Electrophilic Cleavage of Organogold Complexes with Acids. The Mechanism of the Reductive Elimination of Dialkyl(aniono)gold(III) Species

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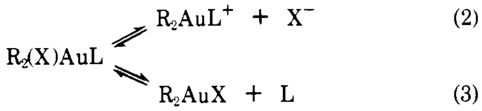
Abstract: Protonolysis of trialkyl(phosphine)gold(III) complexes with a variety of acids HX selectively cleaves one alkyl group to afford high yields of alkane and cis dialkyl(X)phosphinegold(III) complexes in which X = ClO_4, CF_3SO_3, NO_3, I, Br, Cl, CF_3CO_2, and CH_3CO_2. Isotopic labeling studies show unequivocally that only alkyl groups cis to phosphine are removed, consistent with the large trans effect of alkyl ligands. Examination of various *cis*- and *trans*-$R(CH_3)_2AuPPh_3$ indicates that alkyl groups are subject to large steric hindrance during protonolysis. The rates of protonolysis are also highly sensitive to the strengths of the acids. These results suggest that proton transfer to carbon and concomitant breaking of the bond to gold provide the principal driving force for the substitution. This electrophilic mechanism is contrasted with a process involving oxidative addition of acid, previously proposed for the protonolysis of methylplatinum(II) and alkylgold(I) complexes. The reductive elimination of the resultant $R_2(X)Au^{III}PPh_3$ proceeds by first-order kinetics to afford R-R and $XAu^{I}PPh_3$, the rate constants decreasing in the order: X = TfO ≫ NO_3 ≫ CF_3CO_2, Cl > CH_3CO_2. Enlarging the steric bulk of the phosphine ligand PR'_3 as well as homologating the alkyl groups R lead to decreasing stability of $R_2(X)AuPR'_3$. Small amounts of added PPh_3 severely retard reductive elimination, and there is a small negative common-ion effect on the rates. A mechanism is proposed for reductive elimination involving the dissociation of phosphine followed by the decomposition of the three-coordinate intermediate R_2AuX. Evidence for this coordinatively unsaturated species is sought from a study of the phosphine-free $(CH_3)_2AuOTf$, existing as a dimer. The existence of three-coordinate intermediates is consistent with the intermolecular scrambling of methyl groups in $CH_3(CD_3)(X)AuPPh_3$ and in mixtures of $(CD_3)_2(X)AuPPh_3/(CH_3)_2(X)AuPPh_3$ prior to and/or during the reductive elimination. Comparisons are drawn between the mechanistic scheme proposed for the reductive elimination of $R_2(X)AuPPh_3$ and that previously proposed for the trialkyl analogue R_3AuPPh_3. Thus, the replacement of a methyl group in $(CH_3)_3AuPPh_3$ by X effects large variations in the rates of reductive elimination, from $(CH_3)_2AuPPh_3(OAc)$, which is more stable than $(CH_3)_3AuPPh_3$ on one extreme, to $(CH_3)_2AuPPh_3(OTf)$, which is much less stable, on the other. In every case CH_3-CH_3 is eliminated with high selectivity compared to CH_3-X, even with carbon-centered ligands such as X = cyano.

Organogold compounds are valuable probes for the study of the chemistry of organometallic intermediates in catalytic reactions.[1] Thus, trisalkylgold(III) complexes (R_3AuL where L = phosphines) undergo rearrangement of the alkyl ligand R, cis-trans isomerization of the square planar configuration, substitution of the ligand L, and reductive elimination of R-R, all processes characteristic of reactive organometallic species.[2] The latter, reductive elimination, is particularly pertinent to the roles which organometals play in catalytic processes. Replacement of an alkyl ligand in R_3AuL results in a series of bisalkyl derivatives $R_2(X)AuL$, which present an opportunity to examine the effects of anionic ligands X on the chemistry of organometallic species, particularly with respect to ligand substitution and the formation of cationic species in reductive eliminations.

Acidolysis of transition metal-alkyl complexes is known to afford alkanes.[3] Even such thermally unstable species as $(CH_3)_3Au$, prepared only at low temperatures react with hydrogen chloride and various carboxylic acids to give dimethylgold compounds.[4] The latter are usually aggregated as dimers and polymers, which are cleaved into monomeric $Me_2(X)AuL$ complexes by added phosphines (L). Some dimethylgold derivatives can also be obtained from the tetrameric $(Me_2AuOH)_4$,[5] but the yields are usually poor due to the instability and insolubility of the latter.[6] Dimethylgold(III) complexes with a variety of phosphine and anionic ligands have been prepared and characterized.[3-8] They all have square planar cis configurations, the two inequivalent methyl groups being characterized in the proton NMR spectra as separate resonances, each split into doublets by the phosphorus ligand.

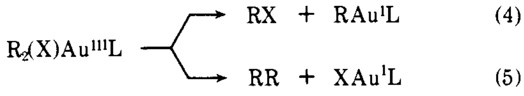
We wish to show that a novel series of bisalkylgold(III) complexes I can be readily prepared by the direct protonolysis of trisalkylgold compounds with various acids. Structural and stereochemical factors in these electrophilic substitutions on gold have been examined. The stability of I with respect to ligand substitution, leading to cationic or neutral three-coordinate intermediates (eq 2 and 3), as well as the structural factors influencing selectivity in reductive elimination, i.e., eq 4 and 5, are the principal objectives of this study.

$$R_3AuL + HX \longrightarrow \underset{\text{I}}{R_2(X)AuL} + RH \qquad (1)$$



$$R_2(X)AuL \rightleftharpoons R_2AuL^+ + X^- \qquad (2)$$

$$R_2(X)AuL \rightleftharpoons R_2AuX + L \qquad (3)$$



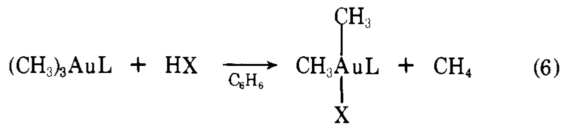
$$R_2(X)Au^{III}L \longrightarrow RX + RAu^{I}L \qquad (4)$$

$$R_2(X)Au^{III}L \longrightarrow RR + XAu^{I}L \qquad (5)$$

Results and Discussion

I. Protonolysis of Trialkyl(phosphine)gold(III) to Dialkyl(aniono)gold(III) Species.

A. Trimethyl(triphenylphosphine)gold(III). The acetolysis of $(CH_3)_3AuL$ (where L = PPh_3 hereafter) proceeds in benzene solution at room temperature to afford 1 equiv of methane and *cis*-acetoxydimethyl(triphenylphosphine)gold(III) according to eq 6. Analogous



$$(CH_3)_3AuL + HX \xrightarrow[C_6H_6]{} CH_3\overset{CH_3}{\underset{X}{Au}}L + CH_4 \qquad (6)$$

substitution reactions of halide may be performed by hydrochloric and hydrobromic acid as well as gaseous hydrogen iodide with similar facility (Table I). Trifluoroacetolysis affords *cis*-trifluoroacetoxydimethyl(triphenylphosphine)gold(III). In every case, only one methyl group is cleaved from $(CH_3)_3AuL$ and the dimethylgold(III) product can be isolated in high yields. However, only derivatives $(CH_3)_2AuL(X)$ with

Table I. Protonolysis of Trimethyl(triphenylphosphine)gold(III) with Acids[a]

