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Reactions of (Triphenylphosphine)gold(I) Enolates and Homoenolates

Masahiro MURAKAMI, Masahiko INOUYE, Michinori SUGINOME, and Yoshihiko ITO*
Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Yoshida, Kyoto 606
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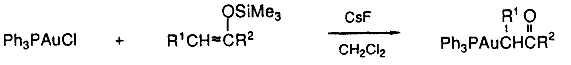
Some reactions of (triphenylphosphine)gold(I) enolates and homoenolates, which are respectively prepared by the reaction of trimethylsilyl ethers of enols and cyclopropanols with (triphenylphosphine)gold(I) chloride in the presence of cesium fluoride, are described. The aldol reaction of (triphenylphosphine)gold(I) enolates with carbonyl compounds is efficiently promoted by Lewis acids such as titanium tetrachloride and diethylaluminum chloride to produce β-hydroxy carbonyl compounds. (Triphenylphosphine)gold(I) enolate reacts with phenyl acetylene to afford (triphenylphosphine)gold(I) phenylacetylide in good yield. Reaction of (benzoylmethyl)(triphenylphosphine)gold(I) (**3a**) with chlorotrimethylsilane produces α-(trimethylsilyloxy)styrene and (triphenylphosphine)gold(I) chloride, which is the reverse of the formation of **3a**. Gold(I) enolate undergoes an isocyanide insertion reaction into the linkage of carbon and gold. (2-Benzoylethyl)(triphenylphosphine)gold(I) reacts with 2-methyl-2-propanethiol to afford (triphenylphosphine)gold(I) *t*-butyl sulfide together with propiophenone.

Some gold(I) enolate complexes have been hitherto reported.[1] Carbon-bound gold(I) enolates of so-called active methylene compounds were prepared with thallium salts of active methylene compounds.[2] Carbon-bound gold(I) enolates of methyl ketones such as acetone and acetophenone were prepared by the reaction of methyl ketones with (triphenylphosphine)gold(I) bromide and silver oxide or with $(Ph_3PAu)_3O^+BF_4^-$.[3] Recently we reported a new preparative method for regioselectively forming carbon-bound (triphenylphosphine)gold(I) enolates (**3**) and homoenolates (**5**), in which trimethylsilyl ethers of enols **2** and cyclopropanols (**4**) are respectively treated with (triphenylphosphine)gold(I) chloride (**1**) in the presence of cesium fluoride (Eqs. 1, 2).[4] No reaction of **2** or **4** with **1** occurred in the absence of cesium fluoride.

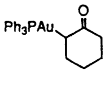


$$\underset{\mathbf{1}}{Ph_3PAuCl} + \underset{\mathbf{2}}{R^1CH{=}\overset{OSiMe_3}{C}R^2} \xrightarrow[CH_2Cl_2]{CsF} \underset{\mathbf{3}}{Ph_3PAu\overset{R^1}{C}H\overset{O}{C}R^2} \quad (1)$$

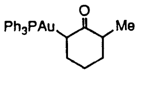
3a: $R^1 = H$, $R^2 = Ph$

3b: $R^1 = H$, $R^2 = CH_2CH_2CH{=}CH_2$

3c:



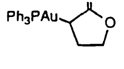
3d:

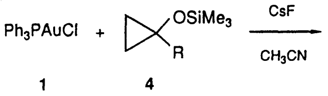


3e:

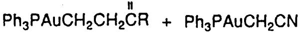
$$Ph_3Au\underset{Me}{C}HCO_2Me$$

3f:





$$\underset{\mathbf{1}}{Ph_3PAuCl} + \underset{\mathbf{4}}{\text{cyclopropane}(OSiMe_3)(R)} \xrightarrow[CH_3CN]{CsF}$$



$$\underset{\mathbf{5}}{Ph_3PAuCH_2CH_2\overset{O}{C}R} + \underset{\mathbf{6}}{Ph_3PAuCH_2CN} \quad (2)$$

5a: R=Ph
b: R=OEt

Unlike the previous method, our method features a regioselective formation of carbon-bound gold(I) enolates via trimethylsilyl ethers of enols from unsymmetrical ketones. X-Ray analyses of (benzoylmethyl)(triphenylphosphine)gold(I) (**3a**) and (2-benzoylethyl)(triphenylphosphine)gold(I) (**5a**) thus prepared unambiguously disclosed the carbon-bound gold(I) enolate and homoenolate structures with almost linear C-Au-P.[4]

Herein, we wish to report some reactions of gold(I) enolates and homoenolates.

