Journal of Organometallic Chemistry, 433 (1992) 337–351
Elsevier Sequoia S.A., Lausanne
JOM 22564

Stereoselective formation and reactions of tetraalkylaurates(III)

Sanshiro Komiya, Satoshi Ozaki, Isao Endo, Kunihiko Inoue, Noriko Kasuga and Yasushi Ishizaki

Department of Applied Chemistry, Faculty of Engineering,
Tokyo University of Agriculture and Technology, 2-24-16 Nakamachi, Koganei, Tokyo 184 (Japan)

(Received November 1, 1991)

Abstract

Reactions of *cis*- (or *trans*-) dimethylalkyl(triphenylphosphine)gold(III), $Au(R^1)(R^2)(R^3)(PPh_3)$ with alkyllithiums (R^4Li) lead to selective displacement of the triphenylphosphine ligand by the alkyl anion to give square planar *cis*- (or *trans*-)tetraalkylaurates(III), $[Au(R^1)(R^2)(R^3)(R^4)]^- Li^+$ (R^1 = Me, R^2 = R^3 = Me or Et, R^4 = Me, Et, ^{n}Pr, ^{i}Pr, ^{n}Bu or Ph) in benzene. The reactions are stereoselective and no isomerization is observed. Rates of the reactions between the trialkylgold(II) complex and alkyllithiums are first order in the concentration of the gold(III) complex, and an associative mechanism involving the neutral trimethylgold(III) complex and alkyllithiums for the formation of tetraalkylaurates(III) has been proposed as a result from the kinetic study. Hydrolyses of *cis*- or *trans*-dimethyldiethylaurates(III) in the presence of triphenylphosphine afford *cis*-methyldiethyl(triphenylphosphine)gold(III) or *trans*-dimethylethyl(triphenylphosphine)gold(III) with liberation of an equimolar amount of the corresponding alkane, reflecting the strong *trans* effect of the alkyl group in the reaction. Molecular structure of *cis*-methyldiethyl(triphenylphosphine)gold(III) has been unequivocally determined by X-ray structure analysis (monoclinic, $P2_1/c$, a 10.972(6), b 19.898(9), c 10.683(7) Å, γ 112.42(4)°, V 2156(2) Å^3, $R = 7.8$, $R_w = 11.6$ for 3947 reflections ($|F_o| > 3|F_o|$).

Organometallic ate complexes have recently attracted a growing interest in relation to catalysis as well as in highly specific reactions of hypervalent metal compounds in organic reactions [1]. In these complexes organic groups bonded to the metal are generally highly activated into anionic states. Although such ate complexes containing metal-to-carbon bonds have been widely known in the most of transition and non-transition metal series, the structure and their chemical reactivities are less documented in comparison with neutral and cationic organometallic complexes, probably owing to their instability toward oxygen and moisture as well as owing to difficulties in their isolation. Organogold complexes, which are frequently synthesized as good models of active intermediates in transition metal promoted organic reactions and catalyses, are also known to form

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Correspondence to: Dr. S. Komiya, Department of Applied Chemistry, Faculty of Engineering, Tokyo University of Agriculture and Technology, 2-24-16 Nakamachi, Koganei, Tokyo 184, Japan.

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Table 1

^{1}H NMR data of tetraalkylaurates(III) [a]

Aurate	AuMe	Au–R	
$[AuMe_4]^-Li^+$ (**2a**)	0.24(12H)s	–	–
$[AuMe_3Et]^-Li^+$ (**2b**)	0.19(3H)s, 0.28(6H)s	0.85(2H)q [b],	1.33(3H)t [b]
$[AuMe_3(^nPr)]^-Li^+$ (**2c**) [d]	0.1(3H)s, 0.2(6H)s	[c]	[c]
$[AuMe_3(^iPr)]^-Li^+$ (**2d**) [d]	0.1(3H)s, 0.2(6H)s	[c]	[c]
$[AuMe_3(^nBu)]^-Li^+$ (**2e**) [d]	0.1(3H)s, 0.2(6H)s	[c]	[c]
$[AuMe_3Ph]^-Li^+$ (**2f**)	0.63(3H)s, 0.86(3H)s	–	–
cis-$[AuMe_2Et_2]^-Li^+$ (**2g**)	0.16(6H)s	0.77(4H)q [b],	1.38(6H)t [b]
trans-$[AuMe_2Et_2]^-Li^+$ (**2h**)	0.27(6H)s	0.71(4H)q [b],	1.34(6H)t [b]

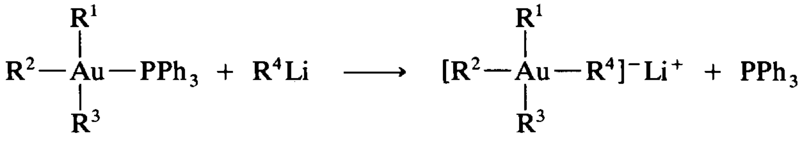
[a] In benzene at room temperature. Chemical shifts were referred to internal TMS. [b] $J = 7.8$ Hz. [c] Signals were obscured by the strong signals of the solvent and alkyl lithium used. [d] 60 MHz in benzene.

stable organometallic ate complexes [2]. The most well described organoaurate complexes are dialkylaurates(I), which are prepared from alkyl(triphenylphosphine)gold(I) and alkyllithiums in ether [2d]. The method provides a variety of mixed dialkylaurates(I). These aurates are susceptible to electrophilic attack of proton and alkyl halide to give corresponding monoalkylgold(I) and triorganogold(III) complexes, respectively. The latter method has been adopted as a convenient preparation of *trans*-dimethylalkyl(triphenylphosphine)gold(III). In contrast to these monovalent organoaurate complexes, examples of trivalent tetraalkylaurates(III) are very limited, and only tetramethylaurate(III) is known [2]. We have recently reported the stereoselective formation of mixed tetraalkylaurates(III) by the reaction of triorgano(triphenylphosphine)gold(III) with alkyllithium [3]. Here we deal with the details of formation and reactivity of mixed tetraalkylaurates(III). The synthesis of new *cis*-methyldialkyl(triphenylphosphine)gold(III) complexes by the selective hydrolysis of the mixed tetraalkylaurates(III) is also described.

