Headline Articles

Synthesis, Structure, and Reactivities of *cis*-Dimethyl(η^1-allyl)gold(III) Complex. Diastereoselective Allylation of Aromatic Aldehyde

Takuo Sone, Satoshi Ozaki, Noriko C. Kasuga,# Atsushi Fukuoka, and Sanshiro Komiya*

Department of Applied Chemistry, Faculty of Technology, Tokyo University of Agriculture and Technology, 2-24-16 Nakacho, Koganei, Tokyo 184

(Received December 8, 1994)

cis-Dimethyl(η^1-allyl)(triphenylphosphine)gold(III), *cis*-[$AuMe_2$(η^1-allyl)(PPh_3)] (η^1-allyl=allyl (**1**), crotyl (**2**), methallyl (**3**)) has been synthesized by reaction of *cis*-[$AuMe_2X(PPh_3)$] (X=I, NO_3) with corresponding Grignard reagents. X-Ray structure analysis of **2** shows that **2** has a typical square planar *cis* configuration and the crotyl ligand binds to Au by η^1-mode: orthorhombic, space group $P2_12_12_1$, a=9.816(2), b=23.208(4), c=9.5290(9) Å, Z=4, $R(R_w)$=0.037(0.041) with use of 2551 reflections. Reactions of **2** with HCl and Br_2 selectively give 1-butene and 3-bromo-1-butene, respectively, indicating γ-regioselectivity of the reactions. Compounds **1**—**3** react with aldehydes and ketones to give the corresponding homoallyl alcohols. C–C bond formation also takes place at the γ-position of η^1-allyl moiety selectively. The rate of the allylation reaction of carbonyl compounds decreases in the order of methallyl (**3**)>allyl (**1**)>crotyl (**2**) gold(III) complexes. The homoallyl alcohol formed by the reaction of **2** with benzaldehyde is a diastereoisomeric mixture of 2-methyl-1-phenyl-3-buten-1-ol, with high *anti* selectivity. Both the reaction rate and *anti* selectivity in the allylation reaction were reduced by addition of tertiary phosphines such as PPh_3 and PCy_3, and a 6-membered transition state has been proposed, which indicates coordination of the carbonyl group to a T-shape Au intermediate produced by dissociation of the PPh_3 ligand.

Allyl metals are important and versatile compounds and have attracted much attention in organic syntheses,[1] since they could serve as convenient synthetic tools involving well stereo-controlled C–C bond formation mediated by metal coordination.[2] Two binding modes of the allyl moiety to the metal are known: one is η^1-allyl and the other η^3-allyl.[1] The former is frequently observed in non-transition metals, and the latter in late transition metals such as Pd and Pt. It is very worthwhile to understand the chemical reactivities of isolated allyl metal complexes, since they would provide us fundamental information and ideas on these important organometallic species. Among the allyl metals, chemistry of structurally established η^3-allyl complexes is quite well documented,[3] but that of η^1-allyl metal complexes is relatively unexplored.[4—6] Especially examples of allylgold are very limited: No allylgold(III) complexes are known and only two examples of an allylgold(I) complex, Au(η^1-$CH_2CR{=}CH_2$)(PPh_3) (R=H, Me)[7] and Au(η^1-C_5H_5)(L) (L=PEt_3, PPh_3)[8,9] have been reported. We have succeeded in isolation of the first η^1-allylgold(III) complexes having a triphenylphosphine ligand by the reaction of *cis*-[$AuMe_2$(X)(PPh_3)] (X=I, NO_3) with an allyl Grignard reagent. This paper gives a full account of the synthesis, structure, and properties of η^1-allylgold(III) complexes involving selective allylation of aldehyde[10] by these complexes. A part of these results has been reported in a preliminary form.[11]

#Present address: Department of Material Science, Faculty of Science, Kanagawa University, 2946 Tsuchiya, Hiratsuka, Kanagawa 259-12.

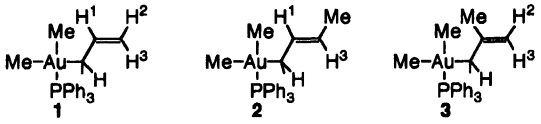
Results and Discussion

Synthesis and Characterization of *cis*-Dimethyl(η^1-allyl)gold(III) Complexes. Reaction of *cis*-dimethyl(iodo or nitrato)(triphenylphosphine)gold(III) with an excess of allylmagnesium bromide in ether at −40 °C gave *cis*-dimethyl(η^1-allyl)(triphenylphos-

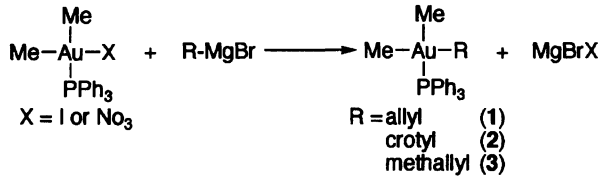
Table 1. ^{1}H NMR and IR Spectral Data of *cis*-[AuMe$_2$(η^1-allyl)(PPh$_3$)]

Complex	^{1}H NMR[a]								IR[c]
	Au–Me (J_{HP} in Hz)		Au–R					PPh$_3$	ν(C=C)
	cis to P	*trans* to P	Au–CH$_2$	H^1	H^2	H^3	Me		
1[b]	0.65 (d, 7.1)	1.76 (d, 8.8)	2.17 (t)	6.15 (ddt)	4.71 (dd)	4.67 (dd)		6.9—7.5 (m)	1608
2[b]	0.63 (d, 7.1)	1.76 (d, 9.0)	2.11 (t)	5.74 (dt)		4.93 (dq)	1.74 (d)	6.9—7.5 (m)	1643
3	0.65 (d, 7.1)	1.73 (d, 9.0)	2.11 (d)		4.5–4.7 (m)		1.59 (s)	6.9—7.5 (m)	1616

a) 200 MHz, ppm from TMS in C_6D_6 at r.t., Abbreviation; d, doublet; t, triplet; dd, double doublet; dt, double triplet; dq, double quartet; ddt, double double triplet; m, multiplet. b) Coupling constants in the allyl group; **1**, $J_{H^1H^3}=16.5$ Hz, $J_{H^1H^2}=10.3$ Hz, $J_{H^2H^3}=3.1$ Hz, $J_{H^1H}=J_{HP}=9.0$ Hz; **2**, $J_{H^1H^3}=14.9$ Hz, $J_{H^2Me}=6.4$ Hz, $J_{H^1H}=J_{HP}=8.8$ Hz. c) KBr disk, cm^{-1}.



phine)gold(III), (**1**) in good yield. Analogous crotyl and methallyl gold(III) complexes, *cis*-[AuMe$_2$(R)(PPh$_3$)] (R=crotyl or (*E*)-2-butenyl (**2**), methallyl or 2-methyl-2-propenyl (**3**)) were also synthesized by the same procedure (Eq. 1). These complexes were purified by recrystallization from an ether/hexane mixture or pentane as pale yellow crystals and characterized by elemental analysis, IR and NMR spectroscopy, and chemical reactions. The ^{1}H NMR and IR data of η^1-allylgold(III) complexes are summarized in Table 1 and ^{13}C NMR data in Table 2.



(1)

^{1}H NMR of **1** in C_6D_6 gives two doublets at 0.65 and 1.76 ppm due to Au–methyl groups *cis* and *trans* to the triphenylphosphine ligand, respectively. This result suggests a square planar geometry with *cis* configuration of **1**. The η^1-coordination mode of the allyl moiety was deduced by the following spectroscopic analyses. ^{1}H NMR of the methylene protons in the allyl group appears as a triplet at 2.17 ppm due to accidental coincidence of coupling constants with both neighboring protons and P nuclei. Three vinylic protons appear as two double doublets and a double double triplet at 4.67, 4.71, and 6.15 ppm, respectively. Absence of couplings between vinylic protons and a P nucleus suggests uncoordination of the allyl ligand. This is also supported by the ^{13}C NMR: The methylene carbon appears as a doublet at 36.1 ppm by coupling with P nucleus, but vinylic carbons appear as two singlets at 106.4 and 143.0 ppm. Similar spectroscopic data have been obtained for **2** and **3**. For **2**, the coupling constant between two vinylic protons has a large value ($J_{HH}=14.9$ Hz), suggesting a *trans* configuration of the crotyl group. IR spectrum of **1** showing a strong absorption band at 1608 cm^{-1} attributable to ν(C=C) also supports the uncoordinated double bond of the allyl ligand.

