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Synthesis, structure and properties of dimethyl(alkoxycarbonyl)gold(III) complexes having a triphenylphosphine ligand *

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Abstract

cis-Dimethyl(alkoxycarbonyl)(triphenylphosphine)gold(III) (*cis*-$AuMe_2(COOR)(PPh_3)$; R = Me (1), Et (2), ^{i}Pr (3)) has been synthesized by the reaction of carbon monoxide with dimethyl(methoxo)(triphenylphosphine)gold(III) prepared *in situ* from *cis*-dimethyliodo(triphenylphosphine)gold(III) and sodium methoxide in methanol. Thermolysis of 1 in benzene leads to a reductive elimination of both methyl acetate and ethane. Protonolysis of 1 with acids such as hydrogen chloride and acetic acid gives *cis*-dimethyl(aniono)(triphenylphosphine)gold(III) accompanied by liberation of carbon monoxide and methanol. Reaction of 1 with acetyl chloride liberates methyl acetate and carbon monoxide. The square planar structure of 1 is unequivocally confirmed by an X-ray diffraction study. Related gold(I) complex, (methoxycarbonyl)(triphenylphosphine)gold(I) is also isolated by a similar reaction of chloro(triphenylphosphine)gold(I) with carbon monoxide in the presence of sodium methoxide.

Introduction

Carbonylation of organic compounds with carbon monoxide is one of the most important fundamental reactions in organometallic chemistry [1]. In the alkoxycarbonylation of organic substances such as alkyl halides and olefins leading to formation of esters, two routes are conceivable [2]. One consists of an initial formation of an acyl intermediate followed by either nucleophilic attack of alcohol toward acyl carbon or reductive elimination from acyl(alkoxo)metal species to give the corresponding esters. Another route involves an alkyl(alkoxycarbonyl)metal intermediate which leads to reductive elimination of esters. Formation of such an alkoxycarbonyl intermediate has been proposed in the Pd catalyzed oxalate synthesis from CO and methanol [3]. In relation to these mechanisms, competitive

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* Dedicated to Professor Akio Yamamoto upon his retirement from the Tokyo Institute of Technology and in honor of his contribution to organometallic chemistry.

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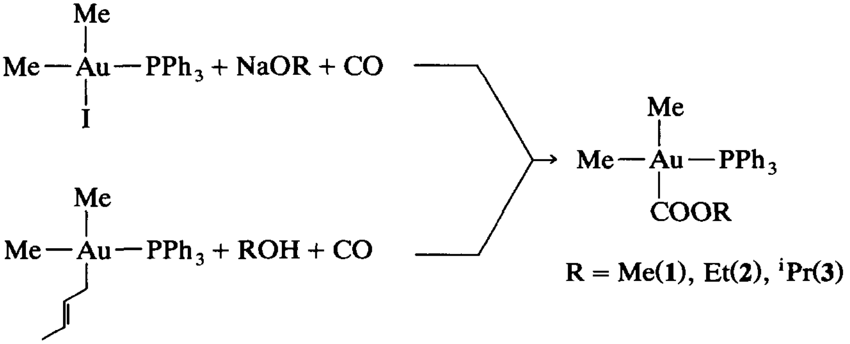
insertion reactions of carbon monoxide into alkyl(alkoxo)nickel(II) [4,5], -palladium(II) [6] and -platinum(II) [7] complexes were reported. In the reaction of alkyl(aryloxo)nickel(II) complexes with CO, insertion of carbon monoxide into the metal carbon bond occurs giving acyl(phenoxo)nickel(II) complex from which the ester can be reductively eliminated on interaction with olefins having electron withdrawing groups or CO [5]. In contrast, methyl(alkoxycarbonyl)platinum(II) complex is isolated in the reaction of methyl(methoxo)platinum(II) complex with CO [7]. However, no reductive elimination of ester was observed. A similar insertion reaction of CO into the perfluoroalkoxopalladium(II) bond in $PdR(OR)L_2$ was also reported [6]. In this reaction an alkyl(alkoxycarbonyl)palladium(II) complex was only determined spectroscopically. In these cases, the formal insertion of carbon monoxide into an alkoxoplatinum or -palladium bond occurs predominantly. We recently found the formation of dimethyl(alkoxocarbonyl)gold(III) complexes by the reaction of *cis*-dimethyliodo(triphenylphosphine)gold(III) with CO in the presence of sodium alkoxide. The paper describes the synthesis, structure and chemical reactivities of alkoxycarbonylgold(III) complexes. Part of these results have been reported in preliminary form [8].

