

The Stability of Organogold Compounds. Hydrolytic, Thermal, and Oxidative Cleavages of Dimethylaurate(I) and Tetramethylaurate(III)

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Abstract: The decomposition of the anionic permethyl derivatives of gold(I) and gold(III) are studied to contrast their stability with other methylgold complexes. The hydrolytic, thermal, and oxidative cleavage of dimethylaurate(I) and tetramethylaurate(III) are examined in two series of complexes: (1) lithium pentamethyldiethylenetriamine (PMDT) chelates and (2) lithium complexes in the presence of triphenylphosphine. First, hydrolysis leads to cleavage of only a single methyl-gold bond from either dimethylaurate or tetramethylaurate, but the gold products depend on the availability of ligands. Thus, in the presence of phosphine, $\text{CH}_3\text{AuPPh}_3$ and $(\text{CH}_3)_3\text{AuPPh}_3$ are obtained, whereas metallic gold (and ethane) are produced from the Li(PMDT) complexes. Second, the thermal decompositions of both dimethyl- and tetramethylaurates proceed at much slower rates than those of the corresponding neutral methyl- and trimethylgold species examined previously. Molecular orbital calculations suggest that fragmentation of the coordinatively saturated tetramethylaurate (which is a symmetry-allowed process) is more difficult than that of trimethylgold owing to unavoidable ligand-ligand interactions. Finally, both dimethyl- and tetramethylaurates, in contrast to their neutral counterparts, undergo rapid decomposition in the presence of dioxygen as well as methyl iodide to produce unusual products. For example, $(\text{CH}_3)_2\text{AuLi}[\text{PPh}_3]$ is converted by dioxygen to a mixture of only $\text{CH}_3\text{AuPPh}_3$ and $(\text{CH}_3)_3\text{AuPPh}_3$ in high yields; and $(\text{CH}_3)_4\text{AuLi}[\text{PPh}_3]$ affords a similar mixture of methylgold products in addition to ethane. Electron transfer processes affording metastable, paramagnetic methylgold(II,IV) species are postulated and are consistent with the dioxygen-induced formation of metallic gold and ethane from the Li(PMDT) chelates of dimethyl- and tetramethylaurates. Theoretical considerations are also given to the possible pathways for oxidative decomposition of these paramagnetic intermediates.

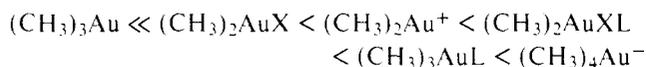
Introduction

A variety of structural types of σ -bonded organogold complexes have been prepared and their chemical properties probed in studies relevant to the modes of cleavage of carbon-gold bonds. For example, among methylgold(I) derivatives the stabilities generally increase in the order¹⁻⁴



where L = phosphine

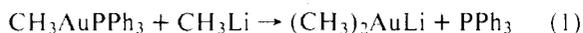
Similarly, the stabilities of a more extensive series of methylgold(III) derivatives follow roughly the order^{4,10}



L = phosphine; X = anion

In both series, the anionic aurate complexes of gold(I) and (III) appear to be uniquely the most stable organometallic species.^{4,10}

Dimethylaurate(I) has been prepared from methyl(phosphine)gold(I) and methyl lithium, after separation of the uncoordinated phosphine.³



It has been isolated in crystalline form as the bispyridine and *N,N,N',N''*-pentamethyldiethylenetriamine (PMDT) derivatives.^{3,10} Similarly, trimethyl(phosphine)gold(III) reacts with methyl lithium to afford lithium tetramethylaurate(III)⁴

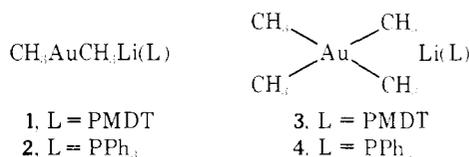


which has also been isolated as the crystalline PMDT derivative.¹⁰ Dimethylaurate(I) and tetramethylaurate(III) have been shown by Rice and Tobias,^{4,10} to have linear and square planar structures, respectively, in accord with other two-coordinate gold(I) and four-coordinate gold(III) complexes.^{9,11}

In this report we wish to compare some chemical properties of these interesting aurate complexes, particularly with regard to the cleavage of the methyl-gold bonds during hydrolysis, thermolysis, as well as oxidative decomposition by molecular oxygen and methyl iodide. The effect of the counterion is examined by comparing the behavior of the lithium derivative with that of the lithium PMDT chelate. Finally, approximate molecular orbital calculations are employed to outline the energy surface for fragmentation of tetramethylaurate, and to compare it with that of the 3-coordinate analogue, trimethylgold, reported recently.¹²

Results and Discussion

In the following studies, dimethylaurate(I) was examined either as the lithium PMDT chelate **1** or as the lithium complex **2** (in the presence of triphenylphosphine). Similarly, tetramethylaurate(III) was examined either as the lithium PMDT chelate **3** or as the lithium complex **4** (in the presence of triphenylphosphine).



Rice and Tobias have clearly shown that **1** and **3** consist of ion pairs, each with discrete $(\text{CH}_3)_2\text{Au}^-$ and $(\text{CH}_3)_4\text{Au}^-$ units, respectively, due to the strong chelation of lithium by PMDT.¹⁰ Similarly, in ethereal solutions, **2** and **4** also exist as ion pairs due to solvation of the lithium ions, but the triphenylphosphine is present only as an innocent, uncoordinated entity^{3,4} and is hereafter included in **2** and **4** as $[\text{PPh}_3]$.

I. Hydrolysis. The dimethylaurate complex **2** reacts rapidly with water in ethereal solution to afford essentially 1 equiv of methane and 1 equiv of the methylgold(I) complex according to eq 3. No significant amounts of ethane are produced (Table I).