Results and discussion

Formation of tetraalkylaurates(III)

Treatment of a benzene solution of the trialkyl(triphenylphosphine)gold(III) (**1**) with an alkyllithium gave a clear colorless solution containing tetraalkylaurate(III) (**2a–2h**) with liberation of a triphenylphosphine ligand after a few hours at room temperature. Table 1 summarizes ^{1}H NMR data of tetraalkylaurates(III). Absence of the triphenylphosphine ligand in the aurates(III) has been confirmed by disappearance of the coupling between methyl protons and phosphorus nuclei in their ^{1}H NMR spectra. The structure of these aurates is considered to be square planar, as previously suggested, using IR and Raman spectra by Tobias [2a,b]. Thus, the reactions of trimethyl(triphenylphosphine)gold(III) (**1a**) with ethyllithium gave trimethylethylaurate(III) (**2b**). The ^{1}H NMR spectrum of **2** exhibits two magnetically inequivalent methyl resonances in 1:2 ratio which have no coupling with the P nucleus. The former is assigned to gold-methyl *trans* to ethyl and the latter to methyls *trans* to each other. The occurrence of these resonances also supports the square planar structure of these tetraalkylaurates(III) complexes. The gold-ethyl resonance appears as a triplet and a quartet at 1.33 and 0.85 ppm, respectively. It is noteworthy that similar reactions of *cis*- and *trans*-dimethylethyl(triphenylphosphine)gold(III) with ethyllithium selectively afforded *cis*- and *trans*-dimethyldiethylaurates (**2g** and **2h**), respectively.



$$\mathrm{R^2{-}\overset{R^1}{\underset{R^3}{Au}}{-}PPh_3 + R^4Li \longrightarrow [R^2{-}\overset{R^1}{\underset{R^3}{Au}}{-}R^4]^-Li^+ + PPh_3} \qquad (1)$$

(1) (2)

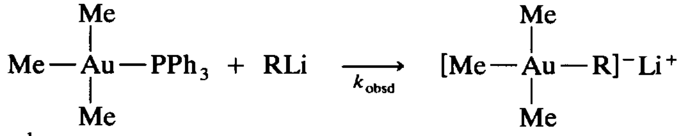
	R^1	R^2	R^3	R^4
2a	Me	Me	Me	Me
2b	Me	Me	Me	Et
2c	Me	Me	Me	^{n}Pr
2d	Me	Me	Me	^{i}Pr
2e	Me	Me	Me	^{n}Bu
2f	Me	Me	Me	Ph
2g	Me	Me	Et	Et
2h	Me	Et	Me	Et

The result clearly indicates that the reactions are stereoselective and that simple displacement of a triphenylphosphine ligand by an alkyl anion took place without configurational rearrangement.

In the ^{1}H NMR spectrum of trimethylethylaurate(III), chemical shift of the methyl group *trans* to each other is slightly lower than that of the methyl *trans* to ethyl, suggesting a higher *trans* influence of ethyl than methyl. The chemical shift of the methyl group in the *cis*-dimethyldiethylaurate(III) is also slightly higher than that in the *trans*-isomer. Independent formation of both isomers and non-fluxional behavior of these aurates in ^{1}H NMR spectra indicate that no facile intramolecular exchange of alkyl groups is taking place at room temperature. Gold alkyls and lithium alkyl anions are also not exchangeable, since both species are observed separately in the presence of excess ethyllithium in the ^{1}H NMR spectra, and other isomers of aurates, which would be formed by inter- and intramolecular alkyl exchange reactions, were not detected (*vide infra*). Similar displacement of tertiary phosphine ligands with alkyllithium in diorganopalladium(II) is known [4].

Mechanism of the formation of tetraalkylaurates

The time-course of the reaction of trialkyl(tertiary phosphine)gold(III) with alkyllithiums was monitored by ^{1}H NMR spectroscopy in benzene. The rates of disappearance of the trimethylgold(III) complex or those of the appearance of the aurate(III) were first order in the concentration of the remaining trimethylgold(III) complex. Table 2 shows the estimated first order rate constants under various conditions.



$$\mathrm{Me{-}\overset{Me}{\underset{Me}{Au}}{-}PPh_3 + RLi \xrightarrow[k_{obsd}]{} [Me{-}\overset{Me}{\underset{Me}{Au}}{-}R]^-Li^+} \qquad (2)$$

$$\frac{\mathrm{d}}{\mathrm{d}t}[\mathrm{AuMe_3R^-}] = k_{\mathrm{obsd}}([\mathrm{Au_{total}}] - [\mathrm{AuMe_3R^-}])$$

where $[\mathrm{Au_{total}}]$ represents the total concentration of gold complexes

Table 2

First order rate constants for the reactions of trialkyl(triphenylphosphine)gold(III) with alkyl lithiums [a]

Complex	RLi (mol/l)	PPh_3 (mol/l)	$10^4 k_{obsd}$ (sec^{-1})
$AuMe_3(PPh_3)$ (**1a**)	EtLi (0.056)	0	2.2
	(0.140)	0	2.7
	(0.140)	0.280	2.2
	(0.140)	0.420	2.2
	(0.140)	0.560	2.4
	(0.280)	0	2.6
	(0.288)	0	2.7
	(0.567)	0	2.9
	^{n}PrLi (0.076)	0	1.9
	(0.108)	0	3.5
	(0.255)	0	9.0
	^{i}PrLi (0.057)	0	3.3
	(0.112)	0	7.2
	(0.243)	0	11
	(0.390)	0	17
	^{n}BuLi (0.117)	0	3.9
	(0.230)	0	5.9
	(0.428)	0	12
cis-$AuMe_2Et(PPh_3)$ (**1b**)	EtLi (0.056)	0	1.4
	(0.140)	0	1.5
	(0.280)	0	1.6
	(0.090)	0.333	2.0
	(0.090)	0.180	2.0
trans-$AuMe_2Et(PPh_3)$ (**1c**)	(0.056)	0	3.1
	(0.140)	0	3.0
	(0.280)	0	3.1
	(0.090)	0.090	3.7
	(0.090)	0.358	3.6
	(0.090)	0.192	3.7
$AuMe_3(PMePh_2)$ (**3**)	(0.057)	0	1.3
	(0.134)	0	1.6
	(0.262)	0	1.9
	(0.423)	0	2.1
$AuMe_3(PMe_2Ph)$ (**4**)	(0.148)	0	0.5
	(0.350)	0	0.7
	(0.486)	0	1.0
$AuMe_3(PMe_3)$ (**5**)	(0.459)	0	0.2
$AuMe_3(PCy_3)$ (**6**)	(0.449)	0	0

[a] $[AuMe_3L] = 0.028$ mol/l, in benzene at 34°C.

Figure 1 shows the dependence of the estimated first order rate constants k_{obsd} on the concentration of various alkyllithiums for the reaction of trimethyl(triphenylphosphine)gold(III). In the case of the reactions with ethyllithium, k_{obsd} values are insensitive to the concentration of ethyllithium, whereas they increase with increase in the concentration of other alkyllithiums, but are apt to level off at constant values. Similar trends were also observed in the reactions of trimethylgold(III) complexes having a different tertiary phosphine ligand with ethyllithium (Fig. 2). Addition of the triphenylphosphine ligand to the system showed no apparent retardation effect on the rate. The present Michaelis–Menten type