Molecular Structure of 2. The molecular structure of **2** was unequivocally confirmed by X-ray structure analysis. A suitable single crystal of **2** was obtained from ether/hexane. Crystal data, atomic coordinates and selected bond lengths and angles for **2** are summarized in Tables 3, 4, and 5, respectively. The molecular structure of **2** is depicted in Fig. 1, where **2** has a typical square planar geometry at Au and the η^1-crotyl ligand lies on the site *cis* to the triphenylphosphine ligand. The results are fully consistent with the above spectroscopic data. The Au–C(1) bond length (2.13(1) Å) is significantly longer than the Au–C(2) (2.07(1) Å), indicating slightly stronger *trans* influence of the crotyl ligand than PPh$_3$. The C(4)–C(5) bond length in the crotyl ligand is 1.34(2) Å, being consistent with the uncoordination of the C=C double bond. The crotyl ligand itself has a *trans* configuration and the vinylic carbons (C(4) or C(5)) stay far from the Au center to avoid the coordination. The observed bond lengths and angles of the allyl moiety are similar to those of well established Pd and Pt η^1-allyl derivatives, which were measured by X-ray structure analysis.[12,13] Other bond lengths and angles in **2** were in the normal range and unusual intra- and intermolecular interactions were not observed.

Reaction of Allylgold(III) Complexes with HCl and Br$_2$. Reaction of (η^1-allyl)gold(III) complex **1** with hydrogen chloride in benzene at room temperature smoothly generated propylene (95%/Au) and *cis*-[AuMe$_2$Cl(PPh$_3$)] (98%), quantitatively. γ-Regioselectivity of the protonolysis was easily understood by the similar acidolysis of (η^1-crotyl)gold(III) complex (**2**)

Table 2. ^{13}C NMR Spectral Data of *cis*-[AuMe$_2$(η^1-allyl)(PPh$_3$)][a)]

Complex	Au–Me		Au–R				PPh$_3$
	cis to P	*trans* to P	C_1	C_2	C_3	Me	
1	10.2 (d, 6.1)	18.4 (d, 118.4)	36.1 (d, 4.9)	143.0	106.4		128–135
2	10.6 (d, 6.1)	18.0 (d, 113.5)	34.5 (d, 4.9)	135.7	116.9	18.6	128–135
3	10.9 (d, 7.3)	21.8 (d, 116.0)	39.0 (d, 3.7)	150.4	106.0	25.9	128–135

a) 50 MHz, ppm from TMS in C_6D_6 at r.t., Numbers in parentheses indicate coupling constants with phosphorus nucleus in Hz., Abbreviation; d, doublet.

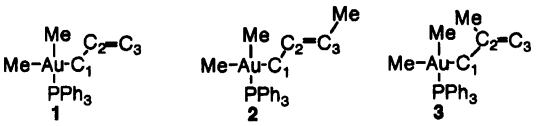


Table 3. Crystal Data and Details of the Structure Determination of **2**

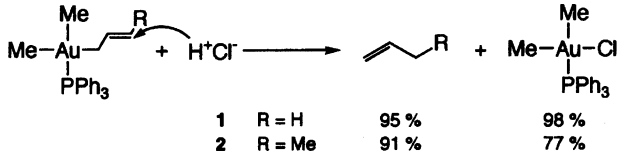
(A) Crystal data	
Empirical formula	$C_{24}H_{28}PAu$
Formula weight	544.43
Space group	$P2_12_12_1$ (#19)
Crystal system	Orthorhombic
Lattice parameter	
a/Å	9.816(2)
b/Å	23.208(4)
c/Å	9.5290(9)
V/Å^3	2170.8(5)
Z	4
D_{calcd}/g cm^{-3}	1.666
F_{000}	1064.00
μ(Mo$K\alpha$)/cm^{-1}	68.79
(B) Data collection and refinement	
Radiation	Mo$K\alpha$ (λ=0.71069 Å)
Temp	23 °C
Scan type	ω–2θ
2θ Range	$3° < 2\theta < 55°$
No. of reflections measured	2805
No. observations ($I > 3\sigma(I)$)	2551
No. variables	236
Structure solution	Patterson method
Residuals: R;[a)] R_w[b)]	0.037; 0.041

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

Table 4. Final Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients (Å^2) of **2**

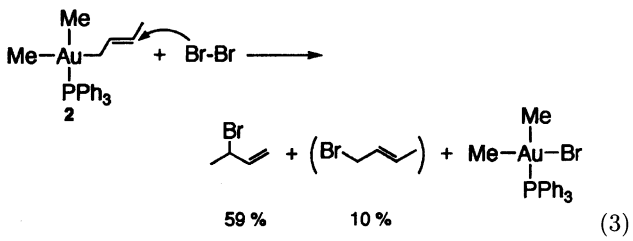
Atom	x	y	z	B_{eq}
Au	−1.01193(4)	−0.18742(2)	−0.67216(4)	3.253(8)
P	−1.0894(3)	−0.1507(1)	−0.7938(3)	2.91(5)
C(1)	−0.852(1)	−0.1410(6)	−0.573(1)	4.9(3)
C(2)	−0.947(1)	−0.2608(5)	−0.569(1)	5.6(3)
C(3)	−1.165(1)	−0.2403(5)	−0.762(1)	4.6(3)
C(4)	−1.115(1)	−0.2760(6)	−0.870(2)	5.5(3)
C(5)	−1.115(1)	−0.2767(6)	−1.005(2)	6.1(4)
C(6)	−1.089(2)	−0.3142(7)	−1.113(2)	9.1(5)
C(7)	−1.257(1)	−0.0806(4)	−0.740(1)	3.2(2)
C(8)	−1.335(1)	−0.1135(5)	−0.650(1)	3.8(2)
C(9)	−1.464(1)	−0.0951(5)	−0.614(1)	5.2(3)
C(10)	−1.518(1)	−0.0452(5)	−0.670(1)	4.7(3)
C(11)	−1.449(1)	−0.0121(5)	−0.759(1)	4.4(3)
C(12)	−1.311(1)	−0.0304(5)	−0.793(1)	3.8(3)
C(13)	−1.099(1)	−0.1202(4)	−0.982(1)	3.2(2)
C(14)	−0.987(1)	−0.1467(4)	−1.046(1)	4.0(2)
C(15)	−0.989(1)	−0.1609(5)	−1.185(1)	4.9(3)
C(16)	−1.106(1)	−0.1504(6)	−1.246(1)	5.1(3)
C(17)	−1.217(1)	−0.1259(6)	−1.201(1)	5.4(3)
C(18)	−1.216(1)	−0.1105(5)	−1.062(1)	4.2(3)
C(19)	−0.987(1)	−0.0401(4)	−0.775(1)	3.4(2)
C(20)	−0.889(1)	−0.0243(5)	−0.871(1)	4.4(3)
C(21)	−0.811(1)	0.0253(6)	−0.850(2)	6.0(4)
C(22)	−0.831(1)	0.0578(5)	−0.732(2)	5.8(4)
C(23)	−0.924(1)	0.0407(6)	−0.634(2)	6.5(4)
C(24)	−1.003(1)	−0.0072(5)	−0.654(1)	5.2(3)

since only 1-butene (91%/Au) was liberated (Eq. 2).



(2)

Reaction of **2** with Br_2 in benzene-d_6 also gave 3-bromo-1-butene (59%/Au) as a main product by γ-attack. A small amount of crotyl bromide (10%/Au) was also formed (Eq. 3). Such preferential γ-attack of H^+ and Br_2 on the η^1-allyl group has been well established for both transition and non-transition metal allylic compounds.[5c,14)]



(3)

Table 5. Selected Bond Lengths and Angles for **2** [a]

	(A) Bond lengths/Å		
Au–C(1)	2.12(1)	P–C(13)	1.82(1)
Au–C(2)	2.07(1)	P–C(19)	1.83(1)
Au–C(3)	2.12(1)	C(3)–C(4)	1.41(2)
Au–P	2.349(3)	C(4)–C(5)	1.33(2)
P–C(7)	1.82(1)	C(5)–C(6)	1.48(2)
	(B) Bond angles/deg		
C(1)–Au–C(2)	88.7(5)	Au–P–C(13)	110.7(3)
C(2)–Au–C(3)	86.3(5)	Au–P–C(19)	116.5(4)
C(3)–Au–P	92.2(3)	Au–C(3)–C(4)	112.7(9)
P–Au–C(1)	92.8(4)	C(3)–C(4)–C(5)	128(1)
Au–P–C(7)	114.5(4)	C(4)–C(5)–C(6)	124(1)

a) Numbers in parentheses indicate standard deviations.