Table I. Hydrolysis of Dimethylaurate(I) and Tetramethylaurate(III)^a in Aqueous Ethers

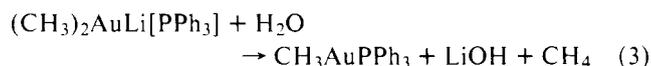
	(CH ₃) _n AuLi(L)	mmol	Alkane liberated, mmol		Gold product (mmol)	Σ(CH ₃), ^b %
			CH ₄	C ₂ H ₆		
2	(CH ₃) ₂ AuLi[PPh ₃]	0.131 E	0.113	0.004	CH ₃ AuPPh ₃ (0.11)	92
1	(CH ₃) ₂ AuLi(PMDT)	0.146 T	0.158	0.065	^c	97
4	(CH ₃) ₄ AuLi[PPh ₃]	0.122 E	0.107	0.011	(CH ₃) ₃ AuPPh ₃ (0.12)	98
3	(CH ₃) ₄ AuLi(PMDT)	0.097 T	0.036	0.057	^d	39

^a In mixture of 1.5 mL of E = ether or T = tetrahydrofuran and 1.0 mL of water at 25 °C, analysis after 17 h. ^b All methyl groups accounted in alkanes plus gold product. Does not include unreacted reactants. ^c Black gold precipitate formed within 5 min. ^d Black precipitate formed slowly (~1 h).

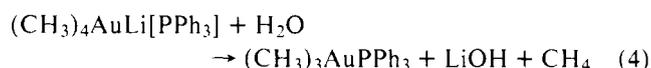
Table II. Thermal Decomposition of Dimethylaurate and Tetramethylaurate

(CH ₃) _n AuLi(L)	mmol	Solvent ^a	Time, h	Temp, °C	Alkane liberated, mmol		Dec ^b %	Σ(CH ₃), ^c %
					CH ₄	C ₂ H ₆		
(CH ₃) ₂ AuLi(PMDT)	0.151	T	4	65	0.009	0	3	78
(CH ₃) ₂ AuLi(PMDT)	0.130	O	1	140	0.003	0	1	77
(CH ₃) ₄ AuLi(PMDT)	0.099	T	4	65	0.009	0.019	12	70
(CH ₃) ₄ AuLi(PMDT)	0.083	O	1	140	0.005	0.043	27	87
CH ₃ AuPPh ₃	0.121	T	4	65	0.005	0	4	^d
CH ₃ AuPPh ₃	0.108	O	1	140	0	0.025	46	^d
(CH ₃) ₃ AuPPh ₃	0.122	T	4	65	0.006	0.091	52	^d
(CH ₃) ₃ AuPPh ₃	0.120	O	1	140	0	0.160	89	^d

^a In T = tetrahydrofuran solution or O = solid material. ^b Based on alkanes liberated during thermolysis only. ^c Based on total alkane determined after hydrolysis of mixture following thermolysis. ^d Not determined.

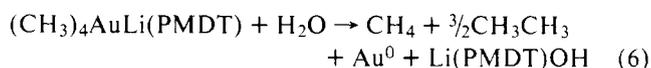
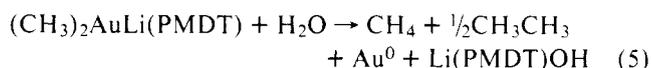


In an analogous manner, the tetramethylaurate complex **4** on hydrolysis also liberates 1 equiv of methane, and the trimethyl(phosphine)gold(III) complex is produced as described in eq 4.



In both cases, the methylgold products are stable triphenylphosphine derivatives.

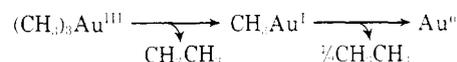
The hydrolysis of the PMDT chelates of dimethyl- and tetramethylaurates **1** and **3** also affords 1 equiv of methane. However, no stable organogold products are formed. The gold appears only as a black precipitate, and the reduction to gold metal is accompanied by the formation of ethane. Equations 5 and 6 describe roughly the stoichiometries for the hydrolysis of the dimethyl- and tetramethylaurate chelates **1** and **3**, respectively.



Among the aurates examined in Table I, the hydrolysis of the PMDT chelate of lithium tetramethylaurate(III) proceeded at a significantly slower rate than the others.

The products formed on the hydrolysis of aurates suggest that the reaction proceeds in two stages. In the first step, the protonolysis of dimethylaurate(I) and tetramethylaurate(III) both produce methane, together with the metastable methylgold(I) and trimethylgold(III) species, respectively. The fate of these coordinatively unsaturated species depends on the availability of ligands. In the presence of triphenylphosphine they are readily intercepted as the relatively stable CH₃Au^IPPh₃ and (CH₃)₃Au^{III}PPh₃, as described in eq 3 and 4, respectively. In the absence of ligands they are known to

readily undergo reductive elimination of ethane and precipitate metallic gold.^{1,2,5} The latter pertain only to the methylgold



intermediates formed during the hydrolysis of chelates **1** and **3**, since PMDT is unavailable for stabilization of the transients, already being tightly chelated to lithium.

II. Thermal Decomposition. The thermolyses of dimethyl- and tetramethylaurates **1** and **3** were examined in the solid state at 140 °C as well as in refluxing tetrahydrofuran (THF) solution under rigorous exclusion of both moisture and air. Decompositions were quite slow and always accompanied by the separation of black gold precipitates and the liberation of minor amounts of methane and ethane. The amounts of unreacted aurate species were estimated in Table II by subsequent hydrolysis of the reaction mixture and quantitative analyses of the alkanes.

The thermal stabilities of dimethylaurate(I) **1** and tetramethylaurate(III) **3** are also compared with that of their uncharged counterparts, methyl(phosphine)gold(I) and trimethyl(phosphine)gold(III), in Table II. As suspected from the results of earlier studies by Rice and Tobias,^{4,10} tetramethylaurate **3** is indeed significantly more stable than trimethyl(phosphine)gold. Since the latter is known¹³ to decompose via a rate-limiting dissociative process involving loss of phosphine, the three-coordinate trimethylgold(III) intermediate must be much less stable than the coordinatively saturated tetramethylaurate(III) species.

We previously carried out molecular orbital calculations to probe the energy surface for ready decomposition of trimethylgold.¹² A correlation diagram for the least motion fragmentation of tetramethylaurate shows no level crossing and should be an allowed reaction, as noted experimentally.¹⁴ Thus, the difference between elimination from four- and three-coordinate gold(III) is not one based on orbital symmetry considerations. In order to investigate this difference further, we now compare the elimination surface from tetramethylaurate starting with a C_{4h} configuration **5** with that of tri-

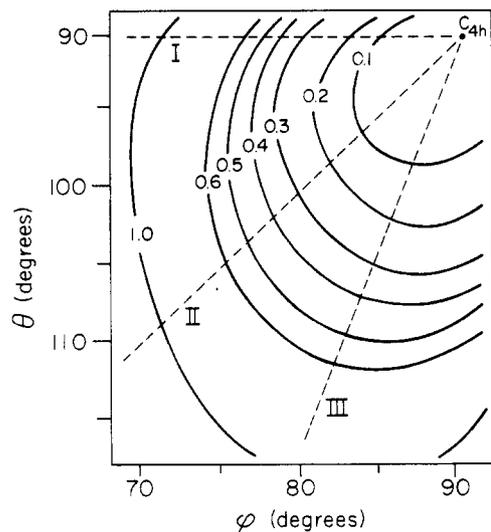
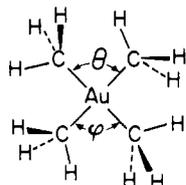


Figure 1. Variation of the two independent C-Au-C bond angles, θ and φ in tetramethylaurate(III). The energies in eV are relative to the square planar, C_{4h} configuration.

methylgold examined recently. (We refer the reader directly to ref 12 for the following discussions pertaining to trimethylgold.)