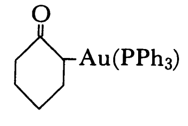
Results and Discussion

Reactions of (Triphenylphosphine)gold(I) Enolates. **[a] Lewis Acid Promoted Aldol Reactions:** (Triphenylphosphine)gold(I) enolates (**3**) did not react with aldehydes. However, addition of Lewis acids efficiently promoted the aldol reaction of (triphenylphosphine)gold(I) enolates with carbonyl compounds to produce β-hydroxy carbonyl compounds (Table 1). Among a variety of Lewis acids, titanium tetrachloride and diethylaluminum chloride gave good results. It is noteworthy that gold(I) enolates readily reacted at −78 °C even with ketones, which are generally unreactive in aldol reaction, in the presence of titanium tetrachloride. Stereoselectivities of the Lewis acid promoted aldol reaction of gold(I) enolates were generally disappointing except for the high diastereoselectivity (91 : 9) observed in the titanium tetrachloride mediated reaction of gold(I) enolate of cyclohexanone with benzaldehyde. Intermediacy of titanium enolate generated by transmetallation of gold(I) enolate with titanium tetrachloride may be suggested in the present reaction, because the very similar diastereoselectivity was found in the reaction of titanium enolate of cyclohexanone with benzaldehyde.[5]

$$\underset{\mathbf{3}}{Ph_3PAu\overset{R^1}{C}H\overset{O}{C}R^2} + \underset{\mathbf{7}}{R^3\overset{O}{C}R^4} \xrightarrow{\text{Lewis acid}} \underset{\mathbf{8}}{R^2\overset{O}{C}CHR^1\overset{OH}{C}R^3R^4} \quad (3)$$

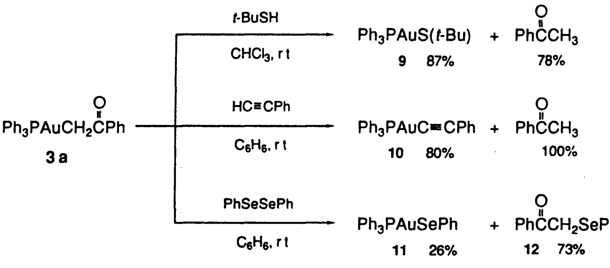
[b] Miscellaneous Reactions: (Triphenylphosphine)gold(I) enolates were relatively stable to oxygen and moisture and could be handled quickly in the open air, but gradually decomposed in solution. Some reactions with (benzoylmethyl)(triphenylphosphine)gold(I) (**3a**) are shown in Eq. 4. Gold(I) enolate **3a** was inert to alcohol. But 2-methyl-2-propanethiol reacted

Table 1. Lewis Acid Promoted Aldol Reaction

Run	3	7	Lewis acid	Conditions	Yield/%	Syn : Anti[a)] (erythro) (threo)
1	$\mathrm{Ph\overset{O}{\overset{\|}{C}}CH_2Au(PPh_3)}$	PhCHO	$BF_3 \cdot OEt_2$	−78 °C, 8 h	33[b)]	—
2			Et_2AlCl	−78 °C, 5.5 h	66[b)]	—
3			$TiCl_4$	−78 °C, 2 h	88[b)]	—
4		$\mathrm{Ph\overset{O}{\overset{\|}{C}}CH_3}$	Et_2AlCl	−78 °C, 9.5 h	38[c)]	—
5			$TiCl_4$	−78 °C, 5 h	64[c)]	—
6		$PhCH_2CH_2CHO$	Et_2AlCl	−78 °C, 4.5 h	63[d)]	—
7		PhCHO	$TiCl_4$	−78 °C, 4 h	54[e)]	91 : 9
8	$\mathrm{MeO\overset{O}{\overset{\|}{C}}\underset{Me}{\underset{\mid}{C}}HAu(PPh_3)}$	PhCHO	Et_2AlCl	−78 °C, 4.5 h	37[f)]	61 : 39
9			$TiCl_4$	−78 °C, 3.5 h	81[f)]	55 : 45
10			$Ti(OPr^i)_3Cl$	0 °C, 5 h	23[f)]	50 : 50
11			$SnCl_4$	0 °C, 4 h	31[f)]	50 : 50