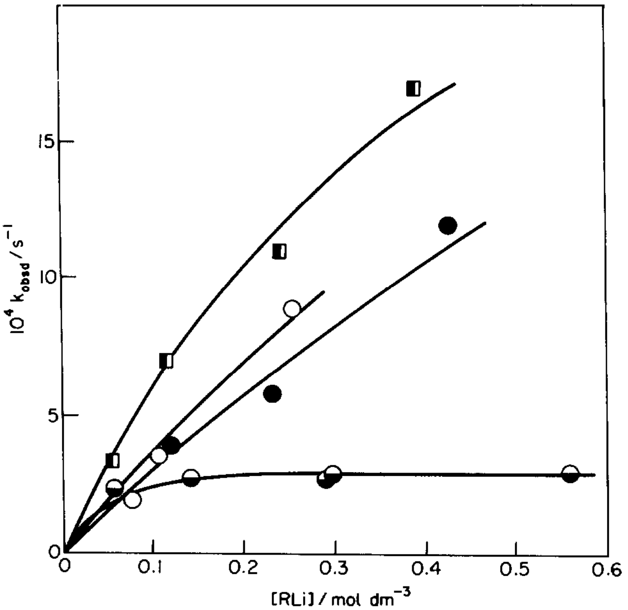
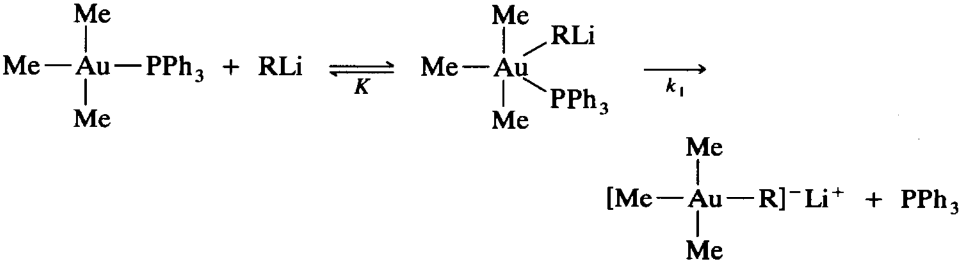


Fig. 1. Dependence of the first order rate constants k_{obsd} on the concentration of alkyl lithiums for the formation reaction of trimethylalkylaurates(III) from $AuMe_3(PPh_3)$ and RLi in benzene at 34°C. $[AuMe_3(PPh_3)] = 0.028$ mol dm^{-3}. R = Et (◒), ^{n}Pr (○), ^{i}Pr (◧), ^{n}Bu (●).

kinetic behavior might reflect the rate-limiting dissociation process of triphenylphosphine ligand, followed by the reaction with alkyllithium. However, if this is the case, the observed rate constant should not exceed the value of limiting rate constant of dissociation of triphenylphosphine ligand. The value was independently estimated as *ca.* $10^{-5}\ s^{-1}$ in the thermolysis of $AuMe_3(PPh_3)$ at 70°C [5]. Thus the limiting k_{obsd} values estimated at room temperature are considered to be much smaller than this value, ruling out the dissociative mechanism. In fact, the reactions proceed smoothly even at room temperature, though the trialkyl(tertiary phosphine)gold(III) is considerably stable under the same reaction conditions. In addition, trimethyl(tricyclohexylphosphine)gold(III), which dissociates the phosphine ligand faster than does the triphenylphosphine complex, shows much less tendency to react with ethyllithium (*vide infra*). Therefore these results are inconsistent with the mechanism involving the prior rate-limiting ligand dissociation process. The following associative mechanism for the reaction, shown in Scheme 1, is now proposed.



$$\mathrm{Me{-}\underset{Me}{\overset{Me}{Au}}{-}PPh_3} + \mathrm{RLi} \underset{K}{\rightleftharpoons} \mathrm{Me{-}\underset{Me}{\overset{Me}{Au}}\genfrac{}{}{0pt}{}{RLi}{PPh_3}} \xrightarrow[k_1]{} [\mathrm{Me{-}\underset{Me}{\overset{Me}{Au}}{-}R}]^-\mathrm{Li}^+ + \mathrm{PPh_3}$$

Scheme 1. An associative mechanism for the formation of tetraalkylaurate(III).

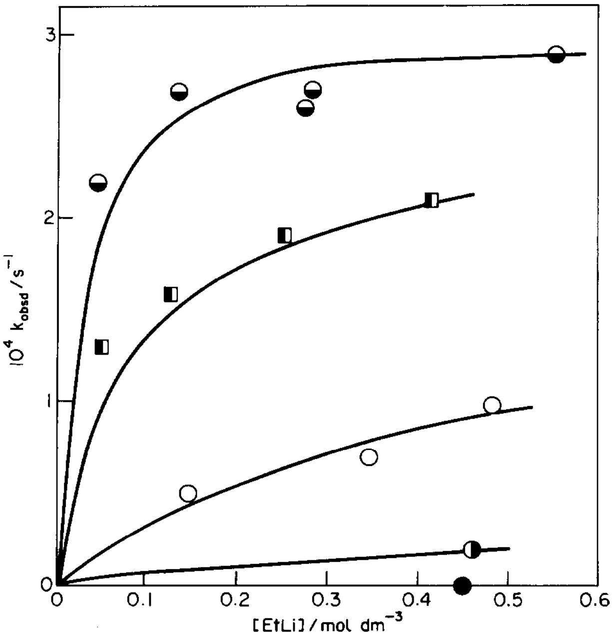


Fig. 2. Dependence of the first order rate constants k_{obsd} on the concentration of EtLi for the formation reaction of trimethylethylaurate(III) from trimethyl(tertiaryphosphine)gold(III) and EtLi in benzene at 34°C. $[AuMe_3(PPh_3)] = 0.028$ mol dm^{-3}. L = PPh_3 (◓), $PMePh_2$ (◧), PMe_2Ph (○), PMe_3 (◑), PCy_3 (●).

As shown in Scheme 1, trialkyl(tertiary phosphine)gold(III) reacts with an alkyllithium to give a 5-coordinate intermediate from which the tertiary phosphine ligand dissociates to afford the tetraalkylaurate(III). The following rate equation has been derived by assuming pre-equilibrium involving a 5-coordinate intermediate and is in good agreement with the kinetic results.

$$-\frac{d}{dt}[Au] = \frac{k_1 K[RLi][Au]}{1 + K[RLi]} = k_{obsd}[Au]$$

where $[Au] = [Au_{total}] - [AuR_4^-]$

When $K[RLi] \ll 1$, k_{obsd} increases linearly with increase in the concentration of RLi, whereas k_{obsd} levels off with increase in the value of $K[RLi]$.

High stereoselectivity of the reactions as mentioned above is also consistent with the proposed mechanism, since the associative ligand displacement of square planar d^8 transition metal complexes generally are known to proceed with high stereoselectivity [6].

Effect of the alkyllithium. As shown in Fig. 1, the more basic alkyllithium complexes such as isopropyllithium show high reactivity toward the gold(III) complex. The results suggest that the displacement reaction of the triphenylphosphine ligand by an alkyllithium is essentially nucleophilic and an alkyl anion is likely to attack the more acidic gold(III) center. However, it is still controversial concerning the different kinetic behaviors between reactions with ethyllithium and other alkyllithiums. Steric bulkiness of alkyllithiums to decrease the equilibrium constant K might be responsible for this type of kinetic behavior. We should await further detailed investigations to resolve the problem why k_{obsd} for the reaction of trimethyl(triphenylphosphine)gold(III) with an ethyllithium shows rate-limiting values under the reaction conditions.