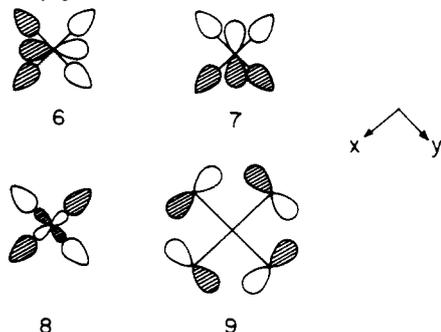
A cut across the potential energy surface of tetramethylaurate, varying the two angles θ and φ , is shown in Figure 1.



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Next, the two lower ligands were gradually removed. Since there is a problem here in determining the rates at which θ opens and φ closes along the reaction coordinate, we studied three paths, marked I-III (Figure 1), which should cover the range of pathways likely for the reductive elimination of ethane. The activation energies calculated for the reductive elimination of ethane from tetramethylaurate by paths I, II, and III are 2.7, 2.5, and 6.4 eV, respectively. While the numbers should not be relied on in a quantitative sense, they are considerably greater than the corresponding barrier of 0.8 eV for $(\text{CH}_3)_3\text{Au}$ studied previously,¹² and in agreement with the experimental trends.

A probe of the origin of the larger barrier for elimination from tetramethylaurate begins with an examination of the orbitals of this complex, which are qualitatively similar to those previously constructed for trimethylgold (see Figure 2, ref 12). However, in this case the HOMO consists of an e_u set, **6** and **7**. [In trimethylgold, there was a similar set of orbitals in C_{3h}



symmetry (see VI and VII in ref 12), but only one of them was occupied.] The LUMO in tetramethylaurate is a b_g orbital, **8**. One additional occupied MO, **9**, which is an analogue of VIII (ref 12), should be mentioned. To this orbital can be traced most of the character of Figure 1, since any angular deformation of θ or φ leads to a destabilization of **9** and the molecule as well.

Path I in Figure 1 corresponds to leaving θ at 90° while φ decreases. In addition to **9** rising in energy, one member of the e_u set, **6**, also increases in energy. (This change is analogous to the variation in energy of VI in trimethylgold in Figure 3, ref 12.) As φ decreases, the antibonding interaction between the cis methyl groups in **6** increases. The latter is not relieved by rocking the methyl groups toward each other. Indeed, that motion destabilizes **6** further, and the greater part of the higher activation energy for fragmentation of tetramethylaurate, $(\text{CH}_3)_4\text{Au}^-$, is assigned to this interaction.

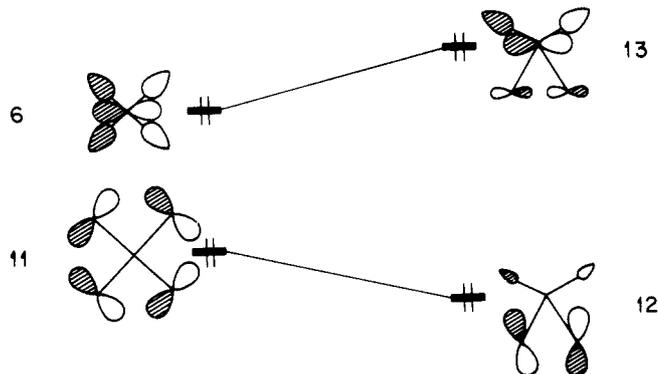
The offending orbital **6**, if followed through the correlation diagram for the total reaction, correlates with a bonding MO **10** of the linear dimethylaurate, $\text{CH}_3\text{AuCH}_3^-$. This rela-



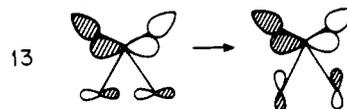
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tionship suggests that the energy of **6** could be kept down if θ were increased at the same time as φ is decreased, and it motivated the study of pathways II and III.

Path II corresponds to increasing θ and decreasing φ uniformly. As a consequence of the reduced symmetry, there are several second-order mixings which are of interest. Thus, there is a low-lying e_u set in C_{4h} geometry. One member of this e_u set, **11**, mixes with **6**, as shown below in a somewhat exaggerated manner.



This mixing is suitable for **12**, since the methyl p orbitals in **12** are reoriented so that their mutual overlap is smaller. However, **13** suffers owing to the greater antibonding methyl-methyl interaction in this occupied orbital. Twisting the methyl groups toward each other also causes **13** to rise in energy because of an increased antibonding interaction between the cis methyl groups and the p orbital on gold, i.e.,

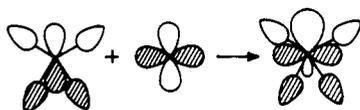


Yet another source of difficulty associated with path II, which is not present in trimethylgold, is that **7** mixes in increased xy character as θ increases and φ decreases. The xy orbital is of lower energy than the level derived by combination of the ligand orbitals in **7**; therefore, the xy orbital is mixed in an out-of-phase relationship with respect to the ligand orbitals.¹⁵ The further path II is followed, the greater is the antibonding overlap between the methyl and gold xy orbitals. Path III suffers from the same problems encountered in path II. There are additional steric effects between the methyl groups that make this route unlikely.