Results and discussion

Interaction of carbon monoxide with a mixture of *cis*-dimethyliodo(triphenylphosphine)gold(III) and sodium alkoxide in the corresponding alcohol at room temperature smoothly gave *cis*-dimethyl(alkoxycarbonyl)(triphenylphosphine)gold(III), $AuMe_2(COOR)(PPh_3)$ (R = Me, **1**; Et, **2**; ^{i}Pr, **3**) in good yield. These compounds were also prepared by the interaction of carbon monoxide with a solution which was obtained by alcoholysis of *cis*-dimethyl(*E*-crotyl)(triphenylphosphine)gold(III) [9] in methanol with a concomitant liberation of butene-1 and -2. In both cases a dimethyl(methoxo)gold(III) complex is considered to be formed prior to the reaction with carbon monoxide (*vide infra*).



These compounds were characterized by elemental analysis, IR and NMR spectroscopy as well as by chemical reactions. Complex **1** has also been unequivocally determined by X-ray structure analysis (*vide infra*). IR spectrum of **1** shows a $\nu(CO)$ band at 1660 cm^{-1} which is characteristic of alkoxycarbonylmetal complexes [10]. ^1H NMR spectrum of **1** also shows a typical singlet at 3.31 ppm assignable to the methoxycarbonylgold moiety in addition to two sets of doublets for gold-methyls at 0.58 and 1.76 ppm, which is consistent with the square planar structure of **1**. The alkoxycarbonyl group is considered to occupy a site *cis* to the triphenylphosphine ligand, since the two gold-methyls are inequivalent as generally observed in *cis*-dimethyl(aniono)(tertiaryphosphine)gold(III) complexes [11]. ^{13}C NMR involving two typical doublets (4.07 ($J(CP)$ = 6.1 Hz) and 9.67 ($J(CP)$ = 106.2 Hz)) and a unique doublet (210.7 ppm ($J(CP) = 12$ Hz) assignable to gold-methyls and a carbonyl carbon, respectively, also supports the above structure.

The reaction is considered to proceed via either an insertion of carbon monoxide into an alkoxometal species formed *in situ* or nucleophilic attack of alkoxide anion towards coordinated carbon monoxide. Such a dimethyl(methoxo)gold(III) intermediate is likely formed by the metathetical reaction of *cis*-dimethyliodogold(III) complex with sodium alkoxide or methanolysis of dimethyl(*E*-crotyl)(triphenylphosphine)gold(III). Formation of dimethyl ether in the reaction of methyl iodide with the solution that was obtained by methanolysis of *cis*-dimethyl(*E*-crotyl)(triphenylphosphine)gold(III) supports the prior formation of such dimethylalkoxogold(III) species. The isolation of an alkoxogold(III) intermediate such as dimethyl(methoxo)(triphenylphosphine)gold(III) was unsuccessful from the reaction mixture and instead only trimethyl(triphenylphosphine)gold(III) was obtained as an isolatable material (see Experimental section). However, the fact that aryloxo and fluoroalkoxo derivatives of dimethylgold(III) can be isolated, also encourages the formation of dimethylmethoxogold(III) complex in these reactions [12]. At present, however, it is difficult to conclude which mechanism is operative in the formation of the alkoxycarbonylgold complexes.

