)_2]ClO_4$ [4].

In several cases, the volatile decomposition products were examined by mass spectrometry. The solid compounds were placed in a sample bulb which then was evacuated. The compounds $[(CH_3)_2Au(AsPh_3)_2]F_3CSO_3$ and $[(CH_3)_2Au(SbPh_3)_2]F_3CSO_3$ eliminate at 25° C, while it was necessary to pyrolyze $[(CH_3)_2Auen]F_3CSO_3$ at 240° C. Only ethane was found upon comparison of the mass spectrum with the reference spectrum of C_2H_6 [30]. The decomposition of a sample of dimethyl[bis(1,2-diphenylarsino)ethane]gold(III) trifluoromethane sulfonate in CH_2Cl_2 solution was followed via the PMR spectrum to completion at 70° C. The sealed tube then was heated to 100° C, frozen in liquid nitrogen, and a portion of the more volatile material was transferred to an evacuated bulb. Only ethane and CH_2Cl_2 were detected by mass spectrometry.

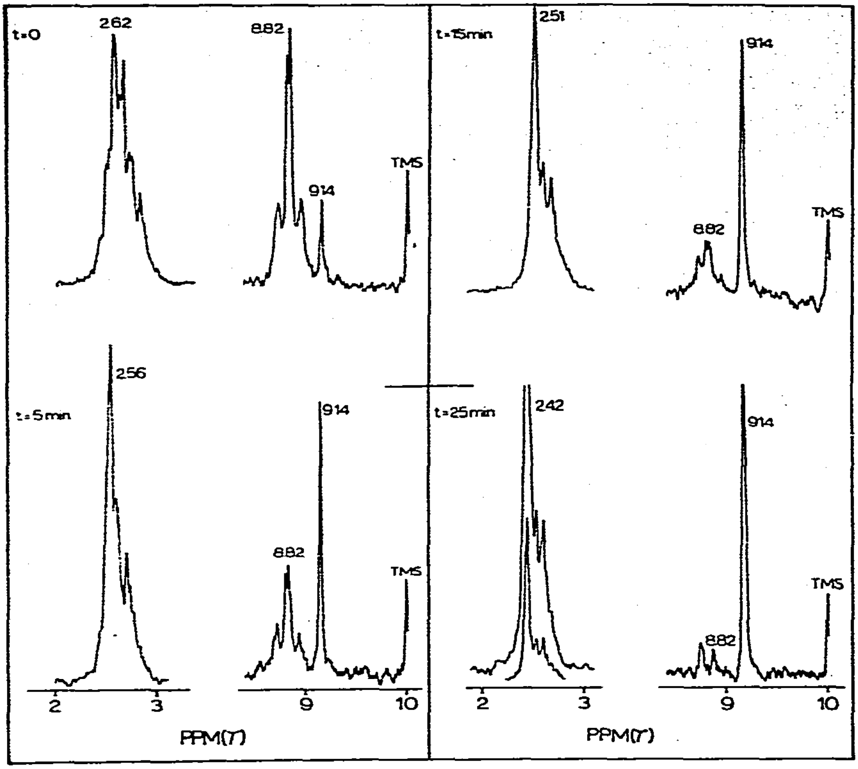


Fig. 2. Proton magnetic resonance spectrum (60 MHz) of [$(CH_3)_2Au(PPh_3)_2$]F_3CSO_3 in CH_2Cl_2 solution at 25.0° C as a function of time after mixing.

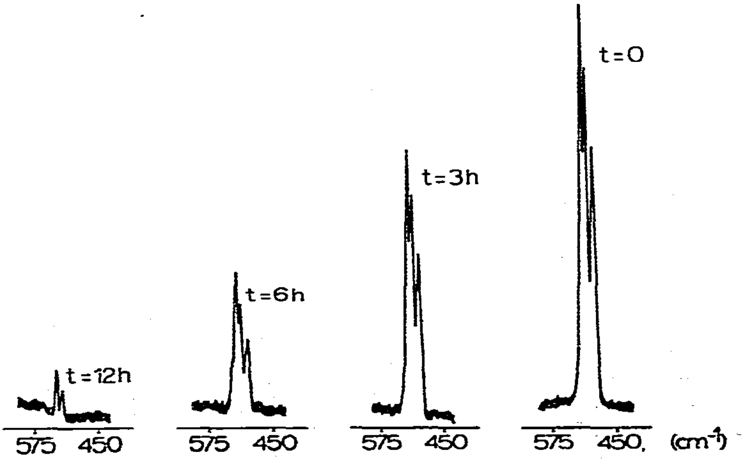


Fig. 3. Raman spectrum of [$(CH_3)_2Au(PPh_3)_2$]BF_4 in the Au—C stretching region, 50.0° C, CH_2Cl_2 solution as a function of time after mixing.