Acid	Concn (M)	$(CH_3)_3AuL$ (M)	Temp (°C)	Solvent	Methane (%)	$(CH_3)_2AuL(X)$ (%)	
CH_3CO_2H	*b*	0.043	25	C_6H_6	77	(CH_3CO_2)[c]	82
CF_3CO_2H	0.030	0.030	25	C_6H_6	95	(CF_3CO_2)[c]	62
HCl[d]	0.065	0.068	25	C_6H_6	75	(Cl)[c]	80
HBr[e]	0.055	0.056	25	C_6H_6	62	(Br)[c]	80
HI[f]	0.050	0.048	25	C_6H_6	74	(I)[c]	66
HNO_3[h]	0.050	0.049	25	$C_6H_5CH_3$	63	(*g*)	63
	0.060	0.061	−20	$C_6H_5CH_3$	86	(NO_3)	49
p-$CH_3C_6H_4SO_3H$	0.040	0.041	25	$C_6H_5CH_3$	58	(*g*)	41
	0.050	0.048	−20	$C_6H_5CH_3$	57	(*g*)	11
CH_3SO_3H	0.055	0.058	25	$C_6H_5CH_3$	98	(*g*)	72
$HClO_4$[h]	0.045	0.045	25	$C_6H_5CH_3$	32	(*g*)	103
CF_3SO_3H	0.11	0.011	25	$C_6H_5CH_3$	93	(*g*)	92
	0.055	0.053	−78	CH_2Cl_2	103	(*g*)	11

[a] Reaction stopped after 24 h. [b] Excess, reaction incomplete after 24 h, result after 3 days. [c] No ethane detected. [d] 37% aqueous. [e] 48% aqueous. [f] Gas. [g] Ethane, no $(CH_3)_2AuL(X)$ detected. [h] 70% aqueous solution.

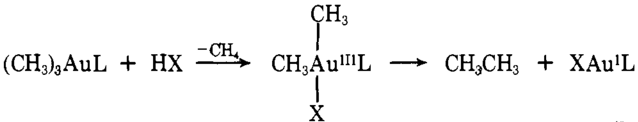
Table II. ^1H and ^{31}P NMR Spectra of Methylgold(III) Complexes[a]

	^1H						
	Cis-CH_3			Trans-CH_3		^{31}P	
Compound	δ	J_{H-P}		δ	J_{H-P}	δ	$\Delta\nu$
$(CH_3)_2Au(PPh_3)OTf$[b]	0.97 (d)	8		1.29 (d)	9		
$(CH_3)_2Au(PPh_3)NO_3$	0.93 (d)	8		1.57 (d)	9	102.87	2
$(CH_3)_2Au(PPh_3)O_2CCF_3$	0.95 (d)	8		1.53 (d)	9	103.53	1
$(CH_3)_2Au(PPh_3)O_2CCH_3$	0.97 (d)	8		1.63 (d)	9		
$(CH_3)_2Au(PPh_3)Cl$	0.92 (d)	8		1.90 (d)	9	107.49	0.6
$(CH_3)_2Au(PPh_3)Br$	1.03 (d)	8		1.97 (d)	9		
$(CH_3)_2Au(PPh_3)I$	1.20 (d)	8		2.05 (d)	9		
$(CH_3)_2Au(PMe_3)O_2CCF_3$	0.80 (d)	8		1.20 (d)	10		
$(CH_3)_3AuPPh_3$	0.68 (d)	8		1.83 (d)	9	111.86	0.6
$(CH_3)_2Au(PPh_3)_2O_2CCF_3$			1.20 (m)				
$(CH_3)_2Au(PPh_3)_2ClO_4$			1.20 (m)				
$(CH_3)_2Au(PPh_3)_2NO_3$			1.20 (m)			108.42	6.3
$(CH_3)_2Au(PPh_3)_2OTf$			1.20 (m)				
$[(CH_3)_2AuI]_2$			1.33 (s)				
$[(CH_3)_2AuOTf]_2$			1.00 (s)				

[a] Chemical shifts in ^1H NMR measured relative to benzene solvent (δ 7.27). Proton decoupled ^{31}P NMR spectra measured relative to external $P(OCH_3)_3$. [b] CH_2Cl_2 at −50 °C, chemical shift relative to ethane (δ 0.85).

cis-X, not trans, can be detected due to their greater thermodynamic stability (vide infra).

When stronger acids such as nitric, *p*-toluenesulfonic, perchloric, or trifluoromethanesulfonic (triflic) acids are employed, 1 equiv of methane is again liberated; the resulting dimethylgold species, however, is unstable and spontaneously liberates an equivalent of ethane according to eq 7. If the acidolysis by nitric acid is carried out at −20 °C, the intermediate $(CH_3)_2AuL(NO_3)$ can be isolated as colorless crystals, and dissolution in benzene is accompanied by the liberation of ethane. No dimethyl derivative can be isolated from $(CH_3)_3AuL$ and triflic acid under similar conditions, only an equivalent of methane and of ethane being observed. (The gold(I) product can be isolated as $Au(PPh_3)_2OTf$ by adding excess PPh_3 after decompoition was complete.) However, the presence of the highly unstable $(CH_3)_2AuL(OTf)$ in solution can be detected by its proton NMR spectrum obtained during acidolysis at −50 °C. The two doublets (δ 0.97, $J_{P-H} = 8$ Hz and δ 1.29, $J_{P-H} = 9$ Hz) of equal intensity are characteristic of cis and trans methyl groups, respectively, in a variety of $(CH_3)_2AuL(X)$ listed in Table II. These resonances slowly disappeared on standing at this temperature and were replaced by that of ethane (0.85), the presence of which was confirmed by gas chromatographic analysis. The large differences in thermal stabilities of various dimethylgold(III) species will be described separately (vide infra).



$$(CH_3)_3AuL + HX \xrightarrow{-CH_4} CH_3\overset{CH_3}{\underset{X}{Au^{III}}}L \longrightarrow CH_3CH_3 + XAu^IL \qquad (7)$$

$$X = ClO_4, CF_3SO_3, C_7H_7SO_3, NO_3$$

If additional ligand PPh_3 is present during acidolysis, the subsequent reductive elimination of the dimethyl intermediate is inhibited since it is readily intercepted and stabilized as the cationic bis-phosphine complex II. Under these conditions

$$(CH_3)_2AuL(X) + L \rightleftharpoons \underset{\text{II}}{(CH_3)_2AuL_2{}^+X^-} \qquad (8)$$

$$X = ClO_4, CF_3SO_3, NO_3, CF_3CO_2$$

even $(CH_3)_3AuL$ and triflic acid afford only 1 equiv of methane but no ethane when the acidolysis is carried out at room temperature (Table III). The cationic dimethyl complex $(CH_3)_2AuL_2{}^+CF_3SO_3{}^-$ formed under these conditions is the analogue of the perchlorate salt prepared previously[7] and other phosphine complexes of dimethylgold(III) halides by the

Table III. Protonolysis of $(CH_3)_3AuPPh_3$ in the Presence of PPh_3[a]

$(CH_3)_3AuPPh_3$ (mmol)	Acid	Concn (mmol)	PPh_3 (mmol)	Alkane (mmol) CH_4	Alkane (mmol) C_2H_6	$(CH_3)_2AuL_2(X)$	(%)
0.12	CF_3SO_3H	0.12	0.72	0.076	0	(CF_3SO_3)	72
0.49	$HClO_4$	0.49	1.12	0.35	0	(ClO_4)	79
0.13	HNO_3	0.13	0.13	*b*	0	(NO_3)	57
0.16	CF_3CO_2H	0.16	0.18	*b*	0	(CF_3CO_2)	63

[a] In benzene at 25 °C for 24 h. [b] Considerable, but not measured.