Effect of ligand. Rates of the formation of tetraalkylaurates from trimethylgold(III) complexes having various tertiary phosphine ligands and alkyl groups are also listed in Table 2. Figure 2 shows the dependence of k_{obsd} on the concentration of ethyllithium for these complexes. As the degree of the phenyl group substitution in PPh_3 ligand by methyl increased, the apparent first order rate constant decreased. Electron donation from the ligand makes the gold center more basic to discourage the nucleophilic reaction of the alkyllithium towards the Au center. Also, the fact that the trimethylgold(III) complex containing a tricyclohexylphosphine ligand showed no tendency to react with ethyllithium under the same reaction conditions, suggested the importance of the steric hindrance in the transition state of the reaction. It is noteworthy that the rate for the reaction of *trans*-$AuMe_2Et(PPh_3)$ (**1b**) with EtLi is larger than those of $AuMe_3(PPh_3)$ (**1a**) and *cis*-$AuMe_2Et(PPh_3)$ (**1c**). Electron donation of two ethyl groups, both of which are placed in the equatorial positions of the possible trigonal bipyramidal intermediate, may enhance the liberation of the triphenylphosphine ligand. However, it is inconsistent that the rate constant of *cis* isomer is smaller than that of $AuMe_3(PPh_3)$. At present we have no appropriate interpretation for this unusual *cis* effect.

Selective hydrolysis of tetraalkylaurates(III)

Hydrolysis of these tetramethylaurates(III) (**2a**) with water in the presence of triphenylphosphine ligand liberated an equimolar amount of methane, giving neutral trimethyl(triphenylphosphine)gold(III) (**1a**) in high yield. It is of interest to analyze the reaction products in the hydrolysis of mixed tetraalkylaurates(III), since the relative nucleophilicity of gold–alkyl bonds toward proton can be estimated by simply analyzing the hydrolyzed organic products. Table 3 summarizes the results of the hydrolysis of various tetraalkylaurates(III). Thus, the

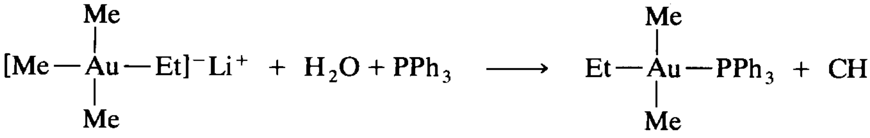
Table 3

Hydrolysis of tetraalkylaurates(III) [a]

Aurate	Gas (%/Au) [b]	Au complex (yield%)
2b	CH_4 (95), C_2H_6 (22)	*trans*-$AuMe_2Et(PPh_3)$ (78) *cis*-$AuMe_2Et(PPh_3)$ (17)
2f	CH_4 (37), C_6H_6 [c]	$AuMe_3(PPh_3)$ (61) *cis*-$AuMe_2Ph(PPh_3)$ (36)
2g	CH_4 (74), C_2H_6 (30)	*cis*-$AuMeEt_2(PPh_3)$ (89) *cis*-$AuMe_2Et(PPh_3)$ (12)
2h [d]	CH_4 (32), C_2H_6 (83)	*trans*-$AuMe_2Et(PPh_3)$ (87)

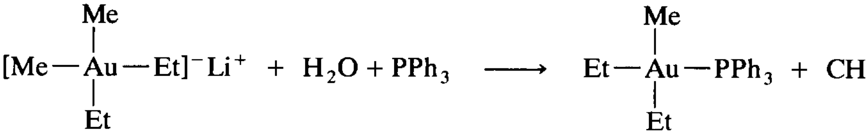
[a] Tetraalkylaurates(III) were prepared *in situ* from a 1:1 mixture of trialkyl(triphenylphosphine)gold(III) and ethyl lithium at room temperature for 1 day. [b] Amounts of gases and resulted organogold(III) complexes were estimated by GC and NMR, respectively. [c] The amount not measured. [d] The sample **2h** contained *ca.* 10% *cis* isomer. A possible minor organogold(III) product, *trans*-$AuMeEt_2(PPh_3)$ was not clearly assigned in ^1H NMR because of overlapping with the large resonances of *trans*-$AuMe_2Et(PPh_3)$ and **1d** (19%).

hydrolysis of trimethylethylaurate(III) (**2b**) afforded mainly *trans*-dimethylethyl(triphenylphosphine)gold(III) accompanied by evolution of methane.

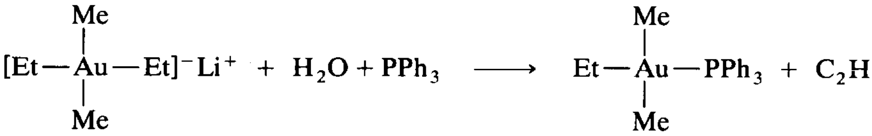


$$[\mathrm{Me}-\underset{\underset{\mathrm{Me}}{|}}{\overset{\overset{\mathrm{Me}}{|}}{\mathrm{Au}}}-\mathrm{Et}]^{-}\mathrm{Li}^{+} + \mathrm{H_2O} + \mathrm{PPh_3} \longrightarrow \mathrm{Et}-\underset{\underset{\mathrm{Me}}{|}}{\overset{\overset{\mathrm{Me}}{|}}{\mathrm{Au}}}-\mathrm{PPh_3} + \mathrm{CH_4} \tag{3}$$

The high selectivity of the reaction was conveniently interpreted by the strong *trans* effect of ethyl group in the hydrolysis, giving higher electron density on the methyl group *trans* to ethyl than that *trans* to methyl. Such *trans* effect is more clearly observed when dimethyldiethylaurates(III) were hydrolyzed. The *cis*-isomer **2g** mainly liberated methane upon hydrolysis, whereas the *trans*-isomer **2h** gave ethane. The resultant triorganogold(III) complexes were found to be *cis*-diethylmethyl(triphenylphosphine)gold(III) (**1d**) and *trans*-dimethylethyl(triphenylphosphine)gold(III) (**1c**) by ^{1}H NMR spectra, respectively. Analogous hydrolysis of *cis*-dialkyldimethylaurates(III), *cis*-$[\mathrm{AuR_2Me_2}]^{-}\mathrm{Li}^{+}$ (R = ^{n}Pr (**1e**); R = ^{n}Bu (**1f**)) also gave corresponding *cis*-dialkylmethyl(triphenylphosphine)gold(III), *cis*-$\mathrm{AuR_2Me(PPh_3)}$ (R = ^{n}Pr (**1e**); R = ^{n}Bu (**1f**)).



$$[\mathrm{Me}-\underset{\underset{\mathrm{Et}}{|}}{\overset{\overset{\mathrm{Me}}{|}}{\mathrm{Au}}}-\mathrm{Et}]^{-}\mathrm{Li}^{+} + \mathrm{H_2O} + \mathrm{PPh_3} \longrightarrow \mathrm{Et}-\underset{\underset{\mathrm{Et}}{|}}{\overset{\overset{\mathrm{Me}}{|}}{\mathrm{Au}}}-\mathrm{PPh_3} + \mathrm{CH_4} \tag{4}$$



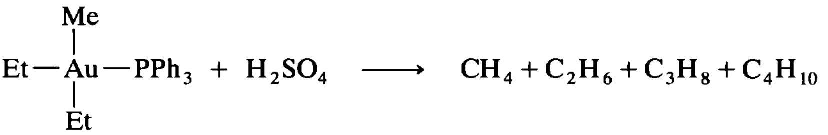
$$[\mathrm{Et}-\underset{\underset{\mathrm{Me}}{|}}{\overset{\overset{\mathrm{Me}}{|}}{\mathrm{Au}}}-\mathrm{Et}]^{-}\mathrm{Li}^{+} + \mathrm{H_2O} + \mathrm{PPh_3} \longrightarrow \mathrm{Et}-\underset{\underset{\mathrm{Me}}{|}}{\overset{\overset{\mathrm{Me}}{|}}{\mathrm{Au}}}-\mathrm{PPh_3} + \mathrm{C_2H_6} \tag{5}$$

Our results indicate the occurrence of the predominant electrophilic attack of a proton toward the alkyl group *trans* to ethyl rather than that *trans* to methyl, in spite of the apparent small difference of electron density of these alkyl groups. It should be mentioned that such a delicate difference in the *trans* effect of the alkyl group effectively controls the regioselectivity of the reaction.