Pyrolysis of solid $[(CH_3)(CD_3)Au(PPh_3)_2]F_3CSO_3$ at 250°C for 15 min and a 0.1 *M* acetone solution at 50°C for 1 h gave peaks in the mass spectrum at 15, 18 and from 25 to 33 *m/e* indicating CH_3CD_3 and perhaps some C_2H_6. No signals above *m/e* 33 which would indicate the presence of C_2D_6 could be observed.

A sample of $[(C_2H_5)_2Au(PPh_3)_2]F_3CSO_3$ in an evacuated bulb was heated for 15 min at 250°C in an oil bath. Analysis of the volatile decomposition product gave the typical mass spectrum [30] of butane with no evidence of any ethane or ethylene. A solution of $[(C_2H_5)_2Au(PPh_3)_2]F_3CSO_3$ in CH_2Cl_2 was heated to 100°C, frozen, and the more volatile products were transferred to an evaccuated bulb. Again, the mass spectrum was characteristic of butane. A sample of $[(n\text{-}C_4H_9)_2Au(PPh_3)_2]F_3CSO_3$ was pyrolyzed at 250°C in vacuum, and the products were extracted with small amounts of $CHCl_3$ or CH_2Cl_2. The mass spectrum clearly indicated the presence of n-octane.

In the decompositions of the $[(CH_3)_2Au(PPh_3)_2]X$ compounds in $CHCl_3$ or CH_2Cl_2 solutions, the production of $[Au(PPh_3)_2]X$ was indicated by the presence of the intense phenyl resonance at τ 2.42 ppm, characteristic of the gold(I) complex. There was no measurable amount of free triphenylphosphine indicating that the gold(I) complex efficiently ties up the free ligand. This is to be expected, since it has been reported that gold(I) forms not only $[AuL_2]X$ but also $[AuL_3]X$ [31,32], and perhaps $[AuL_4]X$ [32] complexes when L is a phosphine and X is a poor nucleophile. The elimination was a homogeneous reaction with all of the unidentate ligand complexes, but the chelates deposited gold metal upon decomposition. The non-volatile residue remaining after pyrolysis of $[(CH_3)_2Au(AsPh_2CH_2)_2]F_3CSO_3$ in 0.1 *M* CH_2Cl_2 solution consisted of gold metal (58% yield based on the starting material) and a yellow oil which eventually crystallized after being maintained at 0°C under vacuum. An ESCA spectrum indicated the presence of both gold(I), binding energies 85.2 ($4f_{7/2}$), 88.8 ($4f_{5/2}$) and gold(III), 86.4 ($4f_{7/2}$), 89.9 eV ($4f_{5/2}$) in an approximate ratio of 2 : 1. These results indicate the chelate ligands are unable to stabilize gold(I) effectively against disproportionation, although binuclear complexes such as [ClAu(diphos)-AuCl] have been reported. The solution PMR also indicated the presence of free ligand as required by material balance: $3\ [Au^IL]X \rightarrow 2\ Au + [Au^{III}L_2]X_3 + L$.

Decomposition rates. The half lives for decomposition of a number of the dialkylgold complexes in sealed NMR tubes were determined at different temperatures by integration of the dimethylgold(III) versus the ethane proton resonances. The results are collected in Table 3.

It became apparent that two of these compounds, $[(CH_3)_2Au(PPh_3)_2]X$ ($X = ClO_4$, F_3CSO_3) eliminated ethane much more rapidly than the others with half lives as short at 15 min. The half lives also varied from sample to sample of the compounds, although the elemental analyses were satisfactory for all.