Table IV. Stereochemistry of Protonolysis of Trimethyl(phosphine)gold(III)

Compound	Concn (mM)	Acid	Concn (mM)	Solvent	Temp (°C)	Methane CH_4	Methane CD_3H
cis-$CD_3(CH_3)_2AuL$[a]	0.049	HNO_3	0.049	$C_6H_5CH_3$	−20	41	59
trans-$CD_3(CH_3)_2AuL$[b]	0.049	HNO_3	0.049	$C_6H_5CH_3$	−20	95	5
$(CD_3)_3AuL$[c]	0.049	HNO_3	0.049	$C_6H_5CH_3$	−20	0	100
$(CD_3)_3AuL$ $(CH_3)_3AuL$	0.049 0.049	HNO_3	0.098	$C_6H_5CH_3$	25	57	43
$(CD_3)_3AuL$ $(CH_3)_3AuL$	0.049 0.049	HNO_3	0.098	Me_2SO	25	52	48

L = PPh_3. Purity: [a] 98%, 1.5% $(CH_3)_3AuL$ and 0.5% trans isomer; [b] 87.5%, 0.5% $(CH_3)_3AuL$ and 12% cis isomer; [c] 99%.

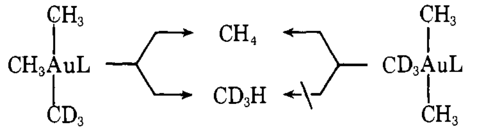
cleavage of the dimer.[6b] The formation of the cationic bis-

$$\tfrac{1}{2}[(CH_3)_2AuX]_2 + 2L' \rightarrow (CH_3)_2AuL'_2{}^+X^- \qquad (9)$$

phosphine complexes in both eq 8 and 9 appears to be favored by poorly coordinating anions X^- and phosphines with small cone angles.

The rates of protonolysis of $(CH_3)_3AuL$ were not measured accurately since they vary over a large span, being highly dependent on the strength of the acid. Thus, a stoichiometric amount of acetic acid ($pK_a = 4.8$) requires more than 3 days to react with $(CH_3)_3AuL$ in benzene solution at room temperatures, whereas protonolysis with trifluoroacetic acid ($pK_a = 0.3$) is complete in several hours. Triflic acid reacts on mixing even at −80 °C in methylene chloride, but nitric acid (about 400 times weaker than triflic acid) reacts with $(CH_3)_3AuL$ at a measureable rate at −20 °C.

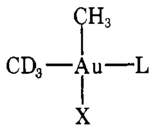
B. Stereochemistry of the Protonolysis. The formation of only the cis-dimethyl derivatives from the protonolysis of trimethyl(phosphine)gold(III) with various acids suggests that a cis-methyl group is preferentially cleaved. However, since it is also possible that the stereochemistry of the product is thermodynamically controlled, i.e., the *cis*-I is more stable than the trans isomer, we examined the isotopic composition of the methane liberated from *cis*- and *trans*-trideuteriomethyldimethyl(triphenylphosphine)gold. The results in Table IV show that only a cis-methyl group is cleaved by nitric acid. The



(10)

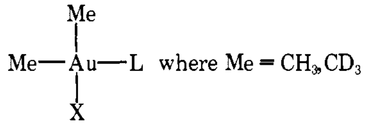
slightly higher yields of CD_3H compared to CH_4 obtained from the cleavage of *cis*-$CD_3(CH_3)_2AuL$ suggest an inverse secondary kinetic isotope effect, but the difference lies within the experimental error in the mass spectral analysis. The latter is supported by the results of the intermolecular labeling study of the protonolysis of an equimolar mixture of $(CH_3)_3AuL$ and $(CD_3)_3AuL$ also included in Table IV.

The stereochemistry of the dimethylgold(III) product of reaction 10 is especially noteworthy. Thus, protonolysis of *trans*-$CD_3(CH_3)_2AuL$ with trifluoroacetic, nitric, or hydrochloric acid (or iodonolysis with iodine) leads to cleavage of only the cis-CH_3–Au bond as described above (i.e., liberation of only CH_4 or CH_3I), but the gold(III) product did not consist of only the expected



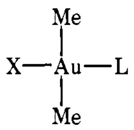
$$CD_3\!-\!\overset{CH_3}{\underset{X}{Au}}\!-\!L$$

Instead, complete scrambling of the methyl groups in the product was indicated by the proton NMR spectrum showing two doublets (due to cis- and trans-CH_3) of equal intensity. Similar results were obtained with *cis*-$CD_3(CH_3)_2AuL$. Since the reactants are not isomerized during the reaction,[20] the scrambling of the two methyl groups must have occurred subsequent to the cleavage of the first methyl group. However, only those dimethylgold(III) products with X cis to L



$$Me\!-\!\overset{Me}{\underset{X}{Au}}\!-\!L \quad \text{where } Me = CH_3, CD_3$$

are produced due to their greater thermodynamic stability compared to the trans isomers



$$X\!-\!\overset{Me}{\underset{Me}{Au}}\!-\!L$$

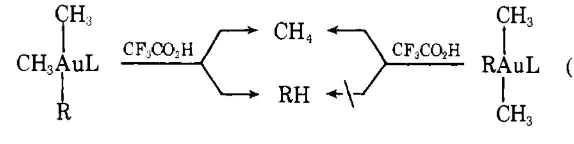
The observation of rapid intramolecular as well as intermolecular scrambling of the methyl groups (vide infra) indicates that these processes are not kinetically limited. Suffice it to emphasize here the caveat that product analysis alone is not a sufficient basis on which to deduce the stereochemistry of the cleavage.[9]

C. *cis*- and *trans*-$R(CH_3)_2AuL$. Structural effects of the alkyl group in the protonolysis were examined in a series of cis and trans alkyldimethylgold complexes listed in Table V. The trans isomer of $R(CH_3)_2AuL$ in the presence of added PPh_3 reacted with stoichiometric amounts of trifluoroacetic acid in benzene to liberate only methane. Under the same conditions, the cis isomer afforded a mixture of methane and the corresponding alkane (RH). A stereospecific cleavage of only cis-alkyl groups is indicated in eq 11, and supports the deuterium labeling

Table V. Trifluoroacetolysis of $R(CH_3)_2AuL$[a]

$R(CH_3)_2AuL$ R	Concn (mM)	CF_3CO_2H (mM)	PPh_3 (mM)	Alkane (%)[b]		
				CH_4	CH_3CH_3	RCH_3
cis-CH_3CH_2	0.043	0.044	0.097	74	5	0
cis-$CH_3CH_2CH_2$	0.040	0.040	0.10	78	0	4
cis-$(CH_3)_2CH$	0.039	0.038	0.093	62	0	0
trans-CH_3CH_2	0.041	0.041	0	100	<0.1	88
trans-CH_3CH_2	0.098	0.098	0.15	70	0	0
trans-$CH_3CH_2CH_2$	0.092	0.092	0.17	62	0	0
trans-$CH_3CH_2CH_2$	0.054	0.053	0	84	0	*c*

[a] In benzene solutions at 25 °C for 1 h. [b] Yields based on $R(CH_3)_2AuL$ (mol/mol). [c] Considerable amounts but not measured, no propane or propylene.



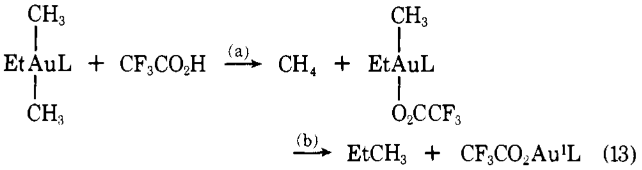
(11)

studies described above. Judging from the relative amounts of CH_4 and RH produced from *cis*-$R(CH_3)_2AuL$, we estimate that the rates of protonolysis proceed in the order: Me ≫ Et > *n*-Pr > *i*-Pr. Under these conditions the gold(III) products appear as bis-phosphine complexes $R(CH_3)AuL_2{}^+O_2CCF_3{}^-$ similar to the dimethyl analogues II in eq 8.