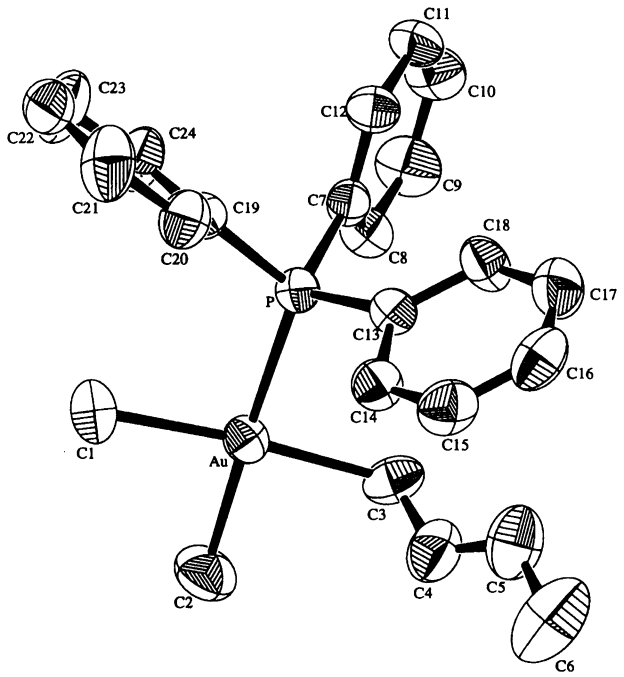


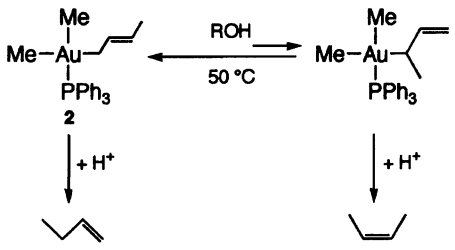
Fig. 1. ORTEP drawing of *cis*-$AuMe_2(\eta^1$-crotyl)-(PPh_3) (**2**) with the probability ellipsoids at the 50% level.

Alcoholysis. Heating of a methanol solution of **1** and **2** at 50 °C also generated only propylene and butenes, respectively, to give a colorless solution (Table 6). Butenes liberated in the methanolysis of **2** contained a 1 : 1 mixture of *cis*-2-butene and 1-butene, but no *trans*-2-butene. Similar results were also obtained in alcoholysis with ethanol or 2-propanol. These results can be interpreted by the similar γ-selective alcoholysis of the crotyl ligands. Especially absence of *trans*-2-butene excludes the direct protonolysis at α-carbon. A notable feature of the reaction is the formation of thermodynamically unstable *cis*-2-butene. This suggests the involvement of facile isomerization of the crotyl ligand into 1-methylallylgold(III) species during the reaction (Eq. 4). The fact probably arises from the preferred conformation of the 1-methylallylgold(III) species in the transition state (Scheme 1).[15,16]

Table 6. Alcoholysis of *cis*-$AuMe_2(\eta^1$-allyl)(PPh_3) in ROH at 50 °C [a]

Run	Complex	ROH	Time (min)	Gas[b] (%/Au)
1	**1**	MeOH	46	Propylene (90)
2	**2**	MeOH	41	1-Butene (48)
				cis-2-Butene (50)
3	**2**	EtOH	104	1-Butene (44)
				cis-2-Butene (47)
4	**2**	*i*-PrOH	174	1-Butene (48)
				cis-2-Butene (44)
				Methane (29)

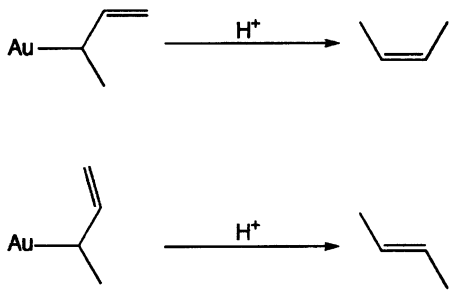
a) Carried out in a vacuum. b) Yields were determined by GC analysis.



(4)

Isolation of the resultant gold complexes in the methanolysis of **2** has failed. Workup of the resulted methanol solution gave $[AuMe_3(PPh_3)]$[17] as an only isolable material. However, addition of MeI to the reaction mixture after the alcoholysis gave Me_2O and the introduction of CO gave *cis*-$[AuMe_2(COOMe)(PPh_3)]$.[18] These results suggest the formation of *cis*-dimethyl(methoxo)-(triphenylphosphine)gold(III) in methanol. Formation of $[AuMe_3(PPh_3)]$ can arise from disproportionation of the dimethyl(methoxo)gold(III) intermediate. In the case of the reaction of **2** with 2-propanol, a considerable amount of methane was evolved in addition to butenes. The mechanism for the methane formation is not now clear, but it is possibly due to decomposition of the *cis*-dimethyl(alkoxo)gold(III) species.

Reaction with Carbonyl Compounds. Reaction of **1** with benzaldehyde in benzene-d_6 at 50 °C led to the formation of 1-phenyl-3-buten-1-ol (77%/Au) (Eq. 5). Similar reactions of **2** and **3** gave corresponding homoallyl alcohols in high yields as listed in Table 7. The reactions were considered to proceed by the insertion of aldehyde into the Au–allyl bond to give



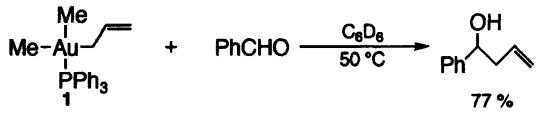
Scheme 1.

Table 7. Reactions of *cis*-[$AuMe_2(\eta^1$-allyl)(PPh_3)] with ArCHO in C_6D_6[a)]

Run	Complex	ArCHO	Additive	Temp °C	Homoallyl alcohol Yield/% Au	*anti* : *syn*	Au complex (Yield/%)
1	**1**	PhCHO	None	50	77[b)]	—	$AuMe_3(PPh_3)$[e)] (26)
2	**2**	PhCHO	None	50	71[c)]	59 : 41	$AuMe_3(PPh_3)$[e)] (28)
3	**3**	PhCHO	None	50	96[d)]	—	$AuMe_3(PPh_3)$[e)] (19)
4	**2**	PhCHO	$CH_2(CN)_2$	50	90[c)]	60 : 40	*cis*-$AuMe_2[CH(CN)_2](PPh_3)$ (84)
5	**2**	PhCHO	$CH_2(CN)_2$	25	92[c)]	84 : 16	*cis*-$AuMe_2[CH(CN)_2](PPh_3)$ (86)
6[f)]	**2**	PhCHO	$CH_2(CN)_2$	0	63[c)]	100 : 0	*cis*-$AuMe_2[CH(CN)_2](PPh_3)$ (26)
7	**2**	*p*-tolCHO	$CH_2(CN)_2$	25	96[c)]	83 : 17	*cis*-$AuMe_2[CH(CN)_2](PPh_3)$ (67)
8	**2**	*o*-tolCHO	$CH_2(CN)_2$	25	96[c)]	83 : 17	*cis*-$AuMe_2[CH(CN)_2](PPh_3)$[g)]
9	**2**	*p*-$MeOC_6H_4CHO$	$CH_2(CN)_2$	25	99[c)]	84 : 16	*cis*-$AuMe_2[CH(CN)_2](PPh_3)$ (100)
10	**2**	*p*-ClC_6H_4CHO	$CH_2(CN)_2$	25	93[c)]	87 : 13	*cis*-$AuMe_2[CH(CN)_2](PPh_3)$ (77)
11	**2**	*p*-NCC_6H_4CHO	$CH_2(CN)_2$	25	99[c)]	84 : 16	*cis*-$AuMe_2[CH(CN)_2](PPh_3)$ (86)

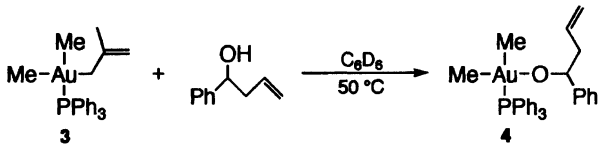
a) Determined by ^1H NMR. b) 1-Phenyl-3-buten-1-ol. c) 2-Methyl-1-phenyl-3-buten-1-ol. d) 3-Methyl-1-phenyl-3-buten-1-ol. e) Unidentified signals due to *cis*-dimethylgold(III) complex were also observed (see experimental). f) In toluene. g) Yield was not determined.

an alkoxogold(III) intermediate followed by protonolysis liberating homoallyl alcohol. The proton source of the reaction seems to be benzaldehyde (vide infra).