Table III. Oxidative Decomposition of Dimethylaurate and Tetramethylaurate by Dioxygen^a

(CH ₃) _n AuLiL	mmol	Time h	Alkane, mmol		CH ₃ OH, ^b mmol	Gold product, mmol		Σ(CH ₃), ^c %
			CH ₄	C ₂ H ₆		CH ₃ AuL	(CH ₃) ₃ AuL	
(CH ₃) ₂ AuLi[PPh ₃]	0.122	24	0.001	0	0.002	0.090	0.045	83
	0.194	3	0.001	0.001		0.128	0.047	72
(CH ₃) ₂ AuLi(PMDT)	0.117	24	0.002	0.086	0	0 ^d	0 ^d	75
	0.135	3	0.002	0.063		0 ^d	0 ^d	47
(CH ₃) ₄ AuLi[PPh ₃]	0.125	24	0.013	0.159	0.012	0.080	0.033	82
	0.170	3	0.018	0.138		0.140	0.010	68
(CH ₃) ₄ AuLi(PMDT)	0.076	24	0.002	0.144	0	0 ^d	0 ^d	97
	0.159	8	0.017	0.142		0 ^d	0 ^d	47
		21	0.021	0.265		0 ^d	0 ^d	87
(CH ₃) ₃ AuPPh ₃ +	0.146	5	0.012	0.155		0.131	0.001	90
(CH ₃) ₄ AuLi[PPh ₃]	0.017							

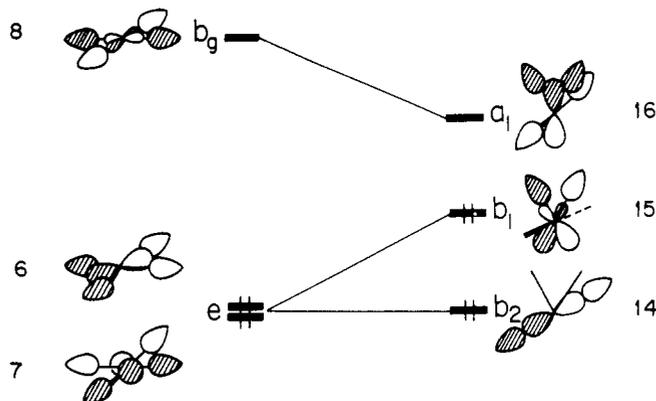
^a In 2 mL of diethyl ether at 25 °C with 0.5 mmol of dioxygen. ^b Analyzed by gas chromatography after acetolysis. ^c All methyl groups in products listed relative to reactant. Does not include unreacted reactant. ^d Black precipitate and gold mirror.



A final possibility considered was trans elimination, by the motion shown below. The C_{2v} distortion splits the e_u set, **6** and



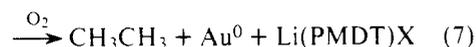
7, into b₂ and b₁ orbitals, **14** and **15**. The LUMO, **8**, in C_{4h} symmetry becomes an a₁ orbital, **16**, in C_{2v} geometry, and it decreases in energy as τ decreases. These changes have been indicated schematically below.



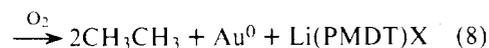
The behavior of these levels is qualitatively similar to that accompanying the C_{2v} distortion in the MCl₄ fragment¹⁶ and needs no further amplification. The point to be made here is that **14** correlates to the 2a_{2u} level, **10**, of dimethylaurate, but **15** must correlate to the unoccupied σ* level of ethane and **16** to the occupied σ level. Therefore, the reaction is symmetry forbidden.

III. Oxidative Decomposition of Methylaurates(I,III) with Dioxygen and Methyl Iodide. The *thermal* stabilities of dimethylaurate and tetramethylaurate examined in the foregoing section are strongly contrasted with the facile *oxidative* decomposition of these aurates induced by molecular oxygen and methyl iodide described below.

A. Dioxygen. The dimethylaurate PMDT chelate **1** reacts readily with dioxygen to produce ethane in high yield as shown in Table III. The gold appears as a mirror and a black precipitate. No significant amounts of methane or methanol were detected. The partial stoichiometry (excluding the as yet undetermined fate of dioxygen) is included in eq 7.

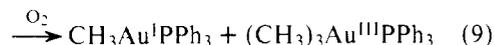


A similar process occurs when the corresponding tetramethylaurate chelate **3** also reacts with dioxygen. Ethane is again formed in high yields according to the partial stoichiometry in eq 8.

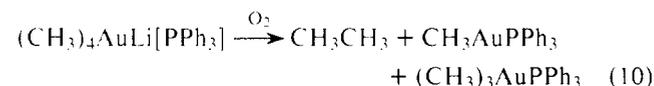


In both processes, the high overall conversion of methyl groups in the reactants to ethane indicates that other products possibly derived from methyl are of minor importance.

The formation of reduced, metallic gold as a result of the oxidation of aurate chelates **1** and **3** is striking. This behavior is in strong contrast to that shown by the aurate complexes **2** and **4** containing phosphine. For example, when the dimethylaurate complex **2** is exposed to dioxygen the reaction mixture remains clear and homogeneous, and only traces of black gold precipitate are perceptible. Significantly, only a small amount of ethane (and methane) is liberated. Instead, the methyl groups can be accounted for in high yields as a mixture of the phosphine complexes of methylgold(I,III), according to the partial stoichiometry in eq 9.



Similarly, only a trace of metallic gold is formed during the treatment of the tetramethylaurate complex **4** with dioxygen, the reaction mixture remaining clear and homogeneous. Roughly 1 mol of ethane is liberated, and the remainder of the methyl groups can be accounted for as the phosphine complexes of methylgold(I,III) according to the partial stoichiometry in eq 10.

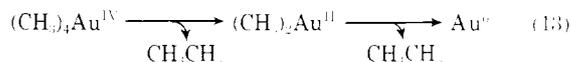


The divergent behavior toward dioxygen of aurate PMDT chelates **1** and **3** compared to complexes **2** and **4** is reminiscent of a similar difference observed upon hydrolysis (*vide supra*). In both sets of reactions, the formation of methylgold products in contrast to metallic gold can be attributed to the interception of metastable, coordinately unsaturated intermediates by phosphine before they undergo reductive elimination and

precipitate gold. With such an interpretation in mind, we tentatively suggest that dimethylaurate and tetramethylaurate initially react with dioxygen by an electron transfer process, e.g.,



to produce metastable, paramagnetic dimethyl- and tetramethylgold intermediates in eq 11 and 12, respectively, which are subject to ready reductive eliminations of ethane, e.g.,



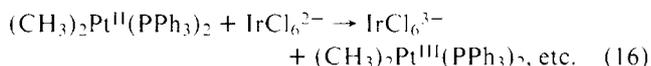
Similar facile reductive eliminations of organometals by dioxygen have been recently described for analogous organocopper, nickel, and cobalt derivatives.^{17,18}