In the absence of added PPh_3, however, *trans*-Et$(CH_3)_2AuL$ gave high yields of both methane and propane ($R\text{-}CH_3$) according to eq 12 with only traces of ethane and *n*-butane.

$$trans\text{-}Et(CH_3)_2Au^{III}L + CF_3CO_2H \rightarrow CH_4 + EtCH_3 + CF_3CO_2Au^{I}L \quad (12)$$

We deduce that trifluoroacetic acid first cleaves one methyl group and leads to the intermediate $Et(CH_3)AuL(O_2CCF_3)$ in eq 13a, followed by its rapid reductive elimination in eq 13b.



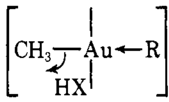
$$\underset{CH_3}{\overset{CH_3}{EtAuL}} + CF_3CO_2H \xrightarrow{(a)} CH_4 + \underset{O_2CCF_3}{\overset{CH_3}{EtAuL}} \xrightarrow{(b)} EtCH_3 + CF_3CO_2Au^{I}L \quad (13)$$

Such a two-step process is consistent with the ready interception of the intermediate by added PPh_3 (cf. eq 8) to form the more stable bis-phosphine complex $Et(CH_3)AuL_2{}^+O_2CCF_3{}^-$.

$$Et(CH_3)AuL(O_2CCF_3) + L \rightleftharpoons Et(CH_3)AuL_2{}^+O_2CCF_3{}^- \quad (14)$$

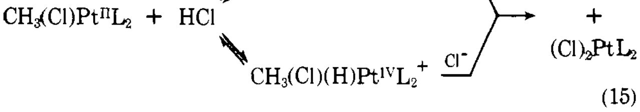
Indeed, such an intermediate can be isolated directly if the protonolysis is carried out with HCl since the chloro analogue, $Et(CH_3)AuL(Cl)$, is more stable than other derivatives. Under similar conditions, the cis-isomer affords a mixture of $Et(CH_3)AuL(Cl)$ and $(CH_3)_2AuL(Cl)$, in addition to methane and ethane, respectively. The large difference in thermal stabilities of $(CH_3)_2AuL(O_2CCF_3)$ which is isolable and $Et(CH_3)AuL(O_2CCF_3)$ which is only a transient intermediate, is noteworthy (vide infra).

D. The Mechanism of Protonolysis. Protonolysis of trialkyl(phosphine)gold(III) complexes with acids HX derive their driving force primarily by proton transfer to the alkyl ligand. The nucleophilic participation by the conjugate base X^- is less important since the rates of protonolysis are highly sensitive to the order of acid strengths: acetic, the weakest acid being the slowest and the strongest acid, triflic, the fastest. Trifluoroacetic, hydrohalic, and nitric acids show intermediate reactivity. The importance of proton transfer, (i.e., electrophilic cleavage) in the activated complex also follows from the order of reactivity of the alkyl group cleaved: viz., Me ≫ Et > *n*-Pr > *i*-Pr which reflects increasing steric hindrance at the site of protonation.[11] The strong trans activating effect by alkyl groups R during electrophilic cleavage of a methyl-gold bond can be interpreted as electron release in the transition state by R during the breaking of the gold-carbon bond,[11b] e.g.,



This description emphasizes the dissociative nature of the driving force for substitution in alkylgold(III) under these acidic conditions. The quantitative effects of alkyl groups in this capacity have been previously delineated in the electrophilic cleavage of the linear dialkylmercurials.[11b] The σ-trans effect of alkyl groups leads to the stereospecific protonolysis of only cis-alkyl groups in the square-planar trialkyl(phosphine)gold(III) complexes. Vibrational analysis of trimethyl(phosphine)gold(III) complexes by Tobias and coworkers indicates an appreciably greater trans influence by a methyl ligand compared to phosphine.[12] Such a ground state property is apparently translated to the activated complex judging from the enhanced trans effect by an alkyl ligand which we observe during protonolysis. A similar strong trans effect by methyl ligands is well-established in substitution reactions of the isoelectronic platinum(II) complexes, mostly proceeding via an associative or nucleophilic mechanism.[13] Further elaboration of the strong trans effects by alkyl ligands in both types of substitution reactions of square planar complexes is desirable.

It is noteworthy that the foregoing mechanism for protonolysis of trialkyl(phosphine)gold(III) contrasts with the mechanism for an analogous cleavage of methylplatinum(II) complexes such as $CH_3(Cl)Pt(PEt_3)_2$, in which a prior protonation of the platinum nucleus was proposed.[14] Such a pre-



(15)

equilibrium oxidative addition of acids should be more favorable for Pt(II) than for Au(III), despite the presence of extra alkyl ligands serving as donors in the latter.[15] Indeed in lower oxidation states, Au(I) complexes particularly in such electron-rich species as dialkylaurate(I), do undergo protonolysis by a two-step mechanism involving prior oxidative addition followed by reductive elimination,[17] similar to that proposed

$$RR'Au^{I}Li + HCl \longrightarrow RR'(H)Au^{III} + LiCl \quad (16)$$

(17)

Table VI. First-Order Rate Constants for Reductive Elimination of Ethane from $(CH_3)_2AuL(X)$

$(CH_3)_2AuL(X)$ X	Concn (M)	Additive (M)	Solvent	Temp (°C)	Rate constant (s^{-1})
Cl	0.075	0	C_6H_6	45	9×10^{-7}
O_2CCF_3	0.075	0	C_6H_6	45	6×10^{-7}
NO_3	0.075	0	C_6H_6	45	3.0×10^{-4}
NO_3	0.075	0	CH_2Cl_2	45	9.7×10^{-4}
NO_3	0.075	0	CH_3OH	45	>0.7
NO_3	0.075	0	C_6H_5Cl	45	2.9×10^{-4}
NO_3	0.075	PPh_3 (0.021)	C_6H_5Cl	45	5.3×10^{-5}
NO_3	0.0090	0	C_6H_5Cl	60	5.8×10^{-4}
NO_3	0.0090	PPh_3 (0.0016)	C_6H_5Cl	60	3.5×10^{-5}
NO_3	0.0090	PPh_3 (0.0039)	C_6H_5Cl	60	2.8×10^{-5}
NO_3	0.0090	PPh_3 (0.0090)	C_6H_5Cl	60	2.7×10^{-5}
NO_3	0.0090	PPh_3 (0.090)	C_6H_5Cl	60	2.1×10^{-5}
NO_3	0.0082	0	CH_3OH	2	6.5×10^{-5}
NO_3	0.0082	$NaNO_3$ (0.054)	CH_3OH	2	5.2×10^{-5}
OTf	0.075	0	C_6H_6	~25	>10
$(CH_3)_2AuL_2NO_3$	0.0090	0	C_6H_5Cl	60	3.0×10^{-5}

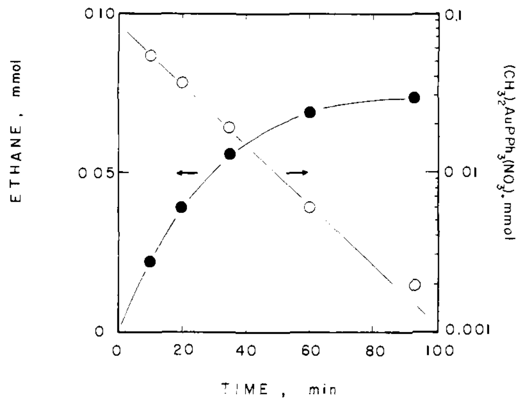


Figure 1. Thermal decomposition of $(CH_3)_2AuPPh_3(NO_3)$ (0.075 mM) in benzene solution at 45 °C, ● experimental data on left scale.

in eq 15 for methylplatinum(II). The reductive elimination of alkanes from the hyridoalkylgold(III) intermediate in eq 17 shows a striking lack of selectivity in the elimination of RH or R′H (when R,R′ = CH_3,CH_3CH_2, $(CH_3)_3C$), in marked contradistinction to the high selectivity observed in the protonolysis of trialkyl(phosphine)gold(*III*) complexes described above. The differences in selectivity effected by structural changes of the alkyl groups in the two systems may be attributed to the differences in the importance of steric effects in (intermolecular) proton transfer and in (intramolecular) reductive elimination.