The presence of excess ligand was observed, in all cases, to inhibit the reaction. The rate of decomposition of the very unstable $[(CH_3)_2Au(PPh_3)_2]F_3CSO_3$ was studied in CH_2Cl_2 solution at 25°C as a function of the added triphenylphosphine concentration, and the results are illustrated in Fig. 4. A small addition of PPh_3 greatly slowed the reaction, but at higher concentrations the half life increased almost linearly with phosphine concentration.

In an analogous fashion, the addition of pyridine to $[(CH_3)_2Au(PPh_3)_2]F_3CSO_3$ inhibited the elimination of ethane. When one equivalent of pyridine was added,

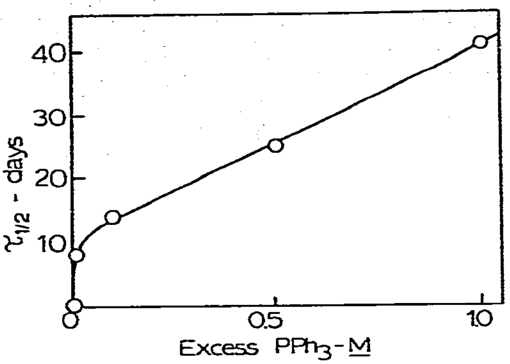


Fig. 4. Effect of added triphenylphosphine on the half life for reductive elimination by 0.1 *M* $[(CH_3)_2Au(PPh_3)_2]F_3CSO_3$ in CH_2Cl_2 solution, 25.0°C.

the PMR spectrum consisted of a doublet, τ 8.78 ppm, $^3J(^{31}P—H)$ 7.5 Hz. Exchange of pyridine and phosphine occurs without dissociation of the remaining phosphine to average the non-equivalent methyl sites.

The eliminations from the reactive $[(CH_3)_2Au(PPh_3)_2]F_3CSO_3$ and $[(CH_3)_2Au(AsPh_3)_2]F_3CSO_3$ in CH_2Cl_2 solution were examined in the presence of the radical trap styrene. No change in the rate of ethane production was observed. When a similar experiment was conducted in the presence of di-t-butyl nitroxide, ethane was found to be produced at a rate comparable to that in the nitroxide-free reaction. No changes occurred during the course of the reaction in the intensity of the nitroxide EPR spectrum (g 2.0065, a_N 17 G, lit. 16.8 G [33]). Methyl radicals have been observed at low temperature during the photolysis of $[(CH_3)_2Pt(PEt_3)_2]$/di-t-butylperoxide mixtures and also detected by the use of spin traps [34].

The kinetics of the decomposition of the somewhat more stable $[(CH_3)_2Au(PPh_3)_2]X$ ($X = BF_4$, PF_6) were followed by measuring the disappearance of the $(CH_3)_2Au$ proton resonance with time in CH_2Cl_2 solution in sealed NMR tubes at 50 ± 0.5°C. The signals were measured relative to an internal TMS reference of known concentration. Although the data could be described approxi-

TABLE 3

HALF LIFE FOR REDUCTIVE ELIMINATION OF ETHANE IN CH_2Cl_2 SOLUTION [a]

Compound	at 25°C	at 50°C	at 75°C	at 100°C	at 125°C
$[Me_2Au(PPh_3)_2]BF_4$	9.3 days	10.1 h	0.5 h	<1 min	[b]
$[Me_2Au(PPh_3)_2]PF_6$	15.7 days	14.8 h	1.2 h	ca. 2 min	[b]
$[Me_2Au(PMePh_2)_2]F_3CSO_3$	[c]	5.3 days	6.0 h	ca. 5 min	[b]
$[Me_2Au(PMe_2Ph)_2]F_3CSO_3$	[c]	8.6 days	18.5 h	ca. 10 min	[b]
$[Me_2Au(PMe_3)_2]F_3CSO_3$	[c]	[d]	8.7 days	10 h	ca. 0.25 h
$[Me_2Au(PPh_2CH_2)_2]F_3CSO_3$	[c]	[e]	26.2 days	1.5 days	4.75 h
$[Me_2Au(AsPh_2CH_2]F_3CSO_3$	[c]	[e]	3.4 days	2.0 h	8 min
$\{Me_2Au[(AsMe_2)_2C_6H_4]\}F_3CSO$	[c]	[e]	43.8 days	2.0 days	0.75 days

[a] Measured to 50% completion by integration of methyl vs. ethane resonance. [b] Too fast to measure. [c] No measurable decomposition. [d] Trace of ethane observed after 30 days. [e] No evidence of ethane after 30 days.