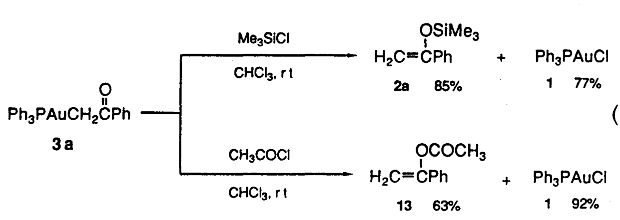
a) Determined by ^{1}H NMR. b) Ref 6. c) Ref 7. d) Ref 8. e) Ref 9. f) Ref 10.

with **3a** at room temperature to give (triphenylphosphine)gold(I) *t*-butyl sulfide (**9**) together with acetophenone. Similarly, reaction of **3a** with phenylacetylene afforded (triphenylphosphine)gold(I) phenylacetylide (**10**) with acetophenone. Gold(I) enolate **3a** did not react with diphenyl disulfide but reacted with diphenyl diselenide to give (triphenylphosphine)gold(I) phenyl selenide (**11**) with (phenylseleno)acetophenone (**12**).



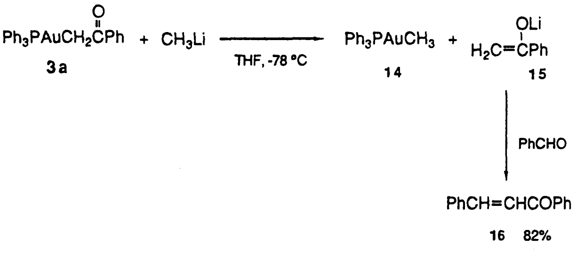
(4)

Reaction of **3a** with chlorotrimethylsilane produced α-(trimethylsilyloxy)styrene (**2a**) and (triphenylphosphine)gold(I) chloride (**1**). The reaction is the reverse of the formation of (triphenylphosphine)gold(I) enolate (**3a**). A similar reaction was observed with acetyl chloride.[3a)] The gold(I) enolate (**3a**) was treated with acetyl chloride to give 1-phenylvinyl acetate (**13**) with (triphenylphosphine)gold(I) chloride (**1**).



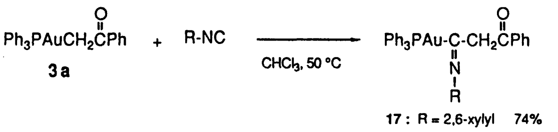
(5)

Reaction of **3a** with methyllithium in tetrahydrofuran (THF) at 0 °C gave rise to the formation of methyl(triphenylphosphine)gold(I) (**14**) after workup with H_2O. Lithium enolate (**15**) of acetophenone, which may be concomitantly generated in the reaction, was indeed trapped. When **3a** was treated with methyllithium in THF at −78 °C and subsequently with benzaldehyde, chalcone (**16**) was isolated in 82% yield.



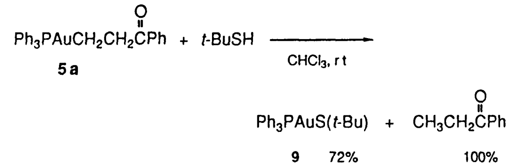
(6)

Gold(I) enolate **3a** underwent an isocyanide insertion reaction into the linkage of carbon and gold according to Eq. 7. NMR spectra revealed that the insertion product **17** exists in an enolized form.