II. Reductive Elimination of Dialkylgold(III) Species. The series of dialkylgold(III) complexes $R_2AuL(X)$ prepared in this study shows a wide range of thermal stabilities, varying from the rather stable chloro complex to the highly unstable triflato species.

A. Kinetics of Reductive Elimination. The liberation of ethane from *cis*-$(CH_3)_2AuL(X)$, in benzene at 45 °C according to eq 18, follows first-order kinetics to the high conversions shown in Figure 1 for X = NO_3. The rate constants listed in Table VI decrease in the order: TfO > NO_3 > CF_3CO_2 > Cl.

$$(CH_3)_2Au^{III}L(X) \rightarrow CH_3CH_3 + XAu^{I}L \qquad (18)$$

Medium effects on the rates of reductive elimination of $(CH_3)_2AuL(NO_3)$ are also shown in Table VI. Methanol is more than 10^3 times more effective than benzene. The faster rate in methylene chloride suggests the importance of polar contributions during decomposition.

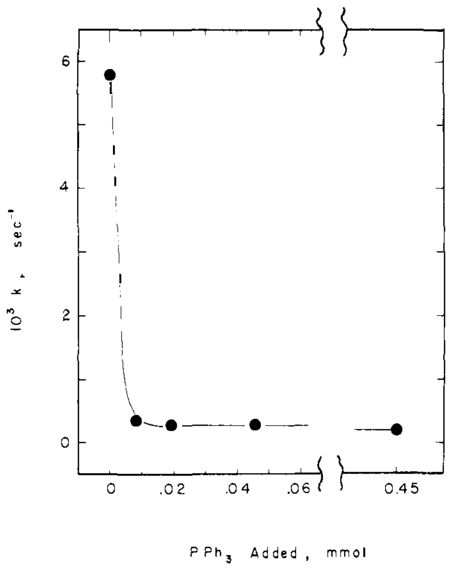


Figure 2. Effect of added triphenylphosphine on the rate of thermal decomposition of 0.045 mmol $(CH_3)_2AuPPh_3(NO_3)$ in 5 ml of chlorobenzene solution at 60 °C.

The studies with added salts are somewhat limited due to restrictions of solubility. Sodium nitrate exerted a minor effect on the reductive elimination of $(CH_3)_2AuL(NO_3)$. The slight retardation observed may be attributed to a salt effect rather than a common ion effect, although a rigorous distinction is difficult to make in these nonaqueous media in which ion-pairing is a significant factor.

Small amounts of triphenylphosphine strongly retard the rate of the reductive elimination of $(CH_3)_2AuL(NO_3)$ in Table VI. Less than a fifth of PPh_3 decreases the first-order rate constant by almost 20-fold. The retardation by added PPh_3 levels off rapidly as shown in Figure 2, despite the fact that the amounts are still stoichiometrically less than that of $(CH_3)_2AuL(NO_3)$. Significantly, when an equivalent of PPh_3 is present, the rate of reductive elimination of $(CH_3)_2AuL(NO_3)$ is quite close to that of $(CH_3)_2AuL_2{}^+NO_3{}^-$ prepared independently.

B. Methyl and Phosphine Exchange in $(CH_3)_2AuL(X)$. The substitution lability of dialkylgold(III) complexes $R_2AuL(X)$ was examined using the dimethyl derivatives. The exchanges of phosphine and the methyl groups in $(CH_3)_2AuL(X)$ are both slow on the NMR time scale, judging by the observation of sharp resonances for the cis and trans CH_3 groups for all the

Table VII. Effects of Phosphine Ligands on the Reductive Elimination of Dialkylgold(III) Complexes[a]

$(CH_3)_3AuL'$ L'	Concn (mM)	CF_3CO_2H (mM)	Methane (%)	$(CH_3)_2AuL'(O_2CCF_3)$ (%)
$P(CH_3)_3$	0.150	0.151	92	87
PPh_3	0.060	0.060	95	62
$P(C_6H_{11})_3$	0.079	0.080	84	*b*

[a] In benzene solution at 25 °C. Yields based on stoichiometry in eq 6 and 18a. [b] 92% ethane formed and no $(CH_3)_2AuL'(O_2CF_3)$ detected.

Table VIII. Effect of Alkyl Groups on the Reductive Elimination of Dialkylgold(III) Complexes

				Alkane (%)			
$R_2AuL(X)$	Concn (10^2M)	Solvent	Temp (°C)	C_2H_6	CH_3CD_3	C_2D_6	Other
$CD_3(CH_3)AuL(NO_3)$[a]	4.9	$C_6H_5CH_3$	25	23	55	21	
$(CH_3)_2AuL(OTf)$ $(CD_3)_2AuL(OTf)$ [b]	4.9 4.9	$C_6H_5CH_3$	25	40	30	30	
$(CD_3)_2AuL(OTf)$ $(CH_3)_2AuL(OTf)$ [b]	4.9 4.9	Me_2SO	25	24	50	25	
$Et(CH_3)AuL(O_2CCF_3)$[c]	4.1	C_6H_6	25				>98[d]
$Et(CH_3)AuL(Cl)$		C_6H_6	80				>98[d]
$n\text{-}Pr(CH_3)AuL(NO_3)$	5.3	C_6H_6	25				*e*

Prepared in situ from [a] *trans*-$CD_3(CH_3)_2AuL + HNO_3$, [b] $(CH_3)_3AuL + (CD_3)_3AuL + TfOH$. [c] *trans*-$Et(CH_3)_2AuL + CF_3CO_2H$. [d] Propane, <0.5% C_2H_6, and n-C_4H_{10}. [e] Large amounts of n-butane only.

derivatives shown in Table II. Chemical studies also show that methyl exchange is minor under reaction conditions. Thus, $CD_3(CH_3)AuL(X)$ undergoes no significant intermolecular scrambling of methyl groups (see Experimental Section), which can only take place if they are exchanged between different gold(III) atoms. However, intramolecular scrambling of methyl groups occurs during reductive elimination starting with a mixture of $(CH_3)_2AuL(X)$ and $(CD_3)_2AuL(X)$ as described in Table VIII (vide infra).

$$2CD_3(CH_3)AuL(X) \rightleftharpoons (CH_3)_2AuL(X) + (CD_3)_2AuL(X) \quad (19)$$

$$X = TfO, NO_3$$

Facile exchange of anions (X) between several $(CH_3)_2AuL(X)$ is suggested by the results of a double labeling experiment. When $(CH_3)_2AuL(Cl)$ and $(CD_3)_2AuL(NO_3)$ mixed, a statistical distribution of cis and trans CH_3 groups in the chloro and nitrato complexes is indicated by the four doublets of equal intensities.[18a] Coupled with the known exchange of X with other anions,[5,6b] we infer that intermolecular methyl and X exchanges occur with similar facility in $(CH_3)_2AuL(X)$.[18b]

C. Steric and Structural Effects of Ligands on Reductive Elimination. Phosphine Ligands. The thermal stabilities of dimethylgold(III) complexes $(CH_3)_2Au(PR_3)X$ vary with the nature of the phosphine ligand. The pattern of stabilities can be obtained from the trifluoroacetolysis of the trimethylphosphine, triphenylphosphine, and tricyclohexylphosphine complexes of trimethylgold shown in Table VII.