mately by a first order decomposition with rate constants (50° C) of $k = 1.9 \times 10^{-5}$ sec^{-1} (BF_4^-), 1.3×10^{-5} sec^{-1} (PF_6^-), it was observed, that increasing the concentration of $[(CH_3)_2Au(PPh_3)_2]BF_4$ from 0.05 to 0.2 *M* approximately doubled the half life for the reaction. It appears that there is inhibition not only by added ligand but also by the gold(I) product, which appears to be typical for these elimination reactions [13]. This is being investigated in more detail. It should be noted that while it is very likely that the $[(CH_3)_2AuL_2]X$ compounds in Table 3 decompose by the same mechanism, this has not been proven. The decomposition products of the complexes with chelate ligands differ from the products of the complexes with monodentate ligands.

Discussion

A number of factors influence the rate of production of alkane from dialkylgold(III) complexes. Among these are the following: (i) cationic complexes $[R_2AuL_2]X$ undergo the most rapid eliminations; (ii) bulky L ligands are required for facile elimination at room temperature; (iii) alkane formation is inhibited by excess L or by the addition of pyridine; (iv) elimination is slower when 2 L are replaced by a bidentate chelating ligand; (v) there is a small but significant anion effect as X is varied. With the $[(CH_3)_2AuL_2]F_3CSO_3$ compounds in CH_2Cl_2 solution, the rate of elimination decreased in the sequence L = $SbPh_3 > AsPh_3 > PPh_3 > PMePh_2 > PMe_2Ph > PMe_3 > PPh_2CH_2CH_2PPh_2$. Upon variation of the alkyl group R with $[R_2Au(PPh_3)_2]F_3CSO_3$, the rate of elimination increased with R = Me < Et ≃ n-Bu.

A dissociative process is indicated by several observations. The fastest reactions by far are those where L = $P(C_6H_5)_3$, $As(C_6H_5)_3$, or $Sb(C_6H_5)_3$, the bulkiest ligands. Among these ligands, the rate decreases as the base strength of the ligand increases. Replacement of one phenyl group by methyl in the ligand, i.e. L = $PMePh_2$, reduces the rate of elimination markedly. The "cone angle" of PPh_3 is 145 ± 2° compared to a value of 118 ± 4° for PMe_3 [35]. Steric effects are an important factor in these elimination reactions. Electronic changes in the series of compounds with $PR_nR'_{(3-n)}$ ligands must be very small as judged by the constancy of $\nu(Au—C_2)$. Complexation by bidentate ligands stabilizes the complexes against elimination. Excess ligands or added pyridine inhibits the decomposition markedly. Stabilization by an associative process is ruled out, because the solubility of $[(CH_3)_2Au(PPh_3)_2]F_3CSO_3$ does not increase in the presence of added phosphine. In addition, the addition of up to five equivalents of PPh_3 has no significant effect on the PMR spectrum. At higher concentrations, there is slight broadening. Exchange of the phosphine ligands is not measurable on the NMR time scale at 40° C, and there is no measurable concentration of a species with three phosphines.

Several observations also indicate that the reaction is an intramolecular, concerted reductive elimination. No traces of methane ever were observed in reactions run in $CHCl_3$ or CH_2Cl_2 solution where methyl radicals would be expected to abstract hydrogen from the solvent. The addition of radical traps such as di-t-butyl nitroxide and styrene had no effect on the rate of ethane production. The decomposition of $[(CH_3)(CD_3)Au(PPh_3)_2]F_3CSO_3$ gives no measurable amount of C_2D_6 by mass spectrometry. In the reactions with the unidentate ligands, the $[Au^IL_2]X$ product could be obtained almost quantitatively from the reaction mixture. The $[R_2AuXL]$ produced by dissociation of L from $[R_2AuL_2]X$ may eliminate itself, or a second L may dissociate before the intramolecular elimination occurs.