Characterization and reactions of cis-*diethylmethyl(triphenylphosphine)gold(III)*

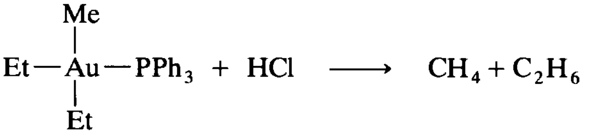
cis-Dialkylmethyl(triphenylphosphine)gold(III) (**1d–1f**) was characterized by NMR and IR spectroscopy, elemental analysis and chemical reactions (see Experimental) as well as by X-ray structure analysis (*vide infra*). Signals assignable to ethyl in ^{1}H NMR of this complex are quite similar to, but slightly different from, the sum of ethyl signals in the spectra of *cis*- and *trans*-dimethylethyl(triphenylphosphine)gold(III) (**1b** and **1c**). The methylgold *cis* to phosphine ligand is observed as a doublet at 0.61 ppm, the value being in the region of methylgold *trans* to alkyl [7].

Acidolysis of **1d** with sulfuric acid liberated methane, ethane, propane and butane. Although methane and ethane were considered to be formed by simple protonolysis of gold–carbon bonds, routes for formation of propane and butane are controversial. One possible interpretation is competitive protonolysis of gold–alkyl bonds, followed by reductive elimination of the remaining two alkyl groups to give propane or butane. In fact, the amounts of liberated methane and ethane are close to those of propane and butane. This is supported further by the fact that reductive elimination from dimethyl(aniono)(triphenylphosphine)gold(III) complexes, whose anion is a good leaving ligand such as triflate and sulfate, is very facile [7].



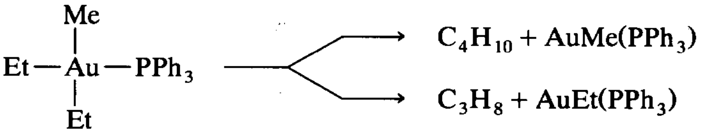
$$\mathrm{Et{-}\overset{\displaystyle Me}{\underset{\displaystyle Et}{Au}}{-}PPh_3 + H_2SO_4 \longrightarrow CH_4 + C_2H_6 + C_3H_8 + C_4H_{10}} \qquad (6)$$

On acidolysis of **1d** with dry hydrogen chloride, only methane and ethane were evolved in 7:3 ratio. Formation of the corresponding diorganochlorogold(III) complexes may be assumed, since the similar acidolysis of trimethyl(triphenylphosphine)gold(III) (**1a**) gave methane and *cis*-dimethylchloro(triphenylphosphine)gold(III) [5]. The result also supports the occurrence of initial protonolysis in these reactions. Similar results were also observed in the protonolysis of **1e** and **1f** (see Experimental).



$$\mathrm{Et{-}\overset{\displaystyle Me}{\underset{\displaystyle Et}{Au}}{-}PPh_3 + HCl \longrightarrow CH_4 + C_2H_6} \qquad (7)$$

Thermolysis of **1d** at 70°C liberated a mixture of propane and butane in a solid state. A small amount of ethane was also detected. The resulting gold complexes were a mixture of methyl(triphenylphosphine)gold(I) and ethyl(triphenylphosphine)gold(I). The yields of these products are compatible with the proposed mechanism involving competitive reductive elimination exemplified by eq. 8. Formation of a small amount of ethane may indicate that, at least in part, an intermolecular alkyl coupling is also involved. However, no β-elimination process is involved in the thermolysis, since no detectable olefins such as ethylene and propylene were produced. Characteristic preference of reductive elimination over β-hydrogen elimination in thermolysis of organogold complexes is in high contrast to the complete disproportionation of alkyl groups in the thermolysis of dialkylplatinum(II) complexes [8]. From the amount of gases evolved, relative ease of reductive elimination can be estimated. Predominant formation of butane in comparison with propane suggests that ethylgold is more susceptible to reductive elimination than methylgold. Thermolysis of complexes **1e** and **1f** also showed a similar trend. These results are consistent with the theoretical anticipation as well as with our previous data that increased electron-donating alkyl groups tend to be reductively eliminated [9].



$$\mathrm{Et{-}\overset{\displaystyle Me}{\underset{\displaystyle Et}{Au}}{-}PPh_3} \; \begin{array}{l} \nearrow \mathrm{C_4H_{10} + AuMe(PPh_3)} \\ \searrow \mathrm{C_3H_8 + AuEt(PPh_3)} \end{array} \qquad (8)$$

Molecular structure of cis-*methyldiethyl(triphenylphosphine)gold(III) (1d)*

The molecular structure of *cis*-methyldiethyl(triphenylphosphine)gold(III) (**1d**) has been unequivocally determined by X-ray structure analysis. Crystal data are

Table 4

Summary of crystallographic data for *cis*-AuMeEt$_2$(PPh$_3$)

	cis-AuMeEt$_2$(PPh$_3$)
Formula	AuPC$_{23}$H$_{28}$
FW	532.41
Space group	$P2_1/c$
Crystal system	monoclinic
a, Å	10.972(6)
b, Å	19.898(9)
c, Å	10.683(7)
γ, deg	112.42(4)
V, Å^3	2156(2)
Z	4
Crystal size, mm	0.2×0.9×0.2
d_{calcd}, g cm^{-3}	1.640
Radiation, Å	Mo-K_α, 0.71068
μ(Mo-K_α) cm^{-1}	66.567
Temp. °C	r.t.
2θ, deg.	$3 < 2\theta < 50$
Scan type	$\omega/2\theta$
No. of data collected	6152
No. of obsd reflns	3947 ($\lvert F_o \rvert > 3\sigma(\lvert F_o \rvert)$)
For refinement	
R [a]	0.0775
R_w [b]	0.1155
Method of phase determination	direct method

[a] $R = \Sigma[\lvert F_o\rvert - \lvert F_c\rvert]/\Sigma\lvert F_o\rvert$, [b] $R_w = [\Sigma(w\lvert F_o\rvert - \lvert F_c\rvert^2)/\Sigma w(\lvert F_o\rvert)^2]^{1/2}$.

summarized in Table 4. Fractional atomic coordinates are listed in Table 5. Tables 6 and 7 show bond distances and angles. ORTEP drawing of **1d** shown in Fig. 3 demonstrates the square planar *cis* structure. Two ethyl groups occupy sites *cis* to each other as suggested from NMR and its chemical reactivities. Bond lengths and angles are normal except for apparently short C–C bond distances of the Au–Et group *cis* to the phosphorus ligand which is probably due to their high thermal motion (see Experimental).