The same electron transfer process can be formulated for the dimethylaurate complex **2**. In this case, the interception by phosphine of the dimethylgold intermediate before it suffers reductive elimination would afford a phosphine complex which can undergo disproportionation to the observed methylgold(I,III) products, e.g.,

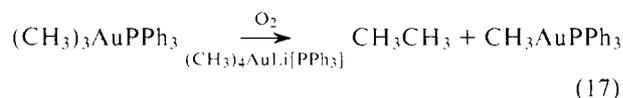


Similarly, electron transfer from the tetramethylaurate complex **4** would afford tetramethylgold. The formation of 1 mol of ethane, irrespective of the presence of phosphine, suggests that tetramethylgold is very unstable, and only the dimethylgold intermediate is intercepted by phosphine before it undergoes reductive elimination in eq 13. [Equivalent results would obtain if disproportionation of dimethylgold were followed by phosphine trapping of the methyl and trimethylgold species (vide supra). The disproportionation of a paramagnetic organotitanium(III) species to organotitanium(II,IV) analogous to that in eq 15 has been recently reported.]^{18d}

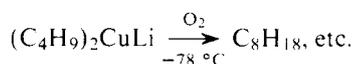
The foregoing scheme includes metastable, paramagnetic organogold species as important intermediates in the oxidative decomposition of both dimethylaurate and tetramethylaurate. Further support for such a mechanism must await their actual detection, but there already exists experimental evidence for similar methylgold(II,IV) intermediates. For example, both $\text{CH}_3\text{Au}^{\text{I}}\text{PPh}_3$ and $(\text{CH}_3)_3\text{Au}^{\text{III}}\text{PPh}_3$ are readily cleaved¹⁹ by the 1-equiv oxidant hexachloroiridate, presumably via the corresponding gold(II) and (IV) intermediates, since an analogous oxidative cleavage of an isoelectronic organoplatinum(II) derivative by hexachloroiridate(IV) has been shown to occur via electron transfer to metastable paramagnetic intermediates,²⁰ e.g.,



Furthermore, $(\text{CH}_3)_3\text{AuPPh}_3$, which is itself stable to dioxygen, readily undergoes reductive elimination in the presence of small amounts of aurate complex **4** (Table III) according to eq 17.

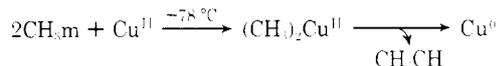


Oxidative decomposition of dimethylaurate(I) in eq 7 has direct analogy with that of dialkylcuprates(I), e.g.,



which can also be effected by other 1-equiv oxidants such as

nitrobenzene, copper(II), and benzophenone.^{18a} Dialkylcopper(II) species are the likely metastable intermediates, since attempts to independently prepare complexes such as dimethylcopper(II) by metathesis of methyl lithium or methylmagnesium bromide under mild conditions with a large series of copper(II) complexes including $\text{Cu}(\text{HMPA})_2(\text{ClO}_4)_2$, $\text{CuBip}_2(\text{ClO}_4)_2$, and $\text{Cu}(\text{OTf})_2$ spontaneously led to almost quantitative yields of ethane.^{18c}

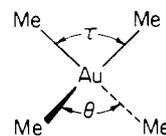


(It is noteworthy that no organocopper(II) compounds have been isolated heretofore, and all attempts at synthesis have led to either reduced organocopper(I) species or copper metal.)

We presently give some theoretical considerations that may be of aid in analyzing the hypothetical reaction pathways of dimethyl- and tetramethylgold. Thus, our calculations on the paramagnetic tetramethylgold(IV) species reveal two shallow minima. One corresponds to **5** with $\theta = \varphi = 86^\circ$. This is found to be only 1.2 kcal/mol more stable than the square planar structure ($\theta = \varphi = 90^\circ$).

In tetramethylgold(IV) the orbital **6** is singly occupied. Upon decreasing θ and φ , this level will rise in energy because of loss of overlap with the gold p orbital and increased antibonding between the cis methyl groups. However, **7** will decrease in energy for the opposite reasons and this orbital has two electrons in it. The important point is that in tetramethylaurate(III), the sizable barrier for cis elimination was set primarily by **6**, but for tetramethylgold(IV), **6** now has one less electron in it. We expect reductive elimination, therefore, to proceed more readily in tetramethylgold(IV).

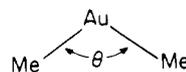
Another local minimum was found for tetramethylgold(IV) in a structure **17** with $\tau = 156^\circ$, $\theta = 170^\circ$. This geometry was



17

found to be only 0.8 kcal/mol more stable than the square planar form. However, trans elimination will still be forbidden for tetramethylgold(IV) since **15** (now with one electron) must cross **16**. Likewise, the tetrahedral geometry ($\tau = \theta = 109.5^\circ$) will be Jahn-Teller unstable with one unpaired electron. However, a quartet state of the molecule may be stable at this geometry.

The optimized structure for dimethylaurate(I) was a linear one, with $\theta = 180^\circ$. Our calculations predict that dimethylgold(II), with one electron less, is bent with $\theta = 138^\circ$. The



18

surface is again a soft one with this geometry 1.9 kcal/mol more stable than that for $\theta = 180^\circ$. A schematic diagram showing this distortion is shown in Figure 2. This b_2 level goes up in energy upon decreasing θ since the methyl orbitals lose overlap with gold p and are antibonding between themselves. There is also some d mixing in an out-of-phase manner. On the other hand, $1a_1$ goes down in energy by mixing p in a bonding fashion. Since b_2 and $1a_1$ have one and two electrons, respectively, in them, θ decreases. On the right side of Figure 2 is a correlation diagram for reductive elimination of ethane from **18**. Since b_2 correlates to a p orbital on gold and $2a_1$ to the s orbital, the concerted elimination to ground state ethane and gold is symmetry forbidden. This is not to say that the reductive

Table IV. Reactions of Dimethylaurate and Tetramethylaurate with Methyl Iodide^a

(CH ₃) _n AuLi(L)	mmol	CH ₃ I, mmol	Alkane, mmol		Gold product, mmol	
			CH ₄	C ₂ H ₆	CH ₃ AuL	(CH ₃) ₃ AuL
(CH ₃) ₂ AuLi[PPh ₃]						<i>b</i>
(CH ₃) ₂ AuLi(PMDT)	0.145	0.59	0.011	0.088	0 ^c	0 ^c
	0.104	0.59	0.007	0.059	0 ^c	0 ^c
(CH ₃) ₄ AuLi [PPh ₃]	0.143	0.68	0.067	0.084	0	0.119
	0.194	~0.9	0.025	0.090	0	0.132
	0.141 ^d	~1	0.027	0.163	0.077	~0.002
(CH ₃) ₄ AuLi(PMDT)	0.099	1.45	0.014	0.083	0 ^c	0 ^c

^a In 2 mL of diethyl ether at 25 °C. ^b See ref 3. ^c Black gold precipitate and mirror. ^d Methyl triflate.