Description of molecular structure of 1

Crystals of **1** were grown from an ether/hexane solution at −30 °C. Crystal data for **1** are summarized in Table 1. Selected bond lengths and bond angles are listed in Tables 2 and 3. The ORTEP drawing of **1** shown if Fig. 1 illustrates the square planar structure of **1**, in which the alkoxycarbonyl ligand is placed *cis* to the triphenylphosphine ligand. The results are consistent with the spectroscopic data. Observed bond lengths and bond angles are quite normal. The carbonyl group in Au-COOMe lies approximately perpendicular to the coordination plane. The bond length of Au–C(2) (2.17(2) Å) is slightly longer than that of Au–C(1) (2.08(2) Å), indicating the stronger *trans* influence of alkoxycarbonyl carbon compared with that of the P ligand. Four bond angles around Au are approximately 90(+2)° and their sum is 360°, indicating a typical square planar structure of **1**.

Reactions of 1 with acetic acid, acetyl chloride and hydrogen chloride

Reactions of **1** with electrophiles such as hydrogen chloride and acetic acid in benzene liberated methanol and carbon monoxide. The resultant gold complexes were *cis*-dimethylchloro(triphenylphosphine)gold(III) and *cis*-dimethyl(acetato)(triphenylphosphine)gold(III), respectively. Acetyl chloride also reacted with **1** to give *cis*-dimethylchloro(triphenylphosphine)gold(III) with liberation of methyl acetate and carbon monoxide.

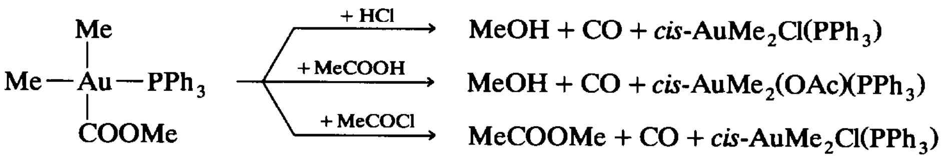


Table 1

Summary of crystallographic data for 1

Formula	$C_{22}H_{24}O_2PAu$
F.W.	518.38
Space group	$P2_12_12_1$
Crystal system	orthorhombic
a (Å)	14.948(5)
b (Å)	18.66(1)
c (Å)	7.374(4)
V (Å^3)	2056(2)
Z	4
Crystal size	$0.2 \times 0.4 \times 0.2$
d_{calc} (g cm^{-3})	1.68
Radiation (Å)	Mo-K_α, 0.71068
μ(Mo-K_α) (cm^{-1})	69.4
Temp.	Room temperature
2θ (deg)	$3 < 2\theta < 50$
Scan type	$\omega/2\theta$
No. of data collected	2699
No. of reflections observed for refinement	2444 ($F_o > 3\sigma(F_o)$)
R [a]	0.0535
R_w [b]	0.0676
Method of phase determination	Direct method

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

A mechanism involving an oxidative addition of these electrophiles such as hydrogen chloride, acetic acid or methyl iodide followed by reductive elimination is not plausible, since no stable organometallic gold(V) complexes are known [13]. The reaction is considered to proceed via an electrophilic reaction of the proton or the acetyl group on the alkoxy group in 1 to liberate methanol. A possible initial gold product is a dimethyl(carbon monoxide)(triphenylphosphine)gold(III) cation which spontaneously liberates carbon monoxide to give *cis*-dimethyl(aniono)(triphenylphosphine)gold(III). The proposed mechanism is considered to be the reverse of the nucleophilic mechanism in the formation of **1** from dimethyliodo(triphenylphosphine)gold(III) with sodium methoxide in the presence of carbon monoxide. However, no definite evidence for the coordination of carbon monoxide toward dimethylgold(III) species prior to the carbon monoxide loss was obtained at present. Thus the addition of carbon monoxide to a benzene solution of *cis*-dimethyl(nitrato)(triphenylphosphine)gold(III) having a relatively good leaving nitrato anionic group [14*], caused no change in its ^{1}H NMR spectrum.

As expected, no reaction of **1** took place with nucleophiles such as sodium ethoxide and triethylamine.

Thermolysis

Thermolysis of most of organogold(III) complexes is known to lead to a reductive elimination involving carbon to carbon bond formation and considerably

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* Reference number with asterisk indicates a note in the list of references.