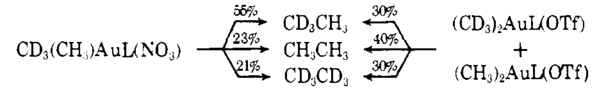
The protonolysis of $(CH_3)_3AuPMe_3$ affords methane and $(CH_3)_2Au(PMe_3)O_2CCF_3$ in high yields at room temperature according to the stoichiometry established in eq 6. Although $(CH_3)_3AuPPh_3$ gives only slightly poorer yields of the corresponding $(CH_3)_3Au(PPh_3)O_2CCF_3$, none of the expected $(CH_3)_2Au(PCy_3)O_2CCF_3$ was obtained from the trifluoroacetolysis of $(CH_3)_3AuPCy_3$ under the same conditions. Instead a high yield of ethane is produced, diagnostic of the rapid reductive elimination of the dimethylgold(III) intermediate previously described in eq 7. The steric size of phosphine ligands (i.e., the cone angle[19]) is known to increase in the order: L' = $PMe_3 < PPh_3 < PCy_3$, and it parallels the tendency for these complexes to undergo reductive elimination.

$$(CH_3)_2Au(PCy_3)O_2CCF_3 \rightarrow CH_3CH_3 + CF_3CO_2AuPCy_3 \quad (20)$$

Alkyl Groups. The reductive elimination of methyl groups from $(CH_3)_2AuL(X)$ is highly dependent on X, but for the same X, homologous alkyl groups are eliminated more rapidly than methyl. For example, $(CH_3)_2AuL(O_2CCF_3)$ is readily isolated, but $Et(CH_3)AuL(O_2CCF_3)$ in Table VIII spontaneously affords propane under the same conditions.

$$Et(CH_3)Au^{III}L(O_2CCF_3) \rightarrow EtCH_3 + CF_3CO_2Au^{I}L \quad (21)$$

Isotopic labeling studies in Table VIII show that the methyl groups are extensively scrambled during the reductive elimination of dimethylgold(III) species. An analogous intermo-



(22)

lecular scrambling of alkyl groups does not appear to be important in the reductive elimination of $Et(CH_3)AuL(NO_3)$, judging by the analysis of only trace amounts of products attributable to exchange, such as n-butane and ethane. Similar results are obtained with n-$Pr(CH_3)AuL(NO_3)$, and we conclude that intramolecular reductive elimination occurs faster than alkyl exchange in these higher homologues.

The high yields of alkanes indicate that reductive elimination of a pair of alkyl groups is the preferred route. However, to determine whether other modes are possible such as the loss of X, we deliberately scrutinized the reaction mixture for their

$$R_2AuL(X) \rightarrow RX + RAuL \quad (23)$$

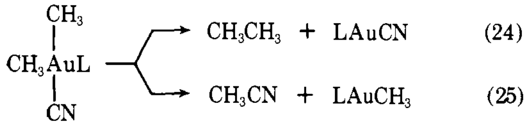
presence. The results in Table IX show that reductive elimination of a pair of methyl groups from $(CH_3)_2AuL(X)$ is always heavily favored over the loss of CH_3–X, even for a carbon-centered group such as cyano. Indeed, we could find no direct evidence for the formation of these alternative products

Table IX. Competition in the Reductive Elimination of CH_3CH_3 and CH_3X in $(CH_3)_2AuPPh_3(X)$

$(CH_3)_2AuPPh_3(X)$ X (mmol)	Solvent[a]	Temp (°C)	Time (h)	Products (%)[b] CH_3CH_3	CH_3X
CH_3CO_2 (0.062)	C_6H_6	70	48	*c*	*c*
(0.062)	*t*-BuPh	160	2	63	<5[c]
I (0.051)	C_6H_6	70	48	*d*	*c*
(0.053)	*t*-BuPh	160	2	90	<1[c]
CN (0.047)	C_6H_6	70	48	*e*	*c*
(0.047)	*t*-BuPh	160	2	83	<1
NO_3 (0.075)	C_6H_6	45	3	96	*f*

[a] In 2 ml of solvent. [b] Based on each mole of product from gold complex during time specified. [c] Beyond detection. [d] Significant amounts, but not measured. [e] Small amount. [f] Not measured.

of reductive elimination from compounds containing such electronegative ligands as those listed in Table IX.



$$CH_3AuL(CH_3)(CN) \rightarrow CH_3CH_3 + LAuCN \quad (24)$$

$$CH_3AuL(CH_3)(CN) \rightarrow CH_3CN + LAuCH_3 \quad (25)$$

D. Mechanism of Reductive Elimination. The first-order kinetics together with the marked effect of PPh_3 in retarding the rate of reductive elimination of $(CH_3)_2AuL(X)$ are most readily accommodated by a dissociative mechanism represented in Scheme I. According to this scheme, dissociation of phosphine in eq 26 is rate limiting. A similar dissociative process was previously shown to be important in the reductive elimination of the trimethyl analogue, that is, $(CH_3)_3AuL$.[20] The existence of the three-coordinate intermediate is difficult to establish in the reductive elimination step 27, because of the facile intermolecular scrambling of methyl groups. The scrambling, however, is consistent with the presence of such a coordinatively unsaturated intermediate since alkyl exchange by a bimolecular process such as,

Scheme I

$$R_2AuL(X) \rightleftharpoons R_2AuX + L \quad (26)$$

$$R_2AuX \xrightarrow{\text{fast}} RR + AuX \quad (27)$$

$$(CH_3)_2AuX + (CD_3)_2AuL(X) \rightleftharpoons CH_3(CD_3)AuX + CH_3(CD_3)AuL(X), \text{etc.} \quad (28)$$

is analogous to that previously described for the role of $(CH_3)_3Au$ in $(CH_3)_3AuL$.[20,21]

The tendency for three-coordinate gold species to undergo self-association is well-established since all of them are known only as dimers.[6c] We prepared the triflate derivative III from the dimeric iodide as a rather stable crystalline solid in 90% yield. Cryoscopic measurements in benzene indicate that it is a dimer. Like other dimeric gold(III) complexes, III is cleaved into mononuclear species by PPh_3.[5,6b] Thus, the addition of excess PPh_3 afforded the bis-phosphine complex described above, $(CH_3)_2AuL_2{}^+OTf^-$, in high yields. The addition of stoichiometric amounts of PPh_3 to III dissolved in benzene caused an immediate evolution of ethane, expected for the reductive elimination of the thermally unstable monophosphine, $(CH_3)_2AuL(OTf)$ described in eqs 7 and 31.

$$[(CH_3)_2AuI]_2 + 2AgOTf \xrightarrow[C_6H_6]{} \underset{\text{III}}{[(CH_3)_2AuOTf]_2} + 2AgI \quad (29)$$

$$[(CH_3)_2AuOTf]_2 + 4PPh_3 \rightarrow 2(CH_3)_2AuL_2{}^+OTf^- \quad (30)$$

$$[(CH_3)_2AuOTf]_2 + 2PPh_3 \rightarrow 2(CH_3)_2AuL(OTf) \quad (31)$$

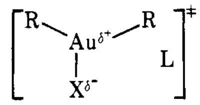
A benzene solution of the dimer III alone evolves only ethane on warming to 45 °C according to the stoichiometry in eq 32.[22]

$$[(CH_3)_2AuOTf]_2 \rightarrow 2CH_3CH_3 + 2AuOTf \quad (32)$$

Reductive elimination of III shows autocatalytic behavior, the apparent rate constant increasing with time, but it occurs too slowly to proceed via dissociation to the unstable $(CH_3)_2AuOTf$.[23] Attempts to prepare and study the three-coordinate intermediate by independent means have been unsuccessful as yet.

$$[(CH_3)_2AuOTf]_2 \not\rightleftharpoons 2(CH_3)_2AuOTf \quad (33)$$

Scheme I accounts for all of the principal data on hand regarding the behavior of $(CH_3)_2AuL(X)$ in reductive elimination as well as ligand exchanges. Thus, the variation in the reactivities of these complexes with different X can be attributed to their influence on the rates of phosphine dissociation in eq 26. The latter also correlates with the rate enhancement observed on increasing the steric size of the departing phosphine. The effects of solvent suggest a rather polar transition state for the T or Y configurations expected for three-coordinate intermediates of gold(III),[20] e.g.,



However, it is not completely clear at this juncture why the stability of such an activated complex is so markedly dependent on the nature of X.