(7)

Reaction of (Triphenylphosphine)gold(I) Homoenolates. In contrast to gold(I) enolates, gold(I) homoenolates were rather unreactive and attempted reactions with gold(I) homoenolates were unsuccessful except for the reaction with 2-methyl-2-propanethiol shown in Eq. 8.



$$Ph_3PAuCH_2CH_2\overset{O}{\overset{\|}{C}}Ph + t\text{-}BuSH \xrightarrow[CHCl_3,\ rt]{} Ph_3PAuS(t\text{-}Bu) + CH_3CH_2\overset{O}{\overset{\|}{C}}Ph \quad (8)$$

5a

9 72% 100%

Experimental

General. Melting points were determined on a Yanaco MP-S3 apparatus and are uncorrected. ^{1}H NMR spectra were recorded on a JEOL JNM-MH 100 spectrometer (100 MHz) with Me_4Si as an internal standard. ^{13}C NMR spectra were obtained on a JNM-GX 400 spectrometer (100 MHz). Infrared spectra were obtained on a Hitachi 270-30 spectrophotometer. Cesium fluoride (Aldrich) was used after drying at ca. 200 °C in vacuo.

Preparation of Gold(I) Enolates 3a—e. Gold(I) enolates **3a—e** were prepared according to the procedure described.[4]

(2-Oxo-5-hexenyl)(triphenylphosphine)gold(I) (3b): 99%; ^{1}H NMR ($CDCl_3$) δ=2.00—2.61 (m, 4H), 2.61—2.87 (br. s, 2H), 4.73—5.12 (m, 2H), 5.61—6.10 (m, 1H), 7.03—7.80 (m, 15H); IR (neat) 1642, 1482, 1102, 910 cm^{-1}.

(2-Oxocyclohexyl)(triphenylphosphine)gold(I) (3c): 81%; ^{1}H NMR ($CDCl_3$) δ=0.86—2.84 (m, 8H), 3.13—3.26 (m, 1H), 7.06—7.85 (m, 15H); IR (neat) 1620, 1440, 1102, 910 cm^{-1}.

(3-Methyl-2-oxocyclohexyl)(triphenylphosphine)gold(I) (3d): 67%; ^{1}H NMR ($CDCl_3$) δ=0.75—2.96 (m, 7H), 1.07 (d, 3H, J=7 Hz), 3.08—3.35 (m, 1H), 7.04—7.86 (m, 15H); IR (neat) 1636, 1482, 1440, 1102 cm^{-1}.

[1-(Methoxycarbonyl)ethyl](triphenylphosphine)gold(I) (3e): 99%; ^{1}H NMR ($CDCl_3$) δ=1.16 (dd, 3H, $J_{H\text{-}H}$=6 Hz and $J_{H\text{-}P}$=6 Hz), 2.65 (dq, 1H, $J_{H\text{-}H}$=6 Hz and $J_{H\text{-}P}$=12 Hz), 3.66 (s, 3H), 7.16—7.69 (m, 15h); IR (neat) 1682, 1438, 1156, 1102 cm^{-1}.

(2-Oxotetrahydro-3-furyl)(triphenylphosphine)gold(I) (3f). To a suspension of anhydrous cesium fluoride (76 mg, 0.5 mmol) and (triphenylphosphine)gold(I) chloride (50 mg, 0.1 mmol) in acetonitrile (1.5 mL), 2-trimethylsilyloxy-4,5-dihydrofuran (**2f**, 32 mg, 0.2 mmol) was added. The mixture was stirred overnight at room temperature and filtered to remove insoluble inorganic salts. The filtrate was evaporated, washed with CH_2Cl_2, and subjected to column chromatography on silica gel pretreated with triethylamine to give **3f**; 28 mg, 51%; mp 149 °C (decomp); ^{1}H NMR ($CDCl_3$) δ=2.42—3.09 (m, 3H), 4.29—4.56 (m, 2H), 7.32—7.74 (m, 15H); ^{13}C NMR ($CDCl_3$) δ=31.1 ($J_{C\text{-}P}$=5 Hz), 42.2 ($J_{C\text{-}P}$=76 Hz), 68.5, 185.4; IR (KBr) 1692 cm^{-1}. Found: C, 48.28; H, 3.61; P, 5.43%. Calcd for $C_{22}H_{20}AuO_2P$: C, 48.54; H, 3.70; P, 5.69%.