The reactants $[(CH_3)_2AuL_2]X$ must exist as intimate ion pairs in the low dielectric constant solvents $CHCl_3$ and CH_2Cl_2 ($D = 4.806$, 9.08 at 20° C, respectively). These chlorinated hydrocarbons were among the very few in which these compounds were soluble without substantial chemical change. This is indicated by the virtually identical Raman spectra for the solutions and microcrystalline powders. Donor solvents displace the bulkier L ligands. That the interaction between cation and anion is essentially a hard sphere Coulombic one is indicated by the lack of any variation in the Raman frequencies or the proton chemical shifts and coupling constants characteristic of the cation as X^- is varied among BF_4^-, PF_6^-, ClO_4^- and $F_3CSO_3^-$ with $[(CH_3)_2Au(PPh_3)_2]^+$.

The very rapid eliminations found with $[(CH_3)_2Au(PPh_3)_2]X$ ($X = ClO_4$ and F_3CSO_3) together with the data in Fig. 4 suggest that the reaction changes at low [L], and $[(CH_3)_2AuXL]$ eliminates more rapidly than it is scavenged by L. If this is true, the complexes $[(CH_3)_2Au(ClO_4)PPh_3]$ and $[(CH_3)_2Au(F_3CSO_3)PPh_3]$ must be very unstable. It was found that the addition of AgF_3CSO_3 to a solution of $[(CH_3)_2AuI]_2$ in THF containing from one to two equivalents of PPh_3 gave an immediate evolution of ethane with effervescence. The difference as X^- is varied among the series ClO_4^-, $F_3CSO_3^-$, BF_4^-, PF_6^- would depend both upon the thermal stability of $[(CH_3)_2AuXL]$ and the tendency of X^- to displace PPh_3 from the coordination sphere of gold. All of the X^- ligands are particularly poor nucleophiles, so no information is available on their nucleophilicity toward heavy transition metal centers. Indeed if X^- is a good nucleophile, e.g. Cl^-, Br^-, or I^-, the equilibrium is shifted entirely in favor of $(CH_3)_2AuXPPh_3$; and the bis-PPh_3 cation cannot be prepared.

Another possible cause for the behavior illustrated in Fig. 4 would be the presence of $[(CH_3)_2Au(F_3CSO_3)PPh_3]$ as a contaminant in the $[(CH_3)_2Au(PPh_3)_2]F_3CSO_3$. This would reduce the effectiveness of scavenging by phosphine. A deficiency of PPh_3 in the system would lead to rapid elimination with the production of $[Au^I(PPh_3)F_3CSO_3]$. This would tend to abstract PPh_3 from $[(CH_3)_2Au(PPh_3)_2]F_3CSO_3^-$, catalyzing the elimination. If the initial effect on $\tau_{1/2}$ of added PPh_3 is attributed to titration of $[(CH_3)_2Au(F_3CSO_3)PPh_3]$, approximately 20% contamination would be required. This is deemed unlikely by: (i) the good agreement between theoretical and calculated elemental analyses (With a 20% PPh_3 deficiency, the theoretical analysis changes as follows: C, 52.0 to 50.1; P, 6.88 to 6.57%. The analytical results do not indicate this degree of non-stoichiometry.); (ii) the lack of any signal attributable to the monophosphine in the PMR spectrum; (iii) the absence of bands in the Raman spectrum assignable to the monophosphine complex. Whatever the basis of the effect, it renders the elimination rates very sensitive to a slight excess or deficiency of phosphine.

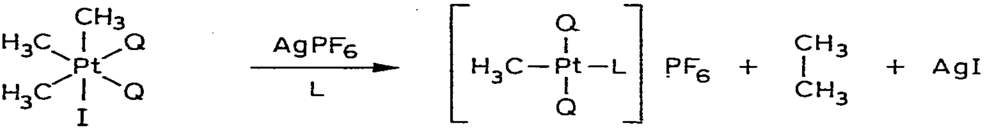
The very rapid eliminations observed with $[(CH_3)_2Au(PPh_3)_2]X$ ($X = ClO_4$, F_3CSO_3) as well as the analogous $AsPh_3$ and $SbPh_3$ systems appear to depend upon a combination of several factors. First the very bulky ligands tend to facilitate dissociation of one L, although the concentration of $[(CH_3)_2AuXL]$ is not measurable by spectroscopic techniques. Unsymmetrical molecules such as

$(CH_3)_2AuXPPh_3$ (X = Cl, Br, I) also eliminate ethane [36], although at a slower rate. The solvents employed are very poor donors. The ligand X^- is a very poor nucleophile, and because of the large Coulombic force in these low dielectric constant solvents X^- probably occupies the site vacated by L. These conditions give information on the type of intermediate which favors reductive elimination of alkane. This involves an electron deficient gold(III) complex. The reduction in electron density at the gold(III) center facilitates transfer of a pair of electrons from the $(CH_3)_2Au^{III}$ framework with concomitant formation of a carbon—carbon bond in a concerted process. It appears that a marked dissimilarity in the two gold—carbon bonds is a necessary condition for a facile elimination. The basis for this is not clear.