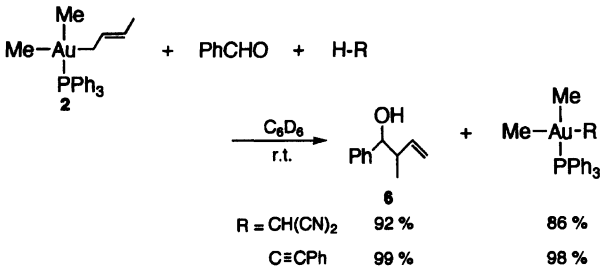


(5)

In the initial stage of the reaction, formation of an alkoxogold(III) intermediate, *cis*-[$AuMe_2$\{OCH(Ph)-$CH_2CH{=}CH_2$\}(PPh_3)] (**4**) was observed by ^1H NMR. Thus new two doublets assignable to *cis* and *trans* Au–Me groups were detected at 0.54 and 1.37 ppm. A triplet signal due to the Au–OCH moiety was also observed at 5.41 ppm. The same ^1H NMR signals due to **4** were also obtained by the reaction of methallylgold(III) complex (**3**) with the corresponding homoallyl alcohol, $PhCH(OH)CH_2CH{=}CH_2$ with liberation of isobutene (Eq. 6). These peaks assignable to **4** gradually disappeared at 50 °C and instead signals due to homoallyl alcohol appeared. At the same time formation of a *cis*-dimethyl(benzoyl)gold(III) species, *cis*-[$AuMe_2(COPh)$-(PPh_3)] (**5**) was also observed. Compound **5** can be independently derived in situ by the reaction of a *cis*-[$AuMe_2(OCH_2CF_3)(PPh_3)$][19)] with benzaldehyde with liberation of 2,2,2-trifluoroethanol. From these results, complexes **4** and **5** were tentatively characterized, since isolation of these alkoxo and benzoyl complexes was not feasible because of their instability in solution as well as difficulty in separation from the contaminating [$AuMe_3(PPh_3)$].[20)] However, when malononitrile or phenylacetylene was added as a proton source, the reactions became more clean: stable dimethylgold(III) complexes such as *cis*-[$AuMe_2(R)(PPh_3)$] (R = $CH(CN)_2$, C≡CPh) were quantitatively formed with concomitant formation of homoallyl alcohol at room temperature (Eq. 7). Such facile abstraction of a proton from active hydrogen compounds by gold(I or III) alkoxides has been established by us recently.[19,21)] Thus, active methylene compounds were always added in the following allylation reaction.



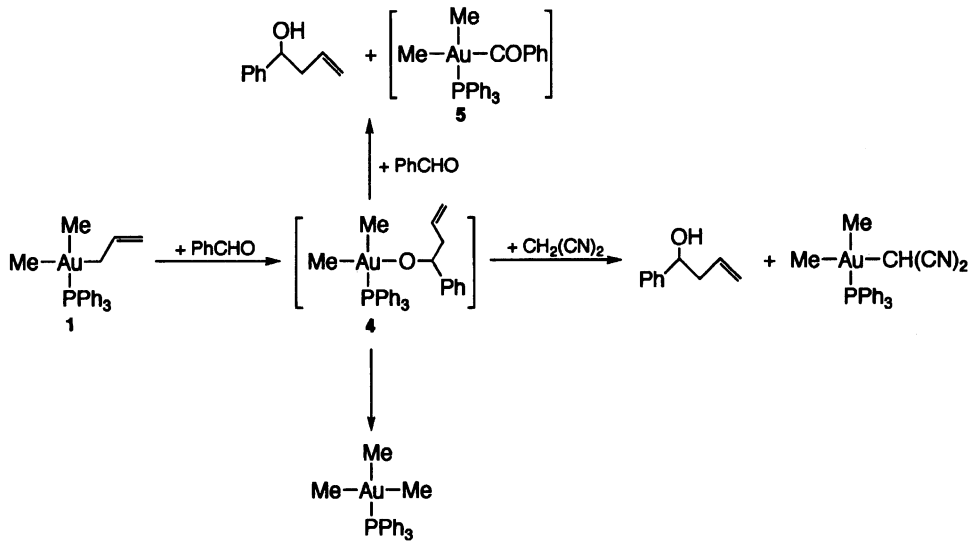
(6)



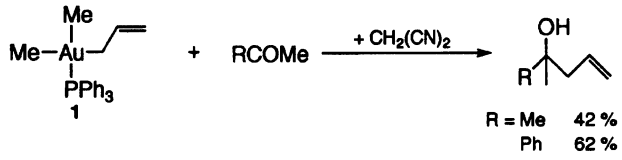
(7)

The proposed mechanism for allylation reaction of benzaldehyde is shown in Scheme 2. Benzaldehyde inserts into the Au-allyl bond in **1** to form an alkoxogold(III) intermediate (**4**). In the presence of malononitrile, **4** abstracts an acidic proton of malononitrile to give homoallyl alcohol and *cis*-[$AuMe_2$\{$CH(CN)_2$\}(PPh_3)]. When proton sources such as malononitrile and phenylacetylene are not present, benzaldehyde acts as a proton donor to give homoallyl alcohol and benzoylgold(III) complex (**5**). Though the routes for formation of [$AuMe_3(PPh_3)$] are not clear at the moment, the disproportionation of unstable alkoxogold(III) intermediate (**4**) may be responsible for this.

Allylation reactions of ketones[22)] such as acetone and acetophenone in the presence of malononitrile proceeded analogously at room temperature in benzene-d_6 to give corresponding homoallyl alcohols (Eq. 8).

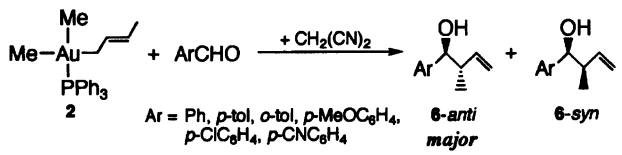


Scheme 2.



(8)

The diastereoselectivities of the reactions were identified. (η^1-Crotyl)gold(III) complex (**2**) reacted with benzaldehyde in the presence of malononitrile in benzene-d_6 at room temperature to give only 2-methyl-1-phenyl-3-buten-1-ol (**6**) (Eq. 9). No 1-phenyl-3-penten-1-ol was formed. This result indicates that the carbonyl carbon only attacks the γ-carbon of the crotyl group similar to the γ-selective electrophilic reactions such as protonolysis and bromination. Diastereoselectivity of the reaction of **2** with various aromatic aldehyde was investigated and the results are summarized in Tables 7 and 8. Aromatic homoallyl alcohols obtained in these reactions were mixtures of diastereomers with high *anti* selectivity at 25 °C (*anti*:*syn*=5:1 Run 5). As seen in Table 7, the *anti* selectivity increases when the temperature is lowered and the complete *anti* selectivity can be attained at 0 °C. Similar *anti* selectivities were observed in the reaction of **2** with *p*- or *o*-substituted benzaldehyde.



(9)

Kinetics of Allylation of Aromatic Aldehyde with Allylgold(III) Complex. To obtain further mechanistic insight into the allylation of carbonyl compounds, the course of the reactions of **1**—**3** with benzaldehyde was examined by ^{1}H NMR in benzene-d_6 at 50 °C. Time-yield curves of the reactions are shown in Fig. 2. The reaction rate decreased in the order of methallyl (**3**)>allyl (**1**)>crotyl (**2**) complexes. Presumably, the lower activity for **2** is due to the steric congestion at the γ-carbon where the C–C bond formation takes place. The result is in accord with the γ-regioselective allylation as mentioned above. On the other hand, the rate for **3** having methyl group at β-carbon is larger than that for **1**. This may reflect the increased nucleophilicity of the allyl unit by the electron-donating methyl group. Figure 3 demonstrates the course of the reactions of **2** with various substituted benzaldehydes. As seen in Fig. 3, substitution at the *p*-position of the phenyl ring by stronger electron-withdrawing groups enhanced the reaction. This is consistent with the nucleophilic allylation toward benzaldehyde. It should be

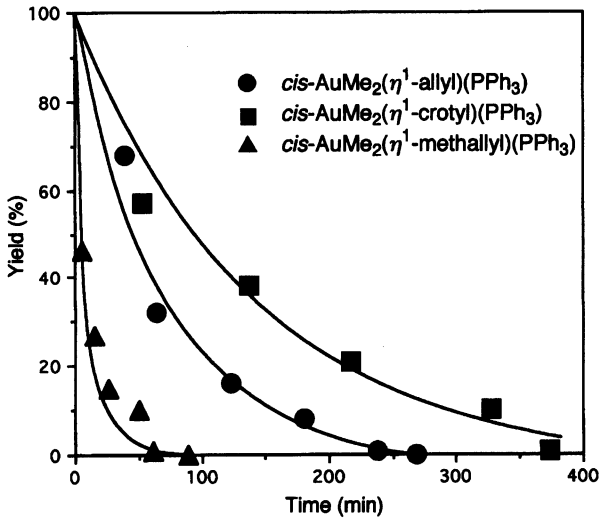


Fig. 2. Time-course of the reaction of *cis*-AuMe$_2$(η^1-allyl)(PPh$_3$) (**1**—**3**) with PhCHO in C_6D_6 at 50 °C. Reaction conditions: (●) [**1**]=0.14 M, [PhCHO]=0.68 M; (■) [**2**]=0.14 M, [PhCHO]=0.74 M; (▲) [**3**]=0.13 M, [PhCHO]=0.68 M, 1 M=1 mol dm^{-3}.