(2-Benzoylethyl)(triphenylphosphine)gold(I) (5a). To a suspension of anhydrous cesium fluoride (286 mg, 1.95 mmol) and (triphenylphosphine)gold(I) chloride (193 mg, 0.390 mmol) in acetonitrile (6 mL), 1-phenyl-1-(trimethylsilyloxy)cyclopropane (111 mg, 0.539 mmol) was added and the mixture was stirred for 4 h at 50 °C. The resulting orange suspension was filtered and the filtrate was evaporated to leave brown oil, which was subjected to column chromatography on silica gel pretreated with triethylamine to give (2-benzoylethyl)(triphenylphosphine)gold(I) (**5a**, 176 mg, 76%) and (cyanomethyl)(triphenylphosphine)gold(I) (**6**, 34 mg, 17%). **5a**: mp 121—122 °C (decomp); ^{1}H NMR ($CDCl_3$) δ=1.48—1.79 (m, 2H), 3.28—3.58 (m, 2H), 7.22—7.74 (m, 18H), 7.99—8.15 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=25.7 (d, $J_{C\text{-}P}$=95.5 Hz), 40.6 (d, $J_{C\text{-}P}$=4 Hz), 204.9 (d, $J_{C\text{-}P}$=5 Hz); IR (KBr) 1670 cm^{-1}. Found: C, 54.47; H, 3.98; P, 5.41%. Calcd for $C_{27}H_{24}OPAu$: C, 54.74; H, 4.08; P, 5.23%. **6**: mp 131—133 °C (decomp); ^{1}H NMR ($CDCl_3$) δ=1.66 (d, 2H, J=10.0 Hz), 7.31—7.76 (m, 15H); IR (KBr) 2200 cm^{-1}. Found: C, 48.00; H, 3.36; N, 2.65; P, 6.07%. Calcd for $C_{20}H_{17}AuNP$: C, 48.11; H, 3.43; N, 2.81; P, 6.20%.

[2-(Ethoxycarbonyl)ethyl](triphenylphosphine)gold(I) (5b): 78%; ^{1}H NMR ($CDCl_3$) δ=1.18 (t, 3H, J=7 Hz), 1.54 (m, 2H), 2.73 (m, 2H), 4.07 (q, 2H, J=7 Hz), 7.40—7.61 (m, 15H); IR (neat) 1728, 1484, 1440, 1100 cm^{-1}.

Lewis Acid Promoted Aldol Reaction. Representative procedure of Lewis acid promoted aldol reaction is given by the preparation of methyl 3-hydroxy-2-methyl-3-phenylpropanoate: To a dichloromethane solution (1 mL) of [1-(methoxycarbonyl)ethyl](triphenylphosphine)gold(I) (48 mg, 0.087 mmol) and benzaldehyde (11 mg, 0.10 mmol), a dichloromethane solution (0.13 mL) of titanium tetrachloride (0.13 mmol) was added at −78 °C, and the reaction mixture was stirred for 5 h at that temperature. Saturated aq. $NaHCO_3$ solution (5 mL) was added and, after usual extractive workup, methyl 3-hydroxy-2-methyl-3-phenylpropanoate (14 mg, 81%) was isolated by preparative TLC on silica gel.

(Triphenylphosphine)gold(I) *t*-Butyl Sulfide (9). A chloroform solution (0.3 mL) of (benzoylmethyl)(triphenylphosphine)gold(I) (**3a**, 24 mg, 0.041 mmol) and 2-methyl-2-propanethiol (5 mg, 0.05 mmol) was sonicated in a sealed tube at room temperature. After 1 h, hexane (0.9 mL) was added to give **9** as colorless crystals: 20 mg, 87%; mp 166—168 °C; ^{1}H NMR ($CDCl_3$) δ=1.60 (s, 9H), 7.27—7.71 (m, 15H). Found: C, 48.08; H, 4.35; P, 5.66%. Calcd for $C_{22}H_{24}AuPS$: C, 48.18; H, 4.41; P, 5.65%.