The rate of phosphine dissociation may not represent the sole factor involved in reductive elimination of all $R_2AuL(X)$ complexes, since there is evidence that the stability of the three-coordinate intermediate R_2AuX itself may vary with X. Thus, Tobias and co-workers have observed with *cis*-$(CH_3)_2AuPy(Cl)$ in CCl_4 solutions the broadened methyl proton NMR resonances due to an exchange process, presumably involving dissociation of pyridine.[5] The absence of concomitant reductive elimination suggests that the three-coordinate intermediate $(CH_3)_2AuCl$ may be more stable than others. Interestingly, the addition of PPh_3 led rapidly and quantitatively to $(CH_3)_2AuL(Cl)$, showing no significant line broadening in the NMR spectrum.

$$(CH_3)_2Au(py)(Cl) \rightleftharpoons (CH_3)_2AuCl + py \quad (34)$$

The ionization of anion X from $(CH_3)_2AuL(X)$ would lead to cationic three-coordinate species IV, which doubtlessly exist as ion-pairs in nonpolar solvents such as benzene.[24] Qualita-

$$(CH_3)_2AuL(X) \rightleftharpoons \underset{\text{IV}}{(CH_3)_2AuL^+X^-} \quad (35)$$

tively, the stabilities of various $(CH_3)_2AuL(X)$ do parallel the coordination ability of X, i.e., CH_3CO_2, Cl > NO_3 > TfO. However, these cationic species do not represent the principal route through which reductive elimination of $(CH_3)_2AuL(X)$ occurs. In particular, the high sensitivity of the rate on the concentration of phosphine (cf. Figure 2) must implicate L and not X as the major cause of the retardation. It is possible, however, that reductive elimination from $(CH_3)_2AuL(X)$ may proceed via several pathways simultaneously, including that proposed in Scheme I as well as a limited contribution from a direct pathway as well as ionization. A somewhat related problem may be encountered in the slower reductive elimination of the cationic complexes $(CH_3)_2AuL_2^+X^-$.[5,7]

The similar mechanisms proposed for reductive eliminations of ethane from $(CH_3)_3AuL$ and $(CH_3)_2AuL(X)$ allow the rate-limiting dissociation of phosphine to be compared in the two systems. The first-order rate constant k_1 for dissociation of $(CH_3)_3AuL$ was evaluated as 3×10^{-5} s^{-1} at 70 °C in

$$(CH_3)_3AuL \xrightarrow{k_1} (CH_3)_3Au + L \qquad (36)$$

benzene by the method described previously.[20] If we assume the ethane formation[25] from $(CH_3)_2AuL(Cl)$ is also related to the rate of phosphine dissociation, we obtain a rate constant $k_1' = 4 \times 10^{-5}$ s^{-1} which is substantially the same as that for

$$(CH_3)_2AuL(Cl) \xrightarrow{k_1'} (CH_3)_2AuCl + L \qquad (37)$$

$(CH_3)_3AuL$. It is known from vibrational analysis that the replacement of a cis-CH_3 group in $(CH_3)_3AuL$ by Cl leads to weakening of the Au–C bonds[8a] (and presumably the Au–P bond by inference). Variations in the ^1H and ^{31}P NMR spectra of various $(CH_3)_2AuL(X)$ have also been observed.[6b] We tentatively conclude that the trans influence of alkyl groups manifested as ground state properties in these complexes may not bear directly on the activated complex,[25] particularly if phosphine dissociation is rate limiting.

Experimental Section

Materials. The preparations of the alkylgold complexes used in this study were described previously.[1] Benzene was redistilled from calcium hydride prior to use. Other solvents were treated similarly. The acids were commercial samples used without further purification.

Trialkyl(phosphine)gold(III) with Acids. A typical procedure is described below for the reaction of trialkyl(phosphine)gold complexes with acids. Details of others are given in the tables. A sample of $(CH_3)_3AuPPh_3$ (30.0 mg, 0.0595 mmol) was placed in a bottle equipped with serum cap and dissolved in 1.0 ml of dry benzene. The flask was evacuated completely while cooling at liquid nitrogen temperatures. Trifluoroacetic acid (4.4 μl) was added with the aid of a microsyringe to the solution. After the evolution of gas (ca. 1 h) was complete, the sample of the gas was analyzed by gas-liquid chromatography. Methane (0.0532 mmol, 95%) was found, but no ethane was detected. The resultant colorless clear solution was evaporated in vacuo to give a solid which was recrystallized from acetone to afford white crystals of $(CH_3)_2Au(PPh_3)O_2CCF_3$ (22.3 mg, 62%) dp 115–116 °C. By adding less than 20% of phosphine ligand to the resultant dimethylgold complex in benzene (X = NO_3, Cl, Br, I), the two doublets in the NMR spectrum broadened to one singlet at room temperature. Anal. Calcd for $C_{22}H_{21}AuO_2PF_3$: C, 43.87; H, 3.51. Found: C, 44.5; H, 3.5.

The reaction of $(CH_3)_3AuPPh_3$ with HSO_3CF_3 at −20 °C in toluene afforded methane and ethane. Workup of the reaction mixture in the presence of triphenylphosphine afforded white crystals which were washed with hexane and dried in vacuo, dp 196 °C. Anal. Calcd for $C_{37}H_{30}F_3AuP_2SO_3(AuL_2OTf)$: Au, 21.6. Found: Au, 22.6. An authentic sample was prepared by the reaction of $AuCl(PPh_3)_2$ with AgOTf to give the same compound (dp 192 °C) characterized by infrared analysis.

$(CH_3)_2AuPPh_3(NO_3)$. A solution of $(CH_3)_3AuPPh_3$ (61.4 mg, 0.122 mmol) in 1 ml of toluene was cooled to −20 °C and 70% aqueous nitric acid (7.7 μl) added. The mixture on standing for 24 h at −20 °C liberated methane (2.36 ml, 86%) and deposited white crystals. After washing with *n*-pentane and drying in vacuo, the colorless crystals (33 mg, 49%) were recrystallized from a mixture of pentane and toluene, mp 88–89 °C dec. Proton NMR spectrum (benzene): δ 0.93 (d, J = 8 Hz) CH_3 cis to PPh_3; δ 1.57 (d, J = 9 Hz) CH_3 trans to PPh_3. Anal. Calcd for $C_{20}H_{21}AuPNO_3$: C, 43.56; H, 3.84; N, 2.54. Found: C, 43.2; H, 3.7; N, 2.4.

$(CH_3)_2AuPPh_3(CN)$. A solution of 165 mg of $(CH_3)_2AuPPh_3(I)$ in 5 ml of acetone was treated with 13.2 mg of NaCN dissolved in 5 ml of acetone. After stirring for 24 h at room temperature, the solvent was removed under reduced pressure. The colorless solid was taken up in toluene and filtered to remove NaI. *n*-Pentane was added and the mixture cooled to −20 °C whereupon colorless crystal was obtained, yield 80 mg (dp 151–152 °C). Proton NMR (C_6H_6): δ 0.64 (d, J = 8 Hz) for cis-CH_3, δ 1.85 (d, J = 9 Hz) for trans-CH_3. The infrared spectrum (KBr disk) showed a weak band at 2150 cm^{-1} for cyano.[27] Anal. Calcd for $C_{21}H_{21}AuPN$: C, 48.94: H, 4.11; N, 2.72. Found: C, 48.6; H, 4.1; N, 2.6.