Table 2

Fractional atomic coordinates ($\times 10^4$) for **1**

Atom	*x*	*y*	*z*	B_{eq} (Å^2)
Au	5581.7(3)	2078.3(2)	6098.9(1)	3.65(5)
P	4733(3)	1305(2)	7989(5)	3.5(1)
C(1)	6308(15)	2737(13)	4353(28)	6.1(6)
C(2)	6193(14)	1162(14)	4785(27)	5.7(6)
C(3)	4037(10)	792(8)	6467(21)	3.6(4)
C(4)	3466(11)	1157(10)	5299(23)	4.1(4)
C(5)	2949(12)	802(9)	4023(29)	4.9(5)
C(6)	3019(11)	49(9)	3959(27)	4.6(4)
C(7)	3591(12)	−322(11)	5082(28)	4.6(5)
C(8)	4092(11)	53(9)	6352(28)	4.3(4)
C(9)	5352(12)	681(8)	9348(22)	4.1(4)
C(10)	4915(13)	222(10)	10544(23)	4.5(5)
C(11)	5390(15)	−249(12)	11573(27)	5.8(6)
C(12)	6292(17)	−261(12)	11540(27)	5.9(6)
C(13)	6734(14)	227(12)	10456(30)	5.2(5)
C(14)	6310(13)	709(12)	9380(32)	5.6(6)
C(15)	3993(10)	1767(8)	9552(20)	3.4(3)
C(16)	4416(11)	2143(10)	10954(19)	4.4(4)
C(17)	3913(15)	2566(12)	12131(26)	5.2(5)
C(18)	3007(14)	2597(10)	11988(28)	5.1(5)
C(19)	2573(12)	2199(10)	10602(28)	5.0(5)
C(20)	3081(11)	1820(11)	9409(24)	4.4(4)
C(21)	5037(15)	2944(14)	7315(27)	5.5(5)
C(22)	3711(15)	3698(14)	7713(36)	7.0(7)
O(1)	4170(9)	3107(8)	6751(19)	5.6(4)
O(2)	5432(11)	3378(9)	8314(33)	9.6(7)

Table 3

Selected bond lengths and angles for **1**

(a) *Bond lengths* (Å)			
Au–P	2.373(4)	P–C(9)	1.79(2)
Au–C(1)	2.08(2)	P–C(15)	1.82(2)
Au–C(2)	2.17(2)	C(21)–O(1)	1.40(3)
Au–C(21)	2.02(3)	C(21)–O(2)	1.24(3)
P–C(3)	1.81(2)	O(2)–C(22)	1.48(3)
(b) *Bond angles* (deg)			
P–Au–C(1)	90.5(6)	P–C(3)–C(4)	119(1)
P–Au–C(2)	90.6(7)	P–C(3)–C(8)	122(1)
C(1)–Au–C(2)	88.3(9)	P–C(9)–C(10)	121(1)
C(1)–Au–C(21)	90.7(9)	P–C(9)–C(14)	120(1)
Au–P–C(3)	105.4(5)	P–C(15)–C(16)	116(1)
Au–P–C(9)	116.5(6)	P–C(15)–C(20)	126(1)
Au–P–C(15)	114.2(5)	Au–C(21)–O(1)	115(1)
C(3)–P–C(9)	107.5(8)	Au–C(21)–O(2)	126(2)
C(3)–P–C(15)	107.2(7)	C(21)–O(1)–C(22)	117(2)
C(9)–P–C(15)	105.5(7)		