Experimental

General

All the manipulations were carried out under deoxygenated nitrogen or argon using Schlenk techniques or under vacuum. Solvents were purified by usual methods under nitrogen and stored under nitrogen prior to use. Benzene-d_6 was used after distillation from sodium. Alkyllithiums, prepared from lithium metal and alkyl chloride in pentane, were purified by recrystallization from pentane and redissolved in benzene for the kinetic study. The concentrations of the alkyllithiums were determined by quantitatively analyzing the gases after hydrolysis of settled amounts of the benzene solution of the alkyllithiums or by acid and base titration of the hydrolyzed aqueous solution. The solutions were stored at −20°C

Table 5

Fractional atomic coordinates ($\times 10^4$) for *cis*-$AuMeEt_2(PPh_3)$

Atom	x	y	z	B_{eq}
Au	2160.4(7)	3784.1(2)	4598.3(6)	6.00
P	3266(5)	4362(2)	6664(5)	5.42
C(1)	1571(28)	4684(12)	3420(20)	9.05
C(2)	1152(29)	3219(13)	2852(27)	8.95
C(3)	−2307(47)	3158(17)	2618(42)	14.49
C(4)	2639(25)	2841(10)	5628(19)	7.69
C(5)	3648(32)	2429(13)	5222(29)	11.02
C(6)	4871(20)	3953(7)	7651(20)	5.55
C(7)	5285(23)	3811(8)	8997(20)	6.54
C(8)	6540(26)	3513(10)	9667(22)	7.29
C(9)	7373(26)	3395(12)	8973(32)	9.05
C(10)	6934(26)	3590(12)	7574(31)	8.80
C(11)	5683(22)	3832(9)	6922(24)	6.89
C(12)	2336(17)	4346(8)	7790(17)	5.24
C(13)	2652(22)	4749(10)	8877(17)	7.05
C(14)	1881(25)	4723(12)	9661(20)	7.98
C(15)	936(25)	4273(11)	9464(23)	7.98
C(16)	603(29)	3800(10)	8318(35)	9.36
C(17)	1335(26)	3851(10)	7575(23)	8.81
C(18)	3595(22)	5275(9)	6615(19)	6.73
C(19)	2534(28)	5712(10)	6138(25)	9.26
C(20)	2832(36)	6409(12)	6078(31)	10.42
C(21)	4111(36)	6624(13)	6497(28)	9.97
C(22)	5204(31)	6177(9)	6915(29)	9.45
C(23)	4938(25)	5470(8)	6981(20)	7.67

and titrated before use. Trialkyl(triphenylphosphine)gold(III) complexes were prepared by the literature methods [10,11]. IR spectra were recorded on Jasco IR A302 and FTIR 5M spectrometers. NMR spectra were measured by JEOL FX-200 and PMX-60 spectrometers.

Table 6

Bond lengths (Å) for *cis*-$AuMeEt_2(PPh_3)$

Au–P	2.371(4)	C(11)–C(6)	1.41(4)
Au–C(1)	2.14(2)	C(12)–C(13)	1.34(3)
Au–C(2)	2.10(3)	C(13)–C(14)	1.40(4)
Au–C(4)	2.14(2)	C(14)–C(15)	1.33(3)
C(2)–C(3)	1.45(6)	C(15)–C(16)	1.47(3)
C(4)–C(5)	1.57(5)	C(16)–C(17)	1.33(5)
P–C(6)	1.86(2)	C(17)–C(12)	1.43(3)
P–C(12)	1.85(2)	C(18)–C(19)	1.39(3)
P–C(18)	1.86(2)	C(19)–C(20)	1.43(3)
C(6)–C(7)	1.36(3)	C(20)–C(21)	1.37(5)
C(7)–C(8)	1.42(3)	C(21)–C(22)	1.42(4)
C(8)–C(9)	1.40(5)	C(22)–C(23)	1.44(3)
C(9)–C(10)	1.44(4)	C(23)–C(18)	1.43(3)
C(10)–C(11)	1.37(3)		

Table 7

Bond angles (deg) for *cis*-$AuMeEt_2(PPh_3)$

P-Au-C(1)	94.3(6)	C(8)-(9)-C(10)	119(2)
P-Au-C(2)	175.9(8)	C(9)-C(10)-C(11)	120(3)
P-Au-C(4)	90.5(5)	C(10)-C(11)-C(6)	120(2)
C(1)-Au-C(2)	89.2(9)	C(13)-C(12)-P	122(1)
C(1)-Au-C(4)	175.2(7)	C(17)-C(12)-P	119(2)
C(2)-Au-C(4)	86.0(8)	C(13)-C(12)-C(17)	119(2)
Au-C(2)-C(3)	111(3)	C(12)-C(13)-C(14)	119(2)
Au-C(4)-C(5)	112(2)	C(13)-C(14)-C(15)	123(2)
Au-P-C(6)	110.7(6)	C(14)-C(15)-C(16)	120(3)
Au-P-C(12)	112.5(5)	C(15)-C(16)-C(17)	116(2)
Au-P-C(18)	118.9(6)	C(16)-C(17)-C(12)	124(2)
C(6)-P-C(12)	105.2(9)	C(19)-C(18)-P	119(2)
C(6)-P-C(18)	106.9(8)	C(23)-C(18)-P	117(1)
C(12)-P-C(18)	101(1)	C(19)-C(18)-C(23)	124(2)
C(7)-C(6)-P	123(2)	C(18)-C(19)-C(20)	117(3)
C(11)-C(6)-P	115(1)	C(19)-C(20)-C(21)	121(3)
C(7)-C(6)-C(11)	121(2)	C(20)-C(21)-C(22)	123(2)
C(6)-C(7)-C(8)	119(2)	C(21)-C(22)-C(23)	118(3)
C(7)-C(8)-C(9)	121(2)	C(22)-C(23)-C(18)	117(2)

Formation of tetraalkylaurates(III) in benzene

Treatment of trimethyl(triphenylphosphine)gold(III) (26.8 mg, 0.0531 mmol) in benzene-d_6 (0.32 cm^3) with ethyllithium (0.108 mmol) at room temperature gave a colorless solution which was extremely air sensitive, as it immediately changed to deep purple when the solution was opened to air. After 5 h the formation of