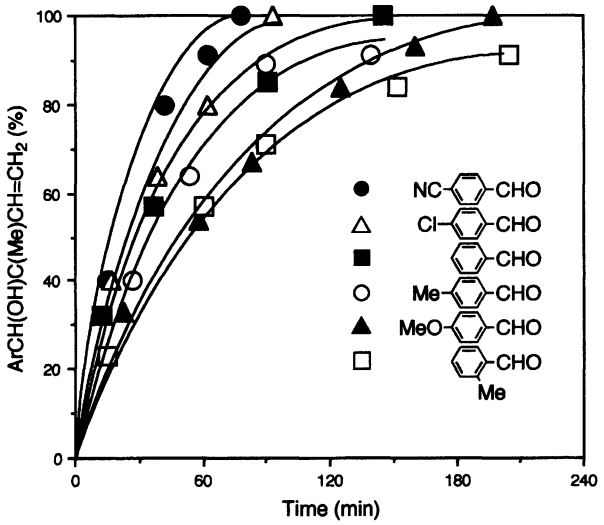


Fig. 3. Time-course of the reaction of *cis*-$AuMe_2(\eta^1$-crotyl)(PPh_3) (**2**) with ArCHO in the presence of HC≡CPh in C_6D_6 at 25 °C. Reaction conditions: [**2**]=0.14 M, [ArCHO]=0.66—0.68 M, [HC≡CPh]=0.42 M.

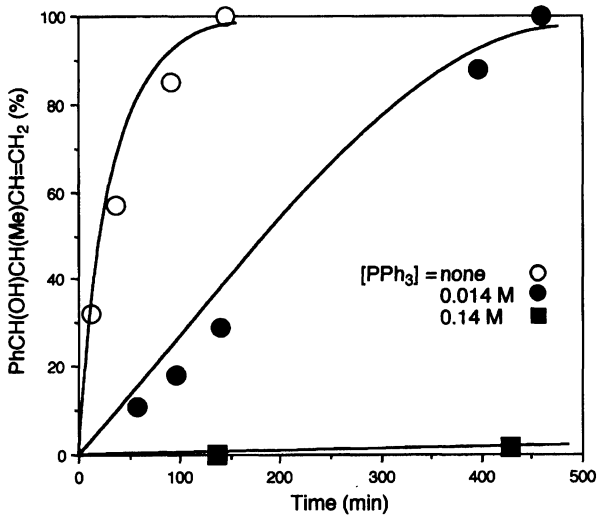


Fig. 4. Time-course of the reaction of *cis*-$AuMe_2(\eta^1$-crotyl)(PPh_3) (**2**) with PhCHO and HC≡CPh in the presence of PPh_3 in C_6D_6 at 25 °C. Reaction conditions: [**2**]=0.14 M, [PhCHO]=0.66—0.68 M, [HC≡CPh]=0.42 M.

noted that reaction rate for *o*-tolualdehyde was slower than that for *p*-tolualdehyde. Steric repulsion between the *o*-methyl group of aldehyde and the crotyl ligand is considered to discourage the reaction.

When PPh_3 was added to the reaction mixture of **2** and benzaldehyde, both the reaction rate and the *anti* selectivity were largely suppressed as shown in Fig. 4 and Table 8. Thus, in the absence of free PPh_3, the reaction was completed in about 2.5 h, but addition of an equimolar amount of PPh_3 greatly suppressed the reaction; it took 1 week to give quantitative amounts of homoallyl alcohol and **6** (Table 8). In this case, contamination of butene by protonolysis significantly increased (Runs 5 and 6). Addition of 10 mol% of PPh_3 per **2** suppressed the initial rate to approximately half (Run 2). These results strongly support the idea that the reaction involves prior dissociation of the PPh_3 ligand.[23]

To investigate the effects of the supporting ligand on the rate and diastereoselectivity, crotylgold(III) complexes having other tertiary phosphine ligands such as PEt_3 or PCy_3 ligand (L=PEt_3 (**7**), PCy_3 (**8**)) were in situ prepared from **2** and the corresponding tertiary phosphine ligand. In both reactions of **7** and **8** with benzaldehyde, the rate decreased considerably and a significant amount of 1-butene was formed for **7** (Runs 6 and 7 in Table 8). *Anti* selectivity for **7** and **8** was lower than that for **2** in the presence of an equimolar amount of PPh_3.

A mechanism of the allylation reaction has been proposed (Scheme 3). The strong retardation effect of added PPh_3 on the reaction rate as well as the high *anti* selectivity suggests the pre-dissociation of the PPh_3 ligand.[23] Then the aldehyde coordinates to the T-shape Au species through the carbonyl oxygen atom giving a 4-coordinate intermediate. To interpret the *anti*/*syn* selectivity, it is possible to assume two configuration for the 6-membered ring transition states (**A** and **B** in Scheme 4). Preferential formation of *anti* isomer arises from structure **B**, where *pseudo*-1,3-diaxial interaction is likely to be small. Such a concept is widely accepted in the reaction of crotylmetal compounds of early transition and non-transition metals with benzaldehyde.[10a,24] In the 6-membered ring transition state, the gold center is considered to serve as a Lewis acid to activate carbonyl group of benzaldehyde. Addition of PPh_3 in the reaction of **2** hinders the coordination of benzaldehyde on Au to discourage the formation of the 6-membered ring transition state, thus decreasing the reaction rate and diastereoselectivity. However, the allylation takes place even without dissociation of PPh_3 though the rate is slow. In this case, benzaldehyde is less likely to coordinate to Au forming a 5-coordinate intermediate, but is apt to react directly toward the γ-allyl carbon making an open chain transition state where no diastereoselectivity is expected. In the case of **7** having a PEt_3 ligand, basicity of the gold center is expected to be increased to hinder the formation of the 6-membered ring. Instead an open chain configuration may be favored to decrease the diastereoselectivity. Decrease in the rate and the *anti* selectivity in **8** having bulky PCy_3 may arise from large steric hindrance in addition to the increased basicity of Au.

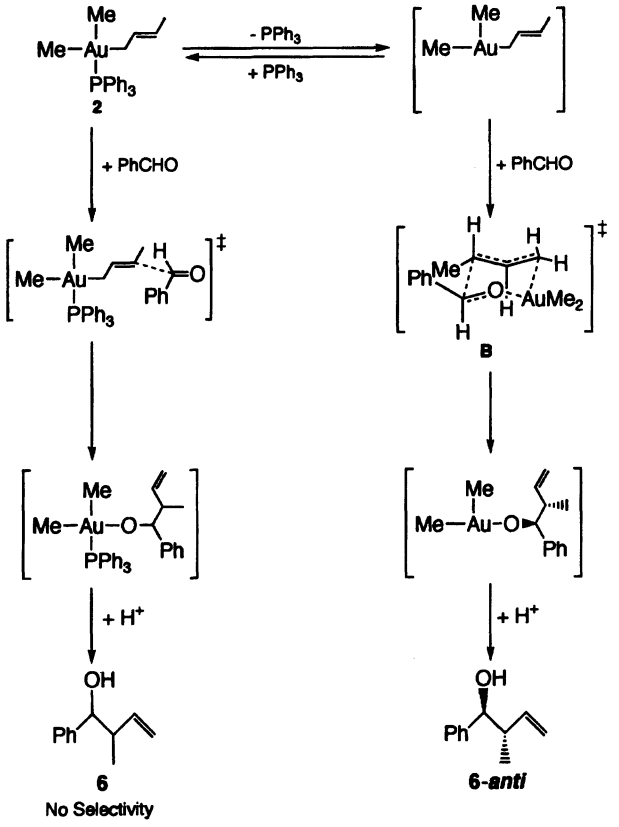
Conclusion

New η^1-allylgold(III) complexes have been synthesized by the reaction of *cis*-dimethyl(aniono)gold(III) complexes with corresponding Grignard reagents. The η^1-mode of the crotyl ligand with *trans* configuration