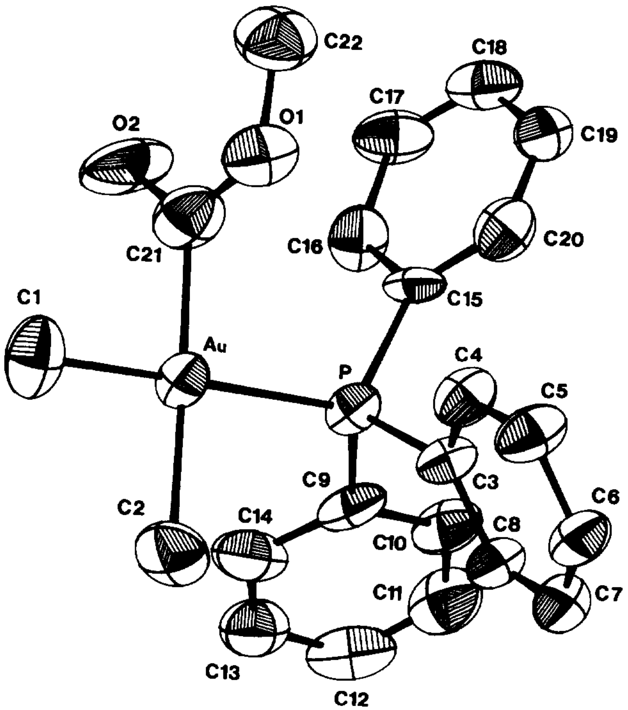
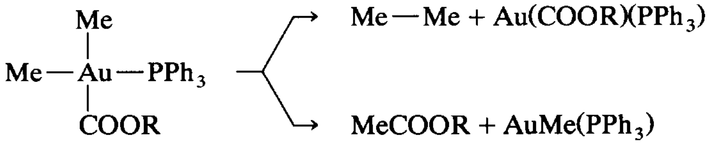


Fig. 1. ORTEP drawing of *cis*-$AuMe_2(COOMe)(PPh_3)$ (**1**) with the probability ellipsoids drawn at the 50% level.

detailed mechanistic investigations have been carried out previously [15,16]. Organic groups *cis* to each other in a T shaped triorganogold(III) intermediate, which is formed by dissociation of a tertiary phosphine ligand, are always reductively eliminated to give coupling products. Since two possible routes for the reductive elimination of these dimethyl(alkoxycarbonyl)gold(III) complexes are conceivable, relative kinetic ease in the reductive elimination of these organic groups can be estimated by simply analyzing the reaction products [17].



$$\begin{array}{c}\text{Me}\\ |\\ \text{Me—Au—PPh}_3\\ |\\ \text{COOR}\end{array} \begin{array}{l}\nearrow \text{Me—Me} + \text{Au(COOR)(PPh}_3)\\ \\ \searrow \text{MeCOOR} + \text{AuMe(PPh}_3)\end{array}$$

Thus the thermolysis of *cis*-dimethyl(alkoxycarbonyl)gold(III) complexes in benzene-d_6 was followed by ^{1}H NMR as well as by GC and the time-yield curve of **1** is shown in Fig. 2. As the reaction proceeded, the amounts of the two reductive elimination products such as ethane and methyl acetate increased. The resulting gold complexes contained mainly the mixture of methyl(triphenylphosphine)gold(I) and (methoxycarbonyl)(triphenylphosphine)gold(I). Since a small amount of trimethyl(triphenylphosphine)gold(III) was also formed during the reaction, a part of the ethane evolved may arise from further decomposition of the trimethylgold (III) complex [15]. Formation of the trimethylgold(III) complex may arise from the disproportionation of the dimethyl(methoxo)gold(III) intermediate (*vide supra*)

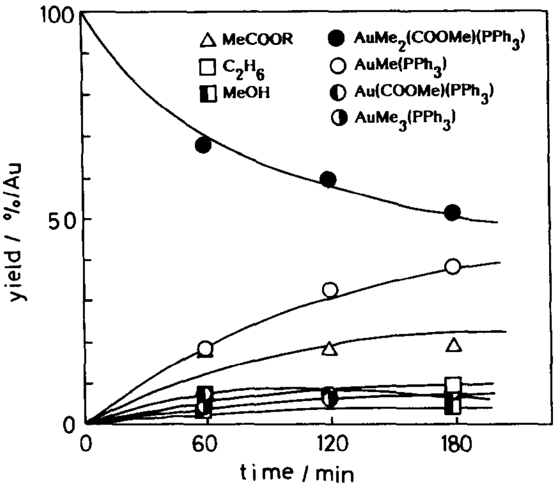


Fig. 2. Time-course of thermolysis of 1 in benzene-d_6 at 70 ° C.