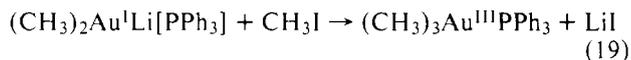
elimination of ethane from dimethylgold will not proceed readily, but only that the unimolecular, concerted process forming a single gold atom does not appear from a theoretical point of view to be an electronically available one.

In the foregoing, we presented experimental evidence and theoretical arguments as to the possible involvement of paramagnetic intermediates such as dimethylgold(II) and tetramethylgold(IV) species in the oxidative decompositions of dimethylaurate(I) and tetramethylaurate(III), respectively. These studies will hopefully guide us in the further elucidation of these interesting processes and allow us to explore the generality of the conclusions. For example, it is possible that other paramagnetic species such as methyl radicals may also be involved in the oxidative decomposition of aurate species. However, methyl radicals are known to react irreversibly with dioxygen at diffusion-controlled rates to afford methanol and formaldehyde.²¹ The small amounts of methanol together with the good accounting of reactant methyl groups as ethane and methylgold products suggest that eq 18 is not an important

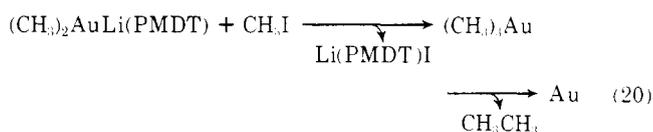


process in these reactions. Such evidence, however, cannot be used to exclude methyl radicals as viable reaction intermediates, since the processes described in eq 14–16 may be exceedingly rapid. Furthermore, the scheme outlined in eq 11–15 does not account for all the experimental observations. For example, CH₃AuPPh₃ and (CH₃)₃AuPPh₃ are not formed in strictly equimolar amounts as predicted by eq 15, and the occurrence of the oxygen-induced reductive elimination of (CH₃)₃AuPPh₃ in eq 17 indicates the presence of other reactive intermediates leading to labilization of the methylgold products. We hope that additional studies will clarify these mechanistic details.

B. Methyl Iodide. The reaction of dimethylaurate **2** with methyl iodide proceeds readily to (CH₃)₃AuPPh₃.³



A similar oxidative addition of methyl iodide probably occurs with the dimethylaurate chelate **1**. However, in the absence of stabilizing ligands, the resultant trimethylgold is unstable and affords ethane and metallic gold according to eq 20.



Other processes may also be involved since the material balance shown in Table IV is limited, including the formation of small but discrete amounts of methane.

The reaction of tetramethylaurate **4** with excess methyl iodide primarily yields ethane and (CH₃)₃AuPPh₃ according to the stoichiometry in eq 21.

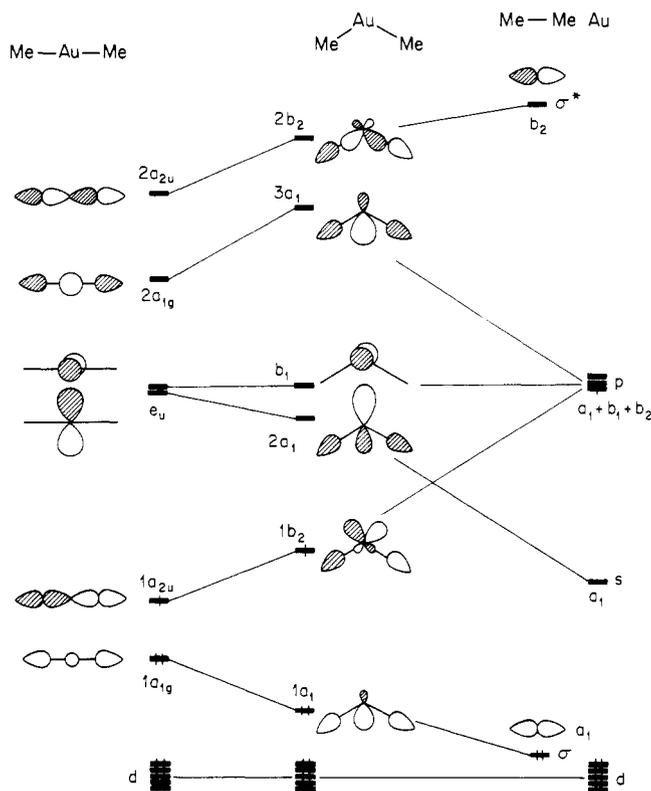
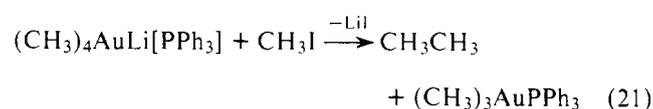


Figure 2. Correlation diagram for the elimination of ethane from dimethylgold. The d block at the bottom is schematic, with the actual level splittings larger than those indicated.



However, a similar reaction with excess methyl triflate affords ethane and CH₃AuPPh₃. In both instances sizable amounts of methane are also formed, and only limited amounts of the reactant methyl groups can be accounted for (particularly if the methyl groups derived from methyl iodide are also considered²²).

These studies suggest that aurates(I,III) do not react with methyl iodide simply by nucleophilic displacement (i.e., S_N2 processes). The possible involvement of paramagnetic intermediates^{23,24} must await the results of isotopic labeling studies and the development of procedures leading to more definitive stoichiometric relationships.