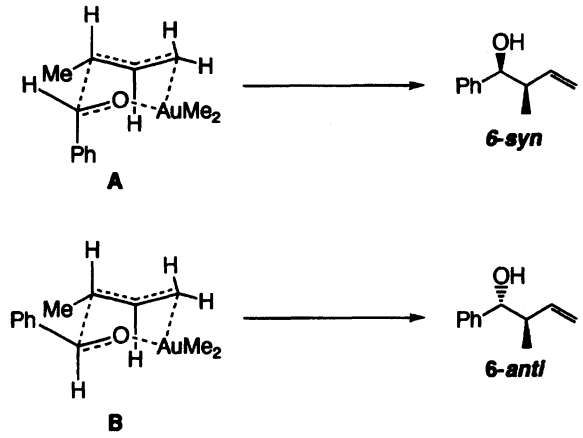
Table 8. Reactions of *cis*-[$AuMe_2(\eta^1$-crotyl)(PPh_3)] (**2**) with PhCHO in the presence of PR_3 and HC≡CPh in C_6D_6 at 25 °C [a)]

Run	**2**	PR_3	Time	Conv	Alcohol[b)]		1-Butene[c)]	Au[d)]
	mol dm^{-3}	mol dm^{-3}	h	%	Yield/%	*anti* : *syn*	%	%
1	0.136	None	2.4	100	>99	89 : 11	0	98
2	0.135	PPh_3, 0.010	7.7	100	>99	89 : 11	0	>99
3	0.134	PPh_3, 0.139	267	81	75	67 : 33	0	82
4	0.136	PPh_3, 0.266	309	87	43	60 : 40	38	86
5	0.139	PPh_3, 0.667	308	80	35	51 : 49	35	80
6	0.136	PEt_3, 0.135	256	64	13	50 : 50	49	e)
7	0.137	PCy_3, 0.147	268	33	28	57 : 43	0	e)

a) Determined by ^{1}H NMR. b) 2-Methyl-1-phenyl-3-buten-1-ol. c) Qualitatively analyzed by GC. d) *cis*-[$AuMe_2$(C≡CPh)(PPh_3)]. e) Not characterized for Au complexes.



Scheme 3.



Scheme 4.

has been confirmed by NMR, IR, and X-ray structure analysis. The η^1-allylgold(III) complexes readily react at γ-carbon with electrophiles such as protons, bromine, and aldehyde to give alkene, allyl bromide, and homoallyl alcohol, respectively. High *anti* selectivity is achieved in the allylation of aldehyde by allylgold(III) complexes, where coordination of aldehyde to a T-shape Au intermediate to form the 6-membered transition state is proposed.

Experimental

All the manipulations were done under deoxygenated N_2 and Ar, or in a vacuum by using standard Schlenk technique unless otherwise noted. Solvents such as benzene, toluene, diethyl ether, THF, pentane, and hexane were dried over Na/benzophenone ketyl. Methanol was dried over magnesium methoxide. These solvents were distilled before use and were stored under N_2. Allyl, crotyl, methallyl, and 1-methylallyl Grignard reagents were prepared from magnesium metal and corresponding organic halides in diethyl ether or THF. *cis*-Dimethyliodo(triphenylphosphine)gold(III)[20] and *cis*-dimethyl(nitrato)(triphenylphosphine)gold(III)[25] were prepared according to the method in the literature. 1-Phenyl-3-buten-1-ol,[26] 2-methyl-1-phenyl-3-buten-1-ol,[27] and 3-methyl-1-phenyl-3-buten-1-ol[28] were prepared by the reaction of corresponding allyl Grignard reagents with aldehyde. All other chemicals were purchased from commercial suppliers and used without further purification. IR spectra were recorded on JASCO A302 and FT-IR 5M spectrometers. ^{1}H and ^{13}C NMR spectra were measured using JEOL FX-200 and GX-400 spectrometers. Chemical shifts are given in ppm from TMS and the coupling constants in Hz. Analytical gas chromatography (GC) was done on a Shimadzu GC-8A instrument equipped with a flame ionization detector and a glass column of Unicarbon A-400 using N_2 as the carrier gas. Elemental analyses were done by a Yanagimoto CHN Autocoder type MT-2.

X-Ray Crystallography. Pale yellow crystals of **2** were obtained by recrystallization from diethyl ether/hexane mixture. Intensity data were collected on a Rigaku AFC-5R diffractometer at room temperature. The data collection was carried out with the program CRYSTAN (Rigaku) on a Facom A-70 computer. The structure was solved by heavy-atom methods and refined by a full-matrix least squares

method and Fourier techniques, which were done using the teXsan crystallographic software package (Molecular Structure Corporation). The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the calculation but not refined. The correct enantiomer was chosen after refinement to convergence of both hands; the one with lower R value was taken as the correct one. Final $R=0.037$ and $R_w=0.041$ for 2551 reflections. The final atomic parameters are listed in Table 4.[29]

Synthesis of *cis*-Dimethyl(η^1-allyl)(triphenylphosphine)gold(III) (1). To a diethyl ether solution (15 ml) of *cis*-[$AuMe_2I(PPh_3)$] (82.5 mg, 0.13 mmol) was added allylmagnesium bromide (1.2 mmol) at −20 °C. After the solution was stirred for 6 h, excess allylmagnesium bromide was slowly hydrolyzed at 0 °C. An ether layer and the ether extracts were combined. Evaporation of the solvent gave a pale yellow solid. Recrystallization from diethyl ether/hexane gave pale yellow crystals. Yield: 42.7 mg (60%). Mp= 100—101 °C (decomp). Found: C, 51.66; H, 5.04%. Calcd for $C_{23}H_{26}PAu$: 52.08; H, 4.94%.

^1H and $^{13}C\{^1H\}$ NMR spectroscopic data of **1**, **2**, and **3** are summarized in Tables 1 and 2, respectively.

Synthesis of *cis*-Dimethyl(η^1-crotyl)(triphenylphosphine)gold(III) (2). The compound was prepared analogously from *cis*-[$AuMe_2I(PPh_3)$] (643.2 mg, 1.17 mmol) and 1-methylallylmagnesium chloride (1.8 mmol). Yield: 457.8 mg (72%). Mp = 103—104 °C (decomp). Found: C, 52.69; H, 5.37%. Calcd for $C_{24}H_{28}PAu$: 52.95; H, 5.18%.

Synthesis of *cis*-Dimethyl(η^1-methallyl)(triphenylphosphine)gold(III) (3). The compound was prepared analogously from *cis*-[$AuMe_2(NO_3)(PPh_3)$] (611.7 mg, 1.11 mmol) and methallylmagnesium chloride (2.0 mmol). Yield: 228.9 mg (39%). Mp=86—87 °C (decomp). Found: C, 52.17; H, 5.18%. Calcd for $C_{24}H_{28}PAu$: 52.95; H, 5.18%.

Reaction of 1 and 2 with HCl. A flask with a rubber septum containing a benzene solution (1 ml) of **1** (21.1 mg, 0.034 mmol) was evacuated. Concd hydrochloric acid (0.0060 ml, 0.068 mmol) was added by a syringe. After this was stirred for 3 h at room temperature, ethylene (1.10 ml) was added as an internal standard. Propylene (0.038 mmol, 95%) evolved in the reaction was quantitatively analyzed by GC. Then the benzene was removed in a vacuum and the residue was dissolved in $CDCl_3$ containing dioxane as an internal standard (0.0010 ml). The formation of *cis*-[$AuMe_2Cl(PPh_3)$] (0.039 mmol, 98%) was observed by ^1H NMR. ^1H NMR ($CDCl_3$) $\delta=0.88$ (3H, d, $J_{HP}=8.5$ Hz, Au-*Me cis* to P), 1.37 (3H, d, $J_{HP}=9.3$ Hz, Au-*Me trans* to P), 7.5—7.7 (15H, m, PPh_3).

Similar acidolysis of **2** (22.0 mg, 0.036 mmol) with hydrochloric acid (0.0040 ml, 0.045 mmol) was done in benzene. The formation of 1-butene (0.036 mmol, 91%) and *cis*-[$AuMe_2Cl(PPh_3)$] (0.0031 mmol, 77%) was confirmed by GC and ^1H NMR, respectively.

Reaction of 2 with Br_2. Compound **2** (22.0 mg, 0.040 mmol) was dissolved in C_6D_6 (0.300 ml) in an NMR tube, and bromine (0.0020 ml, 0.078 mmol) and dioxane as an internal standard (0.0020 ml) were added at room temperature. ^1H NMR analysis showed the formation of 2-bromo-1-butene (0.024 mmol, 59%), 1-bromo-2-butene (0.0040 mmol, 10%), and *cis*-[$AuMe_2Br(PPh_3)$] (0.010 mmol, 26%).