(Triphenylphosphine)gold(I) Phenylacetylide (10). A chloroform solution (0.3 mL) of **3a** (23 mg, 0.040 mmol) and phenylacetylene (7 mg, 0.07 mmol) was sonicated in a sealed tube at room temperature for 4 h. Then the reaction mixture was subjected to column chromatography on silica gel to give **10**: 18 mg, 80%; mp 165—166 °C (lit, 163—164 °C).[11]

Formation of (Triphenylphosphine)gold(I) Phenyl Selenide (11) and (Phenylseleno)acetophenone (12). In a sealed tube, a benzene solution (0.3 mL) of (benzoylmethyl)(triphenylphosphine)gold(I) (**3**, 23 mg, 0.040 mmol) and diphenyl diselenide (13 mg, 0.04 mmol) was sonicated at room temperature. After 12 h, the mixture was subjected to preparative TLC on silica gel to give **11** (6.3 mg, 26%) and **12** (8.0 mg, 73%). **11**: mp 146—149 °C (decomp); ^{1}H NMR ($CDCl_3$) δ=6.70—7.90 (m, 20H). Found: C, 46.81; H, 3.21; P, 5.03%. Calcd for $C_{24}H_{20}AuPSe$: C, 46.85; H, 3.28; P, 5.03%.

Formation of α-Trimethylsilyloxystyrene (2a). In a sealed tube, a $CDCl_3$ solution (0.3 mL) of (benzoylmethyl)(triphenylphosphine)gold(I) (**3**, 23 mg, 0.040 mmol) and chlorotrimethylsilane (9 mg, 0.08 mmol) was sonicated at room temperature for 2.5 h. The formation of **2a** was observed by ^{1}H NMR [δ=0.25 (s), 4.47 (d, J=2 Hz), 4.95 (d, J=2 Hz)] and the yield was determined using an internal standard. (Triphenylphosphine)gold(I) chloride (**1**, 15 mg, 77%) was isolated by column chromatography on silica gel pretreated with triethylamine.

Formation of 1-Phenylvinyl Acetate (13). In a sealed tube, a chloroform solution (0.3 mL) of (benzoylmethyl)(triphenylphosphine)gold(I) (**3**, 23 mg, 0.040 mmol) and acetyl chloride (5 mg, 0.06 mmol) was sonicated at room temperature. After 1 h, the mixture was subjected to column chromatography on silica gel pretreated with triethylamine to give **1** (18 mg, 92%) and **13** (4 mg, 63%).

Formation of Chalcone (16). To a solution of (benzoylmethyl)(triphenylphosphine)gold(I) (25 mg, 0.043 mmol) in THF (1 mL), an ether solution (0.14 mL) of methyllithium (0.055 mmol) was added at −78 °C under a nitrogen atmosphere. After stirring for 30 min, benzaldehyde was added (6.4 mg, 0.06 mmol) and the reaction mixture was allowed to warm gradually to room temperature and quenched with methanol (10 mL). The mixture was subjected to preparative TLC on silica gel to give chalcone (7.3 mg, 82%).

[2-Benzoyl-1-(2,6-xylylimino)ethyl](triphenylphosphine)-gold(I) (17). Under a nitrogen atmosphere, chloroform solution (2 mL) of **3a** (35 mg, 0.060 mmol) and 2,6-xylyl isocyanide (12 mg, 0.090 mmol) was heated at 50 °C for 6 h. Resulting yellow mixture was subjected to column chromatography on silica gel pretreated with triethylamine to give **17**: 32 mg, 74%; mp 160 °C (decomp); ^{1}H NMR ($CDCl_3$) δ= 2.37 (s, 6H), 6.08 (s, 1H), 6.95—8.12 (m, 23H); ^{13}C NMR ($CDCl_3$) δ=19.09, 101.22, 185.2, 209.1; IR (KBr) 1506, 1438 cm^{-1}. Found: C, 59.07; H, 4.58; N, 1.74: P, 4.62%. Calcd for $C_{35}H_{31}AuNOP$: C, 59.24; H, 4.40; N, 1.97, P, 4.37%.

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