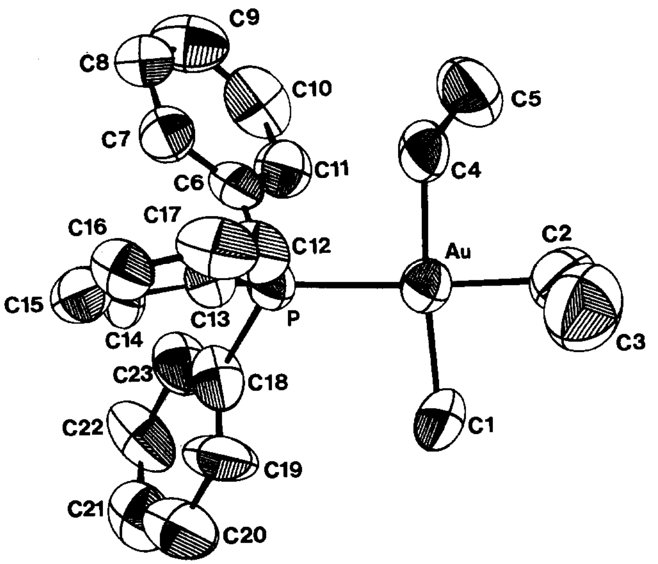


Fig. 3. ORTEP drawing of *cis*-$AuMeEt_2(PPh_3)$, **1d** showing the atomic numbering scheme used. Ellipsoids are drawn at the 50% probability level.

trimethylethylaureate(III) was confirmed by ^{1}H NMR spectroscopy showing two singlets assignable to gold methyls in 1:2 ratio. The ^{1}H NMR data of the trimethylethylaurate and related compounds, which are prepared by the similar reactions of various trialkyl(triphenylphosphine)gold(III) with alkyllithiums, are summarized in Table 1.

Kinetics

A settled amount of trialkyl(triphenylphosphine)gold(III) (*ca.* 10 mg) was taken in the NMR tube with a rubber septum and degassed. Dehydrated benzene (0.3–0.6 cm^3) and anisole (0.0020 cm^3) as an internal standard were added by the hypodermic microsyringe. Then a fixed amount of the benzene solution of alkyllithium was added to start the reaction. The amount of the aurate formed and that of starting trialkylgold(III) complex were estimated by comparing the areas of their signals and the added internal standard periodically.

Hydrolysis of tetraalkylaurates(III) (2)

The benzene solution of tetraalkylaurate(III) was prepared from 1:1 mixture of trialkyl(triphenylphosphine)gold(III) and alkyllithium. After 1 d the formation of aurate was confirmed by ^{1}H NMR spectroscopy. After evacuation of the system, deoxygenated water (0.010 cm^3) was added to hydrolyze the aurate. Gases evolved in the reaction were determined quantitatively by GC using an internal standard (propylene). Evaporation of all the volatile matters gave a colorless solid which was extracted with pentane. ^{1}H NMR of the solid revealed the formation of the corresponding trialkyl(triphenylphosphine)gold(III) complex. The results are summarized in Table 3.

X-Ray structure analysis

The crystals suitable for X-ray structure analysis were obtained by recrystallization from pentane. Intensity data were collected at room temperature on a Rigaku AFC-5R diffractometer. No absorption corrections were applied. The structure was solved by the direct method and refined by a full-matrix least-squares procedure. All the non-hydrogen atoms were refined anisotropically. Empirical absorption corrections were applied [12]. Although high thermal motion of C(3) seems to cause shortening of apparent C(2)–C(3) bond distance, no appropriate disorder of the C(3) atom could be found from the differential map. Hydrogens were included in the calculation, but they were not refined. Data collection and calculation were carried out with the program CRYSTAN (Rigaku).

Tables of fractional atomic coordinates, bond distances, bond angles, and observed and calculated structure factors can be obtained from the authors.

Synthesis of cis-*methyldiethyl(triphenylphosphine)gold(III) (1d)*

The compound can be prepared by hydrolysis of *cis*-dimethyldiethylaurate prepared from *cis*-dimethylethyl(triphenylphosphine)gold(III) with ethyllithium. However, the method shown below is more convenient to synthesize the title compound, since the stereospecific formation of *cis*-dimethylethyl(triphenylphosphine)gold(III) from the reaction of *cis*-dimethyliodo(triphenylphosphine)gold(III) with a stoichiometric amount of ethyllithium is known [2d].

An ether solution (30 cm^3) of *cis*-dimethyliodo(triphenylphosphine)gold(III) (825.0 mg, 1.3 mmol) was treated with ethyllithium (144.0 mg, 4.0 mmol) at room temperature. After 4 h stirring an excess of ethyllithium was slowly hydrolyzed at 0°C. An ether layer and the ether extracts were combined. Evaporation of the solvent to dryness in a vacuum gave a colorless solid which was recrystallized from ether/hexane. Yield 310.0 mg (44%). M.p. 69–70°C. Anal. Found: C, 51.24; H, 5.20. $\mathrm{C_{23}H_{28}PAu}$ calc.: C, 51.89; H, 5.30%. ^{1}H NMR ($\mathrm{C_6D_6}$); δ 0.61 (AuMe, 3H, d, 7.1 Hz); 1.2–1.4 (AuEt *cis* to P, 5H, m); 1.8 ($\mathrm{AuCH_2}\mathit{CH_3}$ *trans* to P, dt, 3H, 13.2, 7.8 Hz); 2.5 ($\mathrm{Au}\mathit{CH_2}\mathrm{CH_3}$ *trans* to P, qui, 2H, 7.8 Hz); 6.9–7.6 ($\mathrm{PPh_3}$, 15H, m). ^{13}C{^{1}H} NMR ($\mathrm{C_6D_6}$): δ 12.5 (AuMe, d, 6.1 Hz); 14.7 ($\mathrm{AuCH_2}\mathit{C}\mathrm{H_3}$ *cis* to P, s); 15.7 ($\mathrm{AuCH_2}\mathit{C}\mathrm{H_3}$ *trans* to P, d, 6.1 Hz); 25.0 ($\mathrm{Au}\mathit{C}\mathrm{H_2CH_3}$ *cis* to P, d, 4.9 Hz); 30.0 ($\mathrm{Au}\mathit{C}\mathrm{H_2CH_3}$ *trans* to P, d, 119.6 Hz), 128–135 ($\mathrm{PPh_3}$).

Similar reactions of *cis*-dimethyliodo(triphenylphosphine)gold(III) with propyl- or butyllithium gave corresponding methyldialkyl(triphenylphosphine)gold(III).

cis-AuMe(Pr)$_2$(PPh$_3$) (**1e**) yield 68%. M.p. 67–68°C. Anal. Found: C, 53.86; H, 5.99. $\mathrm{C_{25}H_{32}PAu}$ calc.: C, 53.58; H, 5.76%. ^{1}H NMR: δ 0.61 (AuMe, 3H, d, 6.8 Hz); 0.97 ($\mathrm{AuCH_2CH_2}\mathit{CH_3}$ *cis* to P, 3H, t, 7.1 Hz); 1.25 ($\mathrm{Au}\mathit{CH_2}\mathrm{CH_2CH_3}$ *cis* to P, 2H, dt, 6.8 and 7.1 Hz); 1.34 ($\mathrm{AuCH_2CH_2}\mathit{CH_3}$ *trans* to P, 3H, dt, 0.8 and 7.1 Hz); 1.64 ($\mathrm{AuCH_2}\mathit{CH_2}\mathrm{CH_3}$ *cis* to P, 2H, sextet, 7.1 Hz); 2.24 ($\mathrm{AuCH_2}\mathit{CH_2}\mathrm{CH_3}$ *trans* to P, 2H septet, 7.5 Hz); 2.51 ($\mathrm{Au}\mathit{CH_2}\mathrm{CH_2CH_3}$ *trans* to P, 2H, q, 7.7 Hz); 6.9–7.6 ($\mathrm{PPh_3}$, 15H, m). ^{13}C{^{1}H} NMR: δ 12.7 (AuMe, d, 6.1 Hz); 19.0 ($\mathrm{AuCH_2}\mathit{C}\mathrm{H_2CH_3}$ *trans* to P, d, 11.0 Hz); 20.4 ($\mathrm{AuCH_2CH_2}\mathit{C}\mathrm{H_3}$, *cis* to P, s); 24.0 ($\mathrm{AuCH_2}\mathit{C}_2\mathrm{CH_3}$ *cis* to P, s); 24.4 ($\mathrm{AuCH_2C_2}\mathit{C}\mathrm{H_3}$ *trans* to P, d, 4.9 Hz); 35.7 ($\mathrm{Au}\mathit{C}\mathrm{H_2CH_2CH_3}$ *cis* to P, d, 4.9 Hz); 39.2 ($\mathrm{Au}\mathit{C}\mathrm{H_2CH_2CH_3}$ *trans* to P, d, 117.2 Hz).