Methanolysis of 1 and 2. A flask with a rubber septum containing a methanol solution (2 ml) of **1** (16.8 mg, 0.032 mmol) was evacuated. After ethylene as an internal standard (1.10 ml) was added, the methanol solution was stirred at 50 °C for 0.5 h. Propylene (0.028 mmol, 90%) evolved in the reaction was quantitatively analyzed by GC. ^1H NMR analysis of the residue in C_6D_6, which was obtained by removal of methanol under vacuum, showed formation of [$AuMe_3(PPh_3)$] (0.0088 mmol, 28%). ^1H NMR (C_6D_6) $\delta=0.61$ (6H, d, $J_{HP}=6.8$ Hz, Au-*Me cis* to P), 1.76 (3H, d, $J_{HP}=6.8$ Hz, Au-*Me trans* to P), 6.9—7.5 (15H, m, PPh_3).

Methanolysis of **2** (16.2 mg, 0.030 mmol) at 50 °C for 0.5 h gave 1-butene (0.014 mmol, 47%), *cis*-2-butene (0.015 mmol, 50%) and [$AuMe_3(PPh_3)$] (0.010 mmol, 34%/Au).

Similar reactions of **2** with other alcohols such as ethanol and 2-propanol were done at 50 °C. Results are summarized in Table 4.

Reaction of 1 with benzaldehyde. The NMR tube was filled with **1** (28.4 mg, 0.056 mmol), C_6D_6 (0.350 ml) and 1,4-dioxane (0.0010 ml) as an internal standard. Benzaldehyde (0.026 ml, 0.26 mmol) was added to the solution and then the NMR tube was heated to 50 °C for 3 h. The ^1H NMR spectrum of the solution indicated the formation of 1-phenyl-3-buten-1-ol (77%) and [$AuMe_3(PPh_3)$] (26%) in addition to *cis*-dimethyl(benzoyl)(triphenylphosphine)gold(III) (**5**). ^1H NMR of **5** showed two doublets at $\delta=0.98$ (3H, d, $J_{HP}=8.3$ Hz, Au-*Me cis* to P) and 1.66 (3H, d, $J_{HP}=9.3$ Hz, Au-*Me trans* to P) ppm. Signals assignable to the benzoyl group and PPh_3 ligand were obscured by the large signal of excess benzaldehyde.

Compound **5** can also be prepared in situ by the reaction of *cis*-[$AuMe_2(OCH_2CF_3)(PPh_3)$] with PhCHO: The NMR tube was filled with *cis*-[$AuMe_2(OCH_2CF_3)(PPh_3)$] (22.7 mg, 0.039 mmol), C_6D_6 (0.350 ml), and 1,4-dioxane (0.0010 ml) as an internal standard. Benzaldehyde (0.020 ml, 0.20 mmol) was added to this solution. After 1 d at room temperature, the ^1H NMR spectrum of the solution indicated the formation of *cis*-dimethyl(benzoyl)(triphenylphosphine)gold(III) (**5**) (0.010 mmol, 25%). In the initial stage of the reaction (after 1 h), formation of an intermediate compound, which was assignable to *cis*-[$AuMe_2\{OCH(Ph)CH_2CH{=}CH_2\}(PPh_3)$] (**4**) was observed. ^1H NMR (C_6D_6 at 50 °C) $\delta=0.54$ (3H, d, $J=8.3$ Hz, Au-*Me cis* to P), 1.37 (3H, d, $J=9.3$ Hz, Au-*Me trans* to P), 5.41 (1H, t, $J=6.4$ Hz, OCH), 2.6 (2H, m, $-CH_2-$), 5.0 (2H, m, $=CH_2$), 6.0 (1H, m, $CH=$), 7.0—7.6 (15H, m, PPh_3). The same ^1H NMR signals were independently obtained by the reaction of **3** with $PhCH(OH)CH_2CH{=}CH_2$: The NMR tube was filled with **3** (14.3 mg, 0.026 mmol), C_6D_6 (0.350 ml), and 1,4-dioxane (0.0010 ml) as an internal standard. $PhCH(OH)CH_2CH{=}CH_2$ (0.010 mg, 0.055 mmol) was added to this solution and then the NMR tube was heated at 50 °C for 1 h. The ^1H NMR spectrum of the solution indicated the formation of *cis*-[$AuMe_2\{OCH(Ph)CH_2CH{=}CH_2\}(PPh_3)$] (**4**) (0.012 mmol, 47%) in addition to [$AuMe_3(PPh_3)$] (0.0062 mmol, 24%).

Diastereoselectivity. ^1H NMR was used to study the diastereoselectivity of 2-methyl-1-aryl-3-buten-1-ol from *cis*-dimethyl(η^1-crotyl)(triphenylphosphine)gold(III) (**2**) and aromatic aldehyde. The ratio of *anti* and *syn* isomers of 2-methyl-1-aryl-3-buten-1-ol was calculated by NMR integration.

The NMR tube containing **2** (about 25 mg) and 1,4-

dioxane (0.0010 ml) as an internal standard in C_6D_6 (0.350 ml) was equipped with a rubber septum cap, and then aromatic aldehyde (about 0.026 ml) and malononitrile (about 0.008 ml) were added at 25—50 °C. ^{1}H NMR spectra of the solution indicated the formation of a diastereoisomeric mixture of 2-methyl-1-aryl-3-buten-1-ol in addition to *cis*-[AuMe$_2${CH(CN)$_2$}(PPh$_3$)]. The *syn*/*anti* ratio of the diastereomers was estimated by NMR integration of C*H*OH signals: ^{1}H NMR (C_6D_6); **6** (*syn*) δ=0.99 (3H, d, J=6.8 Hz, Me), 2.40 (2H, m, C*H*Me), 4.30 (1H, d, J=5.6 Hz, C*H*OH), 4.8—5.2 (2H, m, =CH_2), 5.1—5.3 (1H, m, C*H*=); **6** (*anti*) δ=0.80 (3H, d, J=6.9 Hz, Me), 2.40 (2H, m, C*H*Me), 4.15 (1H, d, J=7.3 Hz, C*H*OH), 4.8—5.2 (2H, m, =CH_2), 5.1—5.3 (1H, m, C*H*=).

When the reaction was done at a low temperature, toluene was used as a solvent. Benzaldehyde (0.24 ml, 0.24 mmol) and malononitrile (0.008 ml, 0.14 mmol) were dissolved in toluene and cooled to 0 °C and then **2** (26.0 mg, 0.048 mmol) was added. After this was stirred for 6 h at 0 °C, toluene was removed in a vacuum and the resulting residue was dissolved in $CDCl_3$ containing dioxane as an internal standard (0.0010 ml). ^{1}H NMR spectrum indicated the formation of **6**-*anti* (0.035 mmol, 74%/Au) and *cis*-[AuMe$_2${CH(CN)$_2$}(PPh$_3$)] (0.013 mmol, 26%).

Results under various reaction conditions are summarized in Tables 7 and 8.

Reaction of 1 with Acetone. The NMR tube containing **1** (21.1 mg, 0.040 mmol) and 1,4-dioxane (0.0010 ml) as an internal standard in C_6D_6 (0.350 ml) was equipped with a rubber septum cap, and to this solution were added acetone (0.014 ml, 0.19 mmol) and malononitrile (0.0022 ml, 0.040 mmol) at room temperature. After 1 d, the ^{1}H NMR spectrum of the solution indicated the formation of 2-methyl-4-penten-2-ol (42%/Au) and *cis*-[AuMe$_2${CH(CN)$_2$}(PPh$_3$)] (73%), which were measured by NMR integration.

The reaction of **1** with acetophenone was done in C_6D_6 analogously to give 2-phenyl-4-penten-2-ol (42%/Au) and *cis*-[AuMe$_2${CH(CN)$_2$}(PPh$_3$)] (70%). A small amount of propylene (14%) was also detected.

Kinetics. ^{1}H NMR spectrometry was used for kinetic study of the formation of homoallyl alcohol from allylgold(III) complexes and aromatic aldehyde. The formation of homoallyl alcohol and the disappearance of starting materials were measured at 23 °C using 1,4-dioxane as an internal standard.