Experimental Section

Materials. The methylgold compounds, CH₃AuPPh₃, (CH₃)₃-AuPPh₃, (CH₃)₂AuLi[PPh₃] (**2**), (CH₃)₄AuLi[PPh₃] (**4**), (CH₃)₂-AuLi(PMDT) (**1**), and (CH₃)₄AuLi(PMDT) (**3**) were synthesized by published procedures.^{2–4,10} The PMDT chelates **1** and **3** were used as crystalline materials, but complexes **2** and **4** were prepared in ether

solution and used in situ. Methyl iodide (Mallinckrodt) was dried over calcium hydride and introduced by trap to trap distillation. Methyl triflate was synthesized from methanol and triflic anhydride and purified by distillation. *N,N,N',N''*-Penta-methyldiethylenetriamine (PMDT, Ames Laboratories) was dried over barium oxide and redistilled (bp 205–207 °C). Tetrahydrofuran and diethyl ether were reagent grade commercial materials, dried over potassium benzophenone and stored in a Schlenk tube. Methylolithium (Foote Mineral Co., halide-free) was diluted with dry ether (K-benzophenone), assayed by acid/base titration after hydrolysis (0.45 M), and stored under argon at –20 °C.

Analysis. The hydrocarbon gases were analyzed by gas chromatography (hydrogen flame, Varian Aerograph 200, 50-cm Porapak Q column at 90 °C or a 20-ft ODPN column). Quantitative analysis was effected by the internal standard method (ethylene) after calibration under reaction conditions. The latter was especially important when solvent was present owing to differential solubility of gases. The analyses were reproducible to $\pm 2\%$. The gold content was determined gravimetrically by digesting the samples in concentrated sulfuric acid. The methylgold products were also analyzed by their ^1H NMR spectra in CDCl_3 solution after removal of the solvent from the reaction mixture in vacuo, using toluene as the internal standard. $(\text{CH}_3)_3\text{AuPPh}_3$: $\delta 0.02$ ppm ($J = 7$ Hz) for cis CH_3 , $\delta 1.10$ ppm ($J = 9$ Hz) for trans CH_3 ; $\text{CH}_3\text{AuPPh}_3$: $\delta 0.56$ ppm ($J = 8$ Hz).

Hydrolysis of Methylaurates. In a typical procedure, a solution of **2** was prepared in 1.5 mL of diethyl ether from 0.131 mmol of $\text{CH}_3\text{AuPPh}_3$ and CH_3Li (0.13 mmol) under argon in a Schlenk tube. Water (1 mL) was added with a hypodermic syringe, whereupon a small amount of black precipitate was formed within 30 min. After 24 h, the methane and ethane were analyzed in the gas phase. The mixture was extracted with methylene chloride and the combined extract concentrated in vacuo to afford $\text{CH}_3\text{AuPPh}_3$. A similar procedure was employed for the hydrolysis of **4**.

Recrystallized **1** (0.146 mmol) was placed in a Schlenk tube under argon, and THF (2 mL) introduced by bulb to bulb distillation. Water (1 mL) was added to the homogeneous solution with a hypodermic syringe, whereupon a copious black precipitate formed immediately. The alkanes were analyzed after 24 h. The same procedure with **3** afforded a black precipitate more slowly than **1**, being significantly visible only after 30 min.

Thermolysis of Methylaurates. The aurates **1** and **3** were weighed into a Schlenk tube under argon. The flask was evacuated completely, and heated to 140 °C for 4 h in an oil bath. Analysis of the gas phase was followed by the addition of water and the contents reanalyzed. A similar procedure was followed for thermolyses carried out in THF solutions, with the exception that solvent (2 mL) was introduced by bulb to bulb distillation. Analysis was carried out after cooling the solution to room temperature.

Oxidative Decomposition of Aurates with Dioxygen. **1** (0.117 mmol) was dissolved in 2 mL of diethyl ether (introduced by bulb to bulb distillation) in a Schlenk tube. When dry dioxygen (0.5 mmol) was introduced with a hypodermic syringe, the mixture turned heterogeneous (black precipitate and gold mirror) within 5 min. The evolved gas was analyzed, and the mixture treated with acetic acid followed by analysis of the solution for methanol by GLC. The same procedure with **3** proceeded significantly slower than **1**, evolving 17% ethane after 3 h, 47% after 8 h, and 87% after 21 h.

Another solution (2 mL) of **2** was prepared from $\text{CH}_3\text{AuPPh}_3$ (0.122 mmol) in a Schlenk tube at 25 °C under argon. Introduction of dioxygen (0.5 mmol) effected no visible changes in the appearance of the solution except for the appearance of a small amount of colorless crystals after 3 h. After analysis of the gas phase, the solvent was removed in vacuo to afford colorless crystals of $\text{CH}_3\text{AuPPh}_3$ and $(\text{CH}_3)_3\text{AuPPh}_3$. A similar procedure was followed with **4**.

Ethereal solutions of $\text{CH}_3\text{AuPPh}_3$ and $(\text{CH}_3)_3\text{AuPPh}_3$ were stable in the presence of 0.5 mmol of dioxygen under conditions described above. A weighed amount of $(\text{CH}_3)_3\text{AuPPh}_3$ (0.163 mmol) was dissolved in 2 mL of dry ether and 0.016 mmol of methylolithium added. The solution was stirred for 15 min and 0.5 mmol of dioxygen added with a hypodermic syringe. Analysis of the gas phase after 3 h showed methane (0.012 mmol) and ethane (0.125 mmol), the amounts of which increased only slightly after 5 h (CH_4 , 0.012 mmol; C_2H_6 , 0.155 mmol). The solution was concentrated in vacuo to afford a colorless, crystalline residue of $\text{CH}_3\text{AuPPh}_3$ (0.131 mmol). A similar treatment of $\text{CH}_3\text{AuPPh}_3$ (0.149 mmol) with methylolithium (0.015 mmol) afforded no alkanes after 13 h, and $\text{CH}_3\text{AuPPh}_3$ could be recovered

Table V. Extended Hückel Parameters

Orbital	H_{ii}	Exponents ^a	
		ζ_1	ζ_2
Au	5d	–15.07	6.163 (0.6851)
	6s	–10.92	2.602
	6p	–5.55	2.584
C	2s	–21.40	1.625
	2p	–11.40	1.625
H	1s	–13.60	1.300

^a Each Slater exponent is followed in parentheses by the coefficient in the double ζ expansion.

(97%) unchanged.

Reaction of Aurates with Methyl Iodide. A suspension of **1** (0.145 mmol) in 2 mL of diethyl ether was prepared in a Schlenk tube at 25 °C in vacuo. Methyl iodide (0.59 mmol) was added by bulb to bulb distillation and the mixture allowed to stand for 24 h. Ethane (0.088 mmol) and methane (0.011 mmol) were detected, together with a black precipitate and a gold mirror. The solvent was removed in vacuo and the residue treated with CDCl_3 .