which would be obtained by decarbonylation of 1. In fact after thermolysis, carbon monoxide and methanol were detected in the reaction vessel. In order to avoid such complications, the initial ratio of methyl acetate and ethane formed was taken as an index of the relative tendency of methoxycarbonyl to methyl toward reductive elimination. The considerably higher molar ratio of 3.0 and 7.0 observed for 1 and 2 is surprising, since electron withdrawing organic groups are generally more stable toward reductive elimination than the electron donating organic groups [16]. Carbonyl carbon with sp^2 character may enhance the coupling reaction. A similar enhancement effect of sp^2 carbon in the reductive elimination has been known in the thermolyses of NiMeR(DMPE) [18] and $AuMe_2R(PPh_3)$ [17,19].

Experimental

General

All the manipulations were carried out under deoxygenated nitrogen or argon, or under vacuum by using standard Schlenk technique unless otherwise noted. Solvents such as benzene, diethyl ether, pentane and hexane were dried over Na/benzophenone ketyl. Methanol and ethanol were dried over magnesium alkoxide. These solvents were distilled under nitrogen and were stored under nitrogen before use. Commercially available carbon monoxide was used after passing through a cold trap at −78 ° C. *cis*-Dimethyliodo(triphenylphosphine)-gold(III) [20], *cis*-dimethyl(*E*-crotyl)triphenylphosphine)gold(III) [9] and chloro(triphenylphosphine)gold(I) [21] were prepared by the literature method. All other chemicals were purchased from a commercial supplier and used without further purification.

IR spectra were recorded on JASCO A302 and FTIR 5M spectrometers. ^1H and ^{13}C NMR spectra were measured using JEOL FX-200 and PMX-60 spectrometers. ^1H and ^{13}C NMR chemical shifts are given in ppm from TMS and the multiplicity, coupling constants in Hz and their assignment are shown in parentheses. Elemental analyses were performed by Yanagimoto CHN Autocorder type

MT-2. Gases and liquids evolved in the reactions were quantitatively analyzed by GC using an internal standard method, or by measuring the gas volume by Toepler pump and analyzing by GC.

X-Ray structure analysis

Crystallographic data including full bond lengths and angles and lists of thermal parameters and of observed and calculated structure factors are available from the authors.

Colorless prismatic crystals of **1** were obtained by slow crystallization from a mixture of ether and pentane. The crystal used for data collection was transferred to a Rigaku AFC 5R diffractometer. Automatic peak search and indexing procedures yielded the reduced orthorhombic primitive cell. The final cell parameters and specific data collection parameters are given in Table 1.

The data collection was carried out with the program CRYSTAN (Rigaku) on a FACOM A-70. Structure was solved by the direct method and refined via standard full matrix least-squares and Fourier techniques. Empirical absorption correction was applied after all the non-hydrogen atoms were located [22]. All the non-hydrogen atoms were anisotropically refined. The correct enantiomer was chosen after refinement to convergence of both hands; the one with the lower R value was taken as the correct one. Final $R = 5.35$, $R_W = 6.67$ for 2444 reflections. Alternative refinement where coordinates x, y, z were replaced by $-x$, $-y$, $-z$ gave $R = 5.83$, $R_W = 8.03$ for 2444 reflections. Hydrogen atoms except those of methyl groups, which were found in the differential map, were included in the calculation and refined isotropically.

cis-Dimethyl(methoxycarbonyl)(triphenylphosphine)gold(III)