$(CH_3)_2AuPPh_3(CH_3CO_2)$. A solution of 200 mg of $(CH_3)_3AuPPh_3$ in 3 ml of benzene was treated with 1 ml of glacial acetic acid and left for 4 days at room temperature. The solvent was removed under reduced pressure and the colorless solid recrystallized from a mixture of toluene and *n*-pentane, yield 100 mg (dp 162–163 °C). Proton NMR (benzene): δ 0.97 (d, J = 8 Hz) for cis-CH_3; δ 1.63 (d, J = 9 Hz) for trans-CH_3, δ 1.86 s for CH_3CO_2. Anal. Calcd for $C_{22}H_{24}AuPO_2$: C, 48.18; H, 4.41. Found: C, 48.4; H, 4.4.

Intermolecular Exchange of Dimethylgold Complexes. *trans*-$CD_3(CH_3)_2Au(PPh_3)$ (25.0 mg) was dissolved in 1.0 ml of benzene and a solution of aqueous HCl (4.1 μl, 37%) was added. Only methane was liberated at room temperature. The ^1H NMR spectrum of the resultant complex showed two doublets (δ 0.92 and δ 1.90) of equal intensity. The benzene was evaporated and dry ether (2 ml) was added in vacuo. CH_3MgI (prepared from Mg (100 mg) and CH_3I (50 μl) in ether) was added to the solution at 0 °C. After an hour, distilled water (5 ml) was added slowly. The ether layer was separated and evaporated to dryness to afford a white solid. The ^1H NMR spectrum of this trimethyl(triphenylphosphine)gold in benzene showed the presence of cis-CH_3 and trans-CH_3 in a ratio of 4.7:1.3. The deuterated trimethyl(triphenylphosphine)gold was dissolved in Me_2SO (2.0 ml) and decomposed at 80 °C for 5 min. The evolved gas consisted of C_2H_6 (39%), CH_3CD_3 (59%), and C_2D_6 (2%) in an overall yield of less than 20%. Reductive elimination of trimethyl(phosphine)gold under these conditions proceeds without intermolecular exchange.[20]

Reaction of *trans*-$CD_3(CH_3)_2Au(PPh_3)$ with Acids. *trans*-$CD_3(CH_3)_2Au(PPh_3)$ (25.0 mg) was dissolved in 0.5 ml of benzene in an NMR tube. CF_3COOH (3.7 μl) was added by means of a microsyringe at room temperature. After gas evolution ceased, NMR spectrum of this solution showed two doublets (δ 0.95 and 1.53 ppm) of equal intensity. Similar reactions with HNO_3 (3.1 μl of 48% aqueous solution), HCl (4.1 μl of 37% aqueous solution), and I_2 (6.3 mg) were also carried out. The NMR spectra of solutions from these reactions all showed doublets (δ 0.93 and 1.57; 0.92 and 1.90; and 1.20 and 2.05, respectively) of equal intensities.

Anion Exchnge Reactions. $(CD_3)_2Au(PPh_3)Cl$ was prepared from 25.0 mg of $(CD_3)_3AuPPh_3$ and 4.1 μl of aqueous HCl solution. It was mixed with 26.0 mg of $(CH_3)_2AuPPh_3(NO_3)$ in 1.0 ml of benzene. The ^1H NMR spectrum taken immediately at room temperature showed four doublets (δ 0.93, 0.92, 1.57, and 1.90 ppm) of equal intensities. The resonances are assigned to *cis*-$(CH_3)_2AuPPh_3(NO_3)$ and *cis*-$(CH_3)_2AuPPh_3(Cl)$, as well as the half-deuterated analogues.

Reaction of *trans*- and *cis*-$Et(CH_3)_2Au(PPh_3)$ with HCl. *trans*-$Et(CH_3)_2AuPPh_3$ (20.0 mg) was dissolved in 1.0 ml of benzene and 0.039 mmol of aqueous HCl added. After the evolution of methane ceased, the benzene layer was separated and the solvent removed in vacuo. The resultant white compound was dissolved in additional benzene. The ^1H NMR spectrum of this solution showed resonances at δ 0.98 (d) for *cis*-CH_3 and δ 1.5–3.0 (m) for Et in *cis*-$Et(CH_3)AuCl(PPh_3)$. Less than 5% yield of $(CH_3)_2AuCl(PPh_3)$ (δ 0.92 (d), 1.90 (d)) was present. $Et_2AuCl(PPh_3)$ could not be observed, due perhaps to the breadth of the resonance.

The reaction mixture resulting from the reactions of *cis*-Et-$(CH_3)_2Au(PPh_3)$ (20.0 mg) and 0.039 mmol of aqueous HCl also gave the same spectrum. However, the amounts of $Et(CH_3)$-

$AuCl(PPh_3)$ formed in this case were less than those obtained from the trans isomer.

The Preparation of Dimethylgold(III) Triflate. $[(CH_3)_2AuI]_2$ (223 mg) was dissolved in benzene and 187 mg of $AgOTf(C_6H_6)_{0.5}$ in benzene was added, and resulted in an immediate precipitation of a yellowish powder consisting of AgI (153 mg, 103%). The colorless clear solution obtained on filtration was concentrated in vacuo to afford a white solid consisting of $(CH_3)_2AuOTf$, yield 90%. The compound is soluble in benzene, toluene, ether, THF, and acetone. It was recrystallized from a mixture of toluene and *n*-pentane, dp 54 °C, mol wt = 738 (cryoscopy in benzene).

Thermal decomposition of $[(CH_3)_2AuOTf]_2$ was carried out at 45 °C in benzene solution in vacuo. Only ethane was evolved. The rate of ethane evolution was measured for only the initial period (<10%). The square of the rate was found to be approximately proportional to the initial concentration of the reactant.

When less than a stoichiometric amount of triphenylphosphine (0.040 mmol) was added to the benzene solution of $[(CH_3)_2AuOTf]_2$ (0.033 mmol), reductive elimination took place immediately to give only ethane. In the presence of excess triphenylphosphine under similar conditions, the reaction afforded dimethylbis(triphenylphosphine)gold complex which was confirmed by its ^1H NMR spectrum (δ 1.20 (m)).

Kinetic Measurements. Weighed amounts of dimethylgold compound and solvent were placed in a round-bottomed flask equipped with a gas-tight rubber septum cap. After complete degas in vacuo, a known amount of methane was added through the rubber septum with the aid of a hypodermic syringe. The reaction flask was placed in a thermostated oil bath and stirred with a Teflon-coated magnet. A small amount of gas sample (less than 1% of the total volume) was extracted periodically with a syringe and analyzed by gas chromatography. Calibration of each component was carried out under identical conditions.

Analysis. Gas samples were analyzed by gas chromatography using a column consisting of 2 ft Porapak Q and 20 ft dibutyl tetrachlorophthalate on Chromosorb P at room temperature. The proton NMR spectra were obtained on a Varian EM360 60-MHz spectrometer and the ^{31}P NMR spectra on a Varian XL100 FT spectrometer. Mass spectra were obtained on an AEI MS-9 spectrometer. Analysis of deuterated ethane and methane was described previously.[20]

Acknowledgment. The authors wish to thank the National Science Foundation for financial support, Dr. R. A. Budnik for the ^{31}P NMR spectra, Mr. R. J. Weber for measuring the mass spectra, and Dr. J. Y. Chen for helpful discussions.

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$$3AuOTf \rightarrow 2Au + Au(OTf)_3$$

This unique material is under further investigation.

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