The NMR tube containing *cis*-dimethylgold(III) complexes, **1**—**3** (about 25 mg), PPh$_3$ (0—0.23 mmol), and 1,4-dioxane (0.0010 ml) in C_6D_6 (0.350 ml) was equipped with a rubber septum cap and to this solution were added aromatic aldehyde and phenylacetylene as a proton source at 23 °C. The amounts of homoallyl alcohol formed and starting materials were estimated by comparing the areas of their signals with the internal standard periodically. Results are summarized in Table 8 and Figs. 2, 3, and 4.

In situ Preparation of 7 and 8 by Phosphine Exchange Reaction. The NMR tube containing **2** (25.9 mg, 0.048 mmol) and C_6D_6 (0.350 ml) was equipped with a rubber septum cap and then an equimolar amount of PEt$_3$ (0.0068 ml, 0.047 mmol) was added at room temperature. ^{1}H NMR indicated the formation of *cis*-[AuMe$_2$(η^1-crotyl)(PEt$_3$)] (**7**) in addition to free PPh$_3$. ^{1}H NMR (C_6D_6) δ=0.56 (Au-*Me cis* to P, d, J=6.6), 1.48 (Au-*Me trans* to P, d, J=8.8), 2.09 (Au-CH_2, t, J=8.1), 5.96 (CH$_2$C*H*=, dt, J=15.0, 8.1), 5.41 (=C*H*Me, dq, J=15.0, 6.2), 1.83 (=CH*Me*, d, J=6.2), 1.37 (quint, PCH_2CH$_3$, J=8.4), 0.63 (PCH$_2$CH_3, dt, J=16.4, 8.4).

Similar exchange reaction of **2** with PCy$_3$ gave *cis*-[AuMe$_2$(η^1-crotyl)(PCy$_3$)] (**8**). ^{1}H NMR (C_6D_6) δ=0.62 (Au-*Me cis* to P, d, J=5.4), 1.46 (Au-*Me trans* to P, d, J=8.3), 2.13 (Au-CH_2, t, J=8.3), 6.09 (CH$_2$C*H*=, ddt, J=16.0, 8.3, 1.0), 5.43 (=C*H*Me, dq, J=16.0, 6.4), 1.86 (=CH*Me*, dd, J=6.4, 1.0), 1.0—2.4 (m, PCy$_3$).

References

1) J. P. Collman, L. S. Hegedus, J. R. Norton, and R. G. Finke, "Principles and Applications of Organotransition Metal Chemistry," University Science Books, Mill Valley, CA (1987), and references cited therein.

2) a) G. Consiglio and R. M. Waymouth, *Chem. Rev.*, **89**, 257 (1989); b) J. Tsuji and I. Minami, *Acc. Chem. Res.*, **20**, 140 (1987); c) Y. Yamamoto, *Acc. Chem. Res.*, **20**, 243 (1987).

3) a) A. Yamamoto, "Organotransition Metal Chemistry Fundamental Concepts and Applications," John Wiley & Sons, Inc., New York (1992); b) R. H. Crabtree, "The Organometallic Chemistry of the Transition Metals," 2nd ed, John Wiley & Sons, Inc., New York (1994).

4) a) P. W. Jolly, *Angew. Chem., Int. Ed. Engl.*, **24**, 283 (1985); b) R. Benn, P. W. Jolly, R. Mynott, B. Raspel, G. Schenker, K. P. Shick, and G. Schroth, *Organometallics*, **4**, 1945 (1985); c) R. Benn, G. Gabor, P. W. Jolly, R. Mynott, and B. Raspel, *J. Organomet. Chem.*, **296**, 443 (1985); d) H. Kurosawa, A. Urabe, K. Miki, and N. Kasai, *Organometallics*, **5**, 2002 (1986); e) H. Kurosawa, M. Emoto, H. Ohnishi, K. Miki, N. Kasai, K. Tatsumi, and A. Nakamura, *J. Am. Chem. Soc.*, **109**, 6333 (1987).

5) a) S. Numata, R. Okawara, and H. Kurosawa, *Inorg. Chem.*, **16**, 1737 (1977); b) B. Henc, P. W. Jolly, R. Salz, S. Stobbe, G. Goddard, and C. Kruger, *J. Organomet. Chem.*, **191**, 449 (1980); c) H. Kurosawa, *J. Organomet. Chem.*, **334**, 243 (1987); c) H. Kurosawa and A. Urabe, *Chem. Lett.*, **1985**, 1839; d) H. Kurosawa, K. Shiba, K. Ohkita, and I. Ikeda, *Organometallics*, **10**, 3941 (1991); e) T. Suzuki, M. Ueda, R. Koumoto, and Y. Nakamura, *Bull. Chem. Soc. Jpn.*, **63**, 804 (1990).

6) W. D. McGhee and R. G. Bergman, *J. Am. Chem. Soc.*, **107**, 3388 (1985).

7) R. Huttel, U. Raffay, and H. Reinheimer, *Angew. Chem., Int. Ed. Engl.*, **6**, 862 (1967).

8) A. N. Nesmeyanov, E. G. Perevalova, D. A. Lemennovskii, A. N. Kosina, and K. I. Grandberg, *Izv. Akad. Nauk USSR, Ser. Khim.*, **1969**, 2030.

9) E. G. Perevalova, K. I. Grandberg, E. I. Smyslova, and V. P. Dyadchenko, *Metalloorg. Khim.*, **2**, 699 (1989).

10) a) R. W. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **21**, 555 (1982); b) A. Hosomi, *Acc. Chem. Res.*, **21**, 200 (1988); c) A. Hafner, R. O. Duthaler, R. Marti, G. Rihs, P. R.-Streit, and F. Schwarzenbach, *J. Am. Chem. Soc.*, **114**, 2321 (1992), and references cited therein.

11) S. Komiya and S. Ozaki, *Chem. Lett.*, **1988**, 1431.

12) F. Dahan, C. Agami, J. Levisalles, and F. R.-Munch, *J. Chem. Soc., Chem. Commun.*, **1976**, 505.

13) A. Scrivanti, G. Carturan, U. Belluco, N. B. Pahor,

M. Calligaris, and L. Randaccio, *Inorg. Chim. Acta*, **20**, L3 (1976).
14) G. Courtois and L. Miginiac, *J. Organomet. Chem.*, **69**, 1 (1974).
15) J. A. Verdone, J. A. Mangravite, N. M. Scarpa, and H. G. Kuivila, *J. Am. Chem. Soc.*, **97**, 843 (1975).
16) S. Bank, *J. Am. Chem. Soc.*, **87**, 3244 (1965).
17) A. Tamaki and J. K. Kochi, *J. Chem. Soc., Dalton Trans.*, **1973**, 2620.
18) S. Komiya, T. Sone, S. Ozaki, M. Ishikawa, and N. Kasuga, *J. Organomet. Chem.*, **428**, 103 (1992).
19) T. Sone, M. Iwata, N. Kasuga, and S. Komiya, *Chem. Lett.*, **1991**, 1949.
20) Formation of $[AuMe_3(PPh_3)]$[21] in the attempted isolation of *cis*-$[AuMe_2(OMe)(PPh_3)]$ from MeOH solution was known.[18]
21) S. Komiya, M. Iwata, T. Sone, and A. Fukuoka, *J. Chem. Soc., Chem. Commun.*, **1992**, 1109.
22) a) L. S. Hegedus, S. D. Wagner, E. L. Waterman, and K. S.-Hansen, *J. Org. Chem.*, **40**, 593 (1975); b) J. F. Ruppert and J. D. White, *J. Org. Chem.*, **41**, 550 (1976); c) T. Hiyama, Y. Okude, K. Kimura, and H. Nozaki, *Bull. Chem. Soc. Jpn.*, **55**, 561 (1982).
23) a) S. Komiya and A. Shibue, *Organometallics*, **4**, 684 (1985); b) S. Komiya, S. Ozaki, and A. Shibue, *J. Chem. Soc., Chem. Commun.*, **1986**, 1555; c) S. Komiya, A. Shibue, and S. Ozaki, *J. Organomet. Chem.*, **319**, C31 (1987).
24) H. E. Zimmerman and M. D. Traxler, *J. Am. Chem. Soc.*, **79**, 1957 (1920).
25) S. Komiya and J. K. Kochi, *J. Am. Chem. Soc.*, **98**, 7599 (1976).
26) G. G. Smith and K. J. Voorhees, *J. Org. Chem.*, **35**, 2182 (1970).
27) Y. Yamamoto, H. Yatagai, and K. Maruyama, *J. Am. Chem. Soc.*, **103**, 1969 (1981).
28) E. G. Corey and M. F. Semmelhack, *J. Am. Chem. Soc.*, **89**, 2756 (1967).
29) The complete F_o-F_c data are deposited as Document No. 68022 at the Office of the Editor of Bull. Chem. Soc. Jpn.