Atomospheric carbon monoxide was introduced into a solution of *cis*-$AuMe_2I(PPh_3)$ (114.9 mg, 0.186 mmol) and sodium methoxide (34.6 mg, 0.641 mmol) in methanol and stirred for 30 min at 50 °C. Hydrolysis of the reaction mixture by water and extraction with ether gave a colorless solution. After evaporation of ether under vacuum, the resulting colorless solid was recrystallized from ether/hexane to give colorless crystals. Yield: 99.0 mg (44%); m.p. = 124–125 °C (dec.). Anal. Found: C, 48.10; H, 4.37. $C_{22}H_{24}O_2PAu$ calc.: C, 48.19; H, 4.41%. IR(KBr disk): 1660, 1190, 1090, 550 cm^{-1}. NMR(C_6D_6): ^1H; 0.58 (d, 7.9, Me *cis* to P), 1.76 (d, 8.8, Me *trans* to P), 3.31 (s, OMe). $^{13}C\{^1H\}$($CDCl_3$); 4.07 (d, 6.1, Me *cis* to P), 9.67 (d, 106.2, Me *trans* to P), 49.4 (s, OMe), 210.7 (d, 12.0, CO).

Compound **1** was also prepared by the reaction of CO with the methanol solution (2 cm^3) which was obtained from *cis*-$AuMe_2$(*E*-$CH_2CH{=}CHCH_3$)(PPh_3) (100.7 mg, 0.185 mmol) at 50 °C for 30 min. Yield, 68%.

Other dimethyl(alkoxycarbonyl)gold(III) complexes were prepared similarly. Only analytical and physical data are shown below.

cis-Dimethyl(ethoxycarbonyl)(triphenylphosphine)gold(III)

Yield, 68%; m.p. = 130–131 °C (dec.). Anal. Found: C, 49.48; H, 4.60. $C_{23}H_{26}O_2PAu$ calc.: C, 49.12; H, 4.66%. IR(KBr disk): 1640, 1190, 1090, 550 cm^{-1}. NMR(C_6D_6): ^1H; 0.59 (d, 7.8, Me *cis* to P), 1.80 (d, 8.6, Me *trans* to P), 0.92 (t, 7.0, OCH_2CH_3), 3.92 (q, 7.0, OCH_2CH_3). $^{13}C\{^1H\}$(C_6D_6); 4.97 (d, 5.1, *cis* to P), 10.94 (d, 106.0, *trans* to P), 14.92 (s, OCH_2CH_3), 57.84 (s, OCH_2CH_3), 207.8 (d, 12.0, CO).

cis-Dimethyl(isopropoxycarbonyl)(triphenylphosphine)gold(III)

Yield, 30%; m.p. = 120–123 °C (dec.). Anal. Found: C, 50.01; H, 4.99. $C_{24}H_{28}O_2PAu$ calc.: C, 50.01; H, 4.90%. IR: 1638, 1190, 1090, 550 cm^{-1}. ^1H NMR(C_6D_6): 0.58 (d, 7.8, Me *cis* to P), 1.80 (d, 8.6, Me *trans* to P), 1.01 (d, 6.4, $OCH(CH_3)_2$), 5.11 (septet, 6.4, $OCH(CH_3)_2$)

Attempted isolation of dimethyl(methoxo)gold(III) complex

Dimethyl(methoxo)gold(III) complex was prepared *in situ* by methanolysis of *cis*-dimethyl(*E*-crotyl)(triphenylphosphine)gold(III) (16.2 mg, 0.0298 mmol) at 50 °C. 1-Butene (0.0141 mmol) and *cis*-2-butene (0.0148 mmol) were detected in the reaction vessel. At this stage in methanol the dimethyl(methoxo)gold(III) species seems to be stable, as suggested from the following chemical reactivities (*vide infra*). However removal of methanol from this solution by evaporation at 0 °C resulted in the formation of only trimethyl(triphenyphosphine)gold(III) which was detected in 34% yield by ^1H NMR. Although no other assignable gold complexes except for trimethylgold(III) complex were detected and the fate of the alkoxide moieties is not clear at present, disproportionation of dimethyl(methoxo) gold(III) complex might explain the formation of trimethyl(triphenylphosphine) gold(III).

An excess of methyl iodide (3.21 mmol) was added to a methanolysis solution prepared from *cis*-dimethyl(*E*-crotyl)(triphenylphosphine)gold(III) (18.3 mg, 0.0336 mmol) and methanol and the solution was stirred for 40 min at room temperature. Dimethyl ether was detected in 52% per mol of Au complex in solution. NMR analysis of the resulting solution revealed the formation of *cis*-dimethyliodo(triphenylphosphine)gold(III) (52%) and trimethyl(triphenylphosphine)gold(III) (39%), suggesting the formation of dimethyl(methoxo)gold(III) species in solution.