An ethereal solution of **4** (2 mL) was prepared from $(\text{CH}_3)_3\text{AuPPh}_3$ (0.143 mmol) and methylolithium (0.14 mmol). The solution was stirred for 15 min and methyl iodide (0.68 mmol) added by bulb to bulb distillation. The gas phase showed the presence of methane (0.067 mmol) and ethane (0.084 mmol). The colorless solution was concentrated in vacuo to afford a colorless residue consisting of $(\text{CH}_3)_3\text{AuPPh}_3$ (83%). No $\text{CH}_3\text{AuPPh}_3$ was detected. A similar reaction with **2** has been described previously to afford $(\text{CH}_3)_3\text{AuPPh}_3$ also.

The ethereal solution of **4** similar to that described above was treated with methyl triflate (~ 1 mmol) which was introduced by bulb to bulb distillation. After 15 min at 25 °C, the mixture turned dark and formed a black precipitate. Analysis after 3 h indicated the presence of methane (0.027 mmol) and ethane (0.163 mmol). Removal of the solvent in vacuo followed by extraction of the dark residue afforded $\text{CH}_3\text{AuPPh}_3$ (0.077 mmol) and small amounts of $(\text{CH}_3)_3\text{AuPPh}_3$ (< 0.001 mmol).

Molecular Orbital Calculations. The calculations on tetramethylaurate were carried out by the extended Hückel method.²⁵ The parameters used are listed in Table V. The gold d functions were taken as double ζ functions.²⁶ An Au–C distance of 2.10 Å, C–H of 1.10 Å, and idealized tetrahedral angles in the methyl groups were used for the computations.

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Silaethylene Intermediates from α -Lithiosilanes.

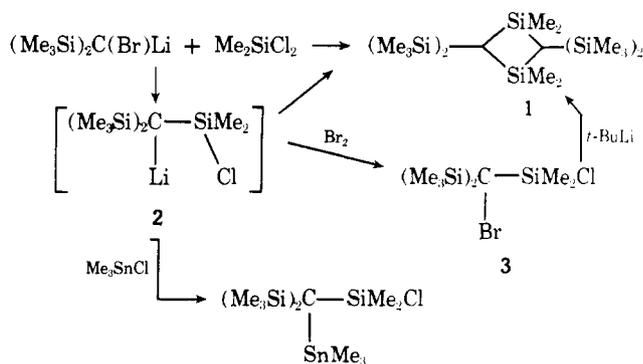
2. Reactions with Chlorosilanes and 1,3-Butadiene

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Abstract: Evidence is presented which indicates that silaethylene intermediates can be produced by the elimination of lithium chloride from α -lithiochlorosilanes under appropriate experimental conditions. The reaction of *tert*-butyllithium with vinyl-dimethylchlorosilane at low temperatures in hydrocarbon solvents gives high yields of *cis*- and *trans*-1,1,3,3-tetramethyl-2,4-dineopentyl-1,3-disilacyclobutanes. Trapping and competition experiments with various chlorosilanes indicate that coupling reactions of the initially produced α -lithiochlorosilane, **5**, are slower than the reactions leading to the 1,3-disilacyclobutanes. When the reaction is carried out in the presence of 1,3-butadiene apparent [2 + 2] and [2 + 4] cycloadducts are produced by the reaction of the silaethylene intermediate with butadiene. Among them is 1,1-dimethyl-2-neopentyl-3-vinylsilacyclobutane, a compound which cannot be formed by the addition of **5** to butadiene followed by ring closure.

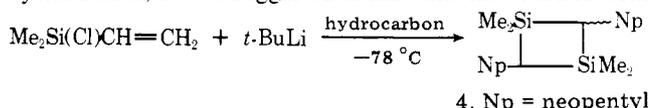
In 1974 Seyferth and Lefferts reported that the reaction of bis(trimethylsilyl)bromomethylithium with dimethylchlorosilane at low temperature in ether solvents gave moderate yields of 1,1,3,3-tetramethyl-2,2,4,4-tetrakis(trimethylsilyl)-1,3-disilacyclobutane (**1**).¹ Subsequently, they demonstrated that an α -lithiochlorosilane, **2**, could be the precursor of **1** by



trapping experiments with trimethyltin chloride. When the reaction mixture was treated with bromine the α -bromo compound **3** was obtained. Furthermore, when **3** was treated with *tert*-butyllithium, a 17% yield of **1** was obtained, presumably by lithium-halogen exchange to re-form **2**.² While other workers have investigated the chemistry of α -lithiohalosilanes produced by metalation,³ and have used such compounds as synthetic intermediates,⁴ the observation of 1,3-disilacyclobutane products from these intermediates was not reported.

We recently discovered that the reaction of *tert*-butyllithium with vinyl-dimethylchlorosilane in hydrocarbon solvents at low temperature gives high yields of the *cis*- and *trans*-1,3-disila-

cyclobutanes, **4**.⁵ We suggested at that time that **4** arises from



the dimerization of a silaethylene intermediate formed by the elimination of lithium chloride from an α -lithiochlorosilane precursor. We now wish to present further evidence that this is the case.

Results and Discussion

It seems reasonable that the first step in the reaction of vinyl-dimethylchlorosilane with *tert*-butyllithium leading to **4** is an addition reaction leading to the α -lithiochlorosilane, **5**. While such additions are known,⁶ the only example of the addition of an organolithium reagent to a vinylsilane bearing substituents susceptible to nucleophilic displacement on silicon is contained in the original report of the reaction.^{6a} In order to gain a better understanding of the relative rates of the coupling reaction of *tert*-butyllithium with chlorosilanes and the addition to vinylsilanes, competition experiments in which equimolar mixtures of vinyltrimethylsilane and trimethylchlorosilane were treated with 1 equiv of *tert*-butyllithium in hydrocarbon, ether, or tetrahydrofuran solvents were performed. In these experiments three products were isolated after hydrolytic workup: *trans*-1-trimethylsilyl-3,3-dimethylbutene (**6**); 1,1-bis(trimethylsilyl)-3,3-dimethylbutane (**7**); and 1,1,3-tris(trimethylsilyl)-5,5-dimethylhexane (**8**), all of which clearly arise from the initial addition of *tert*-butyllithium to the vinylsilane. In none of the experiments was any *tert*-butyltrimethylsilane, the anticipated product from an initial coupling reaction, observed. Table I gives the yields of the products in the three solvent systems studied.