One of the observations which initially was puzzling was why certain cations with relatively poor donor ligands, e.g. $[(CH_3)_2Au(OH_2)_2]^+$ [23] and the intermediate in the syntheses described here, $[(CH_3)_2Au(THF)_2]^+$ should be relatively stable compared to the complexes described above. In all cases, these species occur in solution with the ligand as the solvent. Consequently, there should be little tendency for any dissociation to occur to produce an unsymmetrical, electron deficient species. Symmetrical, electron rich gold complexes, e.g. $(CH_3)_4Au^-$, also show relatively high thermal stability [1,2]. Ethane elimination from $[(CH_3)_2AuL_2]^+$ compounds is neither favored when L is a strong nor a weak donor.

The $[R_2AuL_2]F_3CSO_3$ complexes appear to be much less stable thermally than the analogous $[R_2PtL_2]$ compounds. Comparison of the ν(Au—C) values for $[(CH_3)_2Au(PMe_3)_2]F_3CSO_3$, 533, 522 cm^{-1}, with the values reported for $[(CH_3)_2Pt(PMe_3)_2]$, 525, 508 cm^{-1} [37], indicates the bond strengths should be very similar. The absence of any disproportionation of the $[Et_2Au(PPh_3)_2]F_3CSO_3$ or $[(n\text{-}Bu)_2Au(PPh_3)_2]F_3CSO_3$ is in marked contrast to the behavior of $[(n\text{-}Bu)_2Pt(PPh_3)_2]$ [14]. Reductive elimination occurs much more rapidly with the gold complex than β elimination does with the analogous platinum compound. For example, $[(n\text{-}Bu)_2Au(PPh_3)_2]F_3CSO_3$, 0.1 *M* CH_2Cl_2 solution, decomposes completely within minutes at 25° C to give octane. The analogous platinum complex is 50% decomposed (0.1 *M* CH_2Cl_2 solution) at 60° C in 0.56 h [14].

Reactions analogous to the eliminations discussed here have been observed by Clark and coworkers [40,41]. The addition of $AgPF_6$ to solutions of $[(CH_3)_3PtQ_2I]$ in acetone or methanol solutions containing the ligand L resulted in elimination of ethane. For a facile elimination, Q must be a ligand of high *trans* influence, L a ligand of low *trans* influence.



Ethane is eliminated from the *fac*-$[(CH_3)_3Pt(PMe_2Ph)_2X]$ (X = Cl, Br, I) and *fac*-$[(CH_3)_3PtL_2X]$ (L = PMe_3, $PMePh_2$, X = I) compounds upon pyrolysis [40, 41]. The process involves phosphine dissociation and an intramolecular elimination.

Since a number of features are common to eliminations from the dimethylgold(III) and trimethylplatinum(IV) complexes, it seems likely that they have very similar mechanisms.

Acknowledgement

This investigation was supported by the National Science Foundation, Grants GP-23208 and MPS 73-04856 and by the Donors of the Petroleum Research Fund administered by the American Chemical Society Grant 2905-AC3.

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Note added in proof. Since the completion of this work, we have become aware of a study of reductive elimination from dialkyl(aniono)gold(III) species produced in solution by protonolysis of trialkyl(phosphine)gold(III) complexes: S. Komiya and J.K. Kochi, J. Amer. Chem. Soc., (1976) in press. Since one of these species $[(CH_3)_2AuPPh_3F_3CSO_3]$ also has been suggested by us as an intermediate in the decomposition of $[(CH_3)_2Au(PPh_3)_2]F_3CSO_3$, a mutual effort was made to relate these two studies. Because of the complexity of the reactions, it was not possible to do this quantitatively. The rates of elimination appear to decrease in the sequence $R_2AuX >> R_2AuXL > [R_2AuL_2]^+$.