cis-AuMe(Bu)$_2$(PPh$_3$) (**1f**) yield 59%. M.p. 59°C. Anal. Found: C, 54.80; H, 6.28. $\mathrm{C_{27}H_{36}PAu}$ calc.: C, 55.10; H, 6.17%. ^{1}H NMR: δ 0.58 (AuMe, 3H, d, 6.8 Hz); 0.85 ($\mathrm{AuCH_2CH_2CH_2}\mathit{CH_3}$ *cis* to P, 3H, t, 7.1 Hz); 1.11 ($\mathrm{AuCH_2CH_2CH_2}\mathit{CH_3}$ *trans* to P, 3H, t, 7.5 Hz); 1.15–1.35 ($\mathrm{Au}\mathit{CH_2CH_2CH_2}\mathrm{CH_3}$ *cis* to P, 6H, m); 1.71 ($\mathrm{AuCH_2CH_2}\mathit{CH_2}\mathrm{CH_3}$ *trans* to P, 2H, sextet, 7.5 Hz); 2.18 ($\mathrm{AuCH_2}\mathit{CH_2}\mathrm{CH_2CH_3}$ *trans* to P, 2H, sextet, 7.8 Hz); 2.49 ($\mathrm{Au}\mathit{CH_2}\mathrm{CH_2CH_2CH_3}$ *trans* to P, 2H, q, 7.8 Hz). ^{13}C{^{1}H} NMR: δ 12.7 (AuMe, d, 6.1 Hz); 14.4, 14.6 ($\mathrm{AuCH_2CH_2CH_2}\mathit{C}\mathrm{H_3}$ either *cis* or *trans* to P, s); 27.6 ($\mathrm{AuCH_2}\mathit{C}\mathrm{H_2CH_2CH_3}$ *trans* to P, d, 11.0 Hz); 29.0 ($\mathrm{AuCH_2CH_2}\mathit{C}\mathrm{H_2CH_3}$ *cis* to P, s); 32.7 ($\mathrm{Au}\mathit{C}\mathrm{H_2CH_2CH_2CH_3}$ *cis* to P, d, 4.9 Hz); 32.9 ($\mathrm{AuCH_2}\mathit{C}\mathrm{H_2CH_2CH_3}$ *cis* to P, s); 33.5 ($\mathrm{AuCH_2CH_2}\mathit{C}\mathrm{H_2CH_3}$ *trans* to P, d, 6.1 Hz); 36.8 ($\mathrm{Au}\mathit{C}\mathrm{H_2CH_2CH_2CH_3}$ *trans* to P, d, 117.2 Hz).

Acidolysis of ***1d–1f*** *with sulfuric acid*

A flask with a rubber septum containing a settled amount of *cis*-dialkylmethyl(triphenylphosphine)gold(III) was evacuated. Sulfuric acid (*ca.* 0.2 cm^3) was added with a hypodermic syringe. Gases evolved were quantitatively analyzed by GC by the internal standard method after 1 h. Liquid products were collected by dissolving them in toluene or ether (1 cm^3) and were then analyzed by GC. **1d** (0.0188 mmol): $\mathrm{CH_4}$, 0.0141 mmol (75%); $\mathrm{C_2H_6}$, 0.0030 mol (16%); $\mathrm{C_3H_8}$, 0.0040 mmol (21%); n-$\mathrm{C_4H_{10}}$, 0.013 mmol (72%). **1e** (0.0284 mmol): $\mathrm{CH_4}$, 0.025 mmol (87%); $\mathrm{C_3H_8}$, 0.0030 mmol (12%); n-$\mathrm{C_4H_{10}}$, 0.0060 mmol (21%); n-$\mathrm{C_4H_{10}}$, 0.012 mmol (43%). **1f** (0.0199 mmol): $\mathrm{CH_4}$, 0.0152 mmol (76%); n-$\mathrm{C_4H_{10}}$, 0.0012 mmol (6%); n-$\mathrm{C_5H_{12}}$, 0.0022 mmol (11%); n-$\mathrm{C_8H_{18}}$, 0.049 mmol (25%).

Reactions of 1d–1f with dry hydrogen chloride

A settled amount of the complex was taken in a flask equipped with a rubber septum and dissolved in tetralin (1.0 cm^3). An equimolar amount of a tetralin solution of dry hydrogen chloride (0.030 N) was added with a syringe. Gases evolved in the reaction were quantitatively analyzed by GC after 1 h. **1d** (0.0186 mmol): CH_4, 0.0141 (76%): C_2H_6, 0.0032 mmol (17%). **1e** (0.0180 mmol): CH_4, 0.0151 (84%); C_3H_8, 0.0023 mmol (13%). **1f** (0.0175 mmol): CH_4, 0.0158 (90%); n-C_4H_{10}, 0.0024 mmol (14%).

Thermolysis of 1d–1f

A flask containing a settled amount of the complex with a rubber septum was evacuated and was heated at 70°C for 1 h. Gases evolved and liquids formed in the thermolysis were quantitatively analyzed as mentioned in the acidolysis. The resulting gold(I) complex was collected after evaporation of all the volatile matters and then quantitatively analyzed by NMR spectroscopy. **1d** (0.0203 mmol): C_3H_8, 0.005 mmol (22%); n-C_4H_{10}, 0.0140 mmol (69%); AuEt(PPh_3), 0.002 mmol (11%); AuMe(PPh_3), 0.0148 mmol (73%). **1e** (0.0164 mmol): n-C_4H_{10}, 0.030 mmol (18%); n-C_6H_{14}, 0.0093 mmol (57%); Au(^{n}Pr)(PPh_3), 0.021 mmol (13%); AuMe(PPh_3), 0.0116 mmol (71%). **1f** (0.0173 mmol): n-C_5H_{12}, 0.028 mmol (16%); n-C_8H_{18}, 0.0057 mmol (33%); Au(^{n}Bu)(PPh_3), 0.023 mmol (13%); AuMe(PPh_3), 0.0100 mmol (58%).

Acknowledgement

Authors thank the financial support from the Grant-in-Aid for Scientific Research on Special Area from the Ministry of Education, Science and Culture, Japan.

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