(Methoxycarbonyl)(triphenylphosphine)gold(I)

Atmospheric carbon monoxide was introduced into a THF/methanol solution (5 cm^3 each) containing chloro(triphenylphosphine)gold(I) (126.8 mg, 0.2563 mmol) and sodium methoxide (27.8 mg, 0.515 mmol). After stirring for 1 h, all the volatile matter was removed by evacuation. Benzene extracts were recrystallized from toluene/ether to give yellowish white crystals. Yield, 45.6 mg (34%); m.p. = 111–112 °C (dec.). Anal. Found: C, 46.30; H, 3.57. $C_{20}H_{18}O_2PAu$ calc.: C, 46.35; H, 3.50%. IR (KBr disk): 1640, 1060 cm^{-1}. ^1H NMR ($CDCl_3$): 3.59 (s, OCH_3).

Thermolysis of 1 and 2

The NMR tube containing **1** (17.3 mg, 0.0325 mg) and diphenylmethane (0.0119 mmol) as an internal standard in C_6D_6 (0.5 cm^3) was heated to 70 °C. Products were quantitatively determined periodically by NMR integration and also by GC using the internal standard method. After 310 min, methyl acetate (15%), ethane (12%), methyl(triphenylphosphine)gold(I) (38%), (methoxycarbonyl)(triphenylphosphine)gold(I) (4%), trimethyl(triphenylphosphine)gold(III) (4%) and methanol (12%) were obtained. Carbon monoxide was detected in the gas phase but the amount was not measured. The time-yield curve of the thermolysis is shown in Fig.

2. The initial molar ratio of methyl acetate to ethane was 3.0. A similar thermolysis of **2** (17.3 mg, 0.0317 mmol) at 80 ° C for 300 min gave ethane (6%), ethyl acetate (19%), methyl(triphenylphosphine)gold(I) (18%) and trimethyl(triphenylphosphine)gold(III) (7%). The estimated initial molar ratio of ethyl acetate to ethane was 7.0.

Reaction of 1 with hydrogen chloride

Dry hydrogen chloride gas (0.0221 mmol) was added into a THF solution of **1** (39.5 mg, 0.0742 mmol). After stirring for 3 h, carbon monoxide (0.0601 mmol, 81%) and methanol (0.0356 mmol, 48%) were detected in the reaction flask. Removal of all the volatiles gave known *cis*-dimethylchloro(triphenylphosphine) gold(III) [11] in 53% yield.

Reaction of 1 with acetic acid

Acetic acid (0.026 mmol) was added into a C_6D_6 solution (0.30 cm^3) of **1** (14.7 mg, 0.0268 mmol). After 3 h reaction at room temperature, formation of methanol (90%) and *cis*-dimethyl(acetato)(triphenylphosphine)gold(III) (90%) was observed [11]. Carbon monoxide was detected in the gas phase.

Reaction of 1 with acetyl chloride

Acetyl chloride (0.0280 mmol) was added to a C_6D_6 solution (0.30 cm^3) containing **1** (15.0 mg, 1.27 mmol) and diphenylmethane as a standard material. After 4 days reaction at room temperature, methyl acetate (60%) and *cis*-dimethylchloro(triphenylphosphine)gold(III) (60%) were detected by ^1H NMR. In the gas phase carbon monoxide gas was detected by GC.

Reaction of 1 with sodium ethoxide and triethylamine

A THF solution of **1** (36.9 mg, 0.0693 mmol) and sodium ethoxide (0.106 mmol) was stirred for 3 h at room temperature. No gas evolution was observed and after workup, **1** was recovered from the reaction mixture (42%). A mixture of triethylamine (0.229 mmol) and **1** (12.0 mg, 0.225 mmol) in C_6D_6 was stirred for 11 h at room temperature. No change in the NMR spectrum was observed.

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