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Au(I) complexes-catalyzed transfer vinylation of alcohols and carboxylic acids

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Abstract

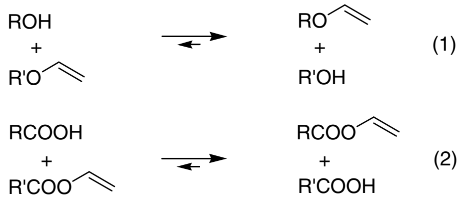
Au(I) complexes-catalyzed transfer vinylation of alcohols and carboxylic acids has been achieved. The catalyst system consists of 2 mol % $AuClPPh_3$ and 2 mol % AgOAc. Primary alcohols and secondary alcohols were converted into corresponding vinyl ethers in good yield (64–93%); however, tertiary alcohols showed poor reactivities. Carboxylic acids were also transformed into corresponding vinyl esters in good yield (78–96%).

Vinyl ethers and esters are highly valuable class of compounds that have been used for vinyl polymer synthesis[1] as well as organic synthesis including Claisen-rearrangement,[2] cycloaddition,[3] cyclopropanation,[4] hydroformylation,[5] metathesis,[6] and Heck reaction[7]. Recently, we have utilized vinyl ethers as substrates for asymmetric hydrolysis and alcoholysis reactions[8] and achieved an efficient kinetic resolution of axially chiral compounds.[8b]

With respect to atom efficiency, alcohol and carboxylic acid addition to acetylene (C_2H_2) is desirable for the synthesis of their vinyl derivatives and indeed the method is used in industry.[9] However, the process requires rather harsh condition and suffered from safety problems due to explosive nature of acetylene.

Vinyl transfer reactions from vinyl ethers or esters to alcohols and acids are an alternative practical route to access them. Mercury[10] and palladium[11] catalysts have been known for long years and recently iridium complex catalysts have been developed.[12] On another front, recently gold catalysts received much attentions due to their versatile catalytic functions including C–C multiple bond activations.[13] Since previous vinyl transfer reactions include olefin activation in their catalytic cycle, we focused attention to utilize gold catalysts in vinyl transfer reactions (Scheme 1).

Transfer vinylation of 1-phenylethanol with ethyl vinyl ether was examined with several kinds of Au-complexes. The reactions were carried out with 2 mol % catalyst and 10 equiv vinyl ether at 50 °C for 10 h in the absence of solvent (Table 1). A commercially available Au(I) complex, $AuClPPh_3$ did not afford desired vinyl ether but formation of undesired acetals was observed (entry 1). However, the addition of AgOAc (OAc = CH_3COO^-) to the Au(I) complex suppresses the acetal formation completely and gave the vinylated product in 74% yield (entry 2).[14] Since the reaction is reversible and came to equilibrium in 10 h, the



Scheme 1. Vinyl transfer reactions between alcohols (1) and carboxylic acids (2).

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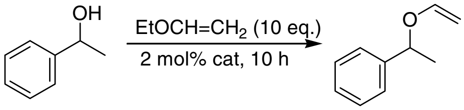
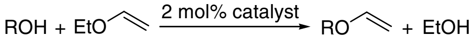
Table 1
Transfer vinylation of 1-phenylethanol with ethyl vinyl ether[a,14]

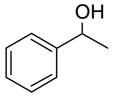
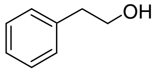
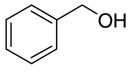
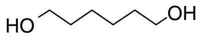
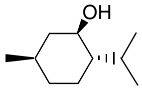
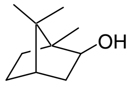
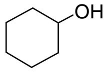
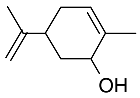
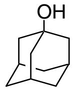
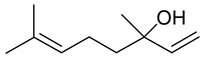


Entry	Catalyst	Yield[b] (%)
1	$AuClPPh_3$	0[c]
2	$AuClPPh_3/AgOAc$	74
3	AgOAc	0[d]
4[e]	$AuClPPh_3/AgOAc$	70
5[f]	$AuClPPh_3/AgOAc$	62
6[g]	$AuClPPh_3/AgOAc$	69
7[h]	$AuClPPh_3/AgOAc$	55
8	$AuClPPh_3/AgTFA$	75[c]
9	$AuClPPh_3/AgTFA/NEt_3$[i]	70
10	$AuClPPh_3/AgOTf$	0[j]

[a] All the reactions were performed in accordance with the general procedure described in Ref. 14, unless otherwise stated.
[b] GC yield.
[c] ~20% of acetals formation.
[d] No reaction.
[e] $AuClPPh_3$ and AgOAc were stirred in CH_2Cl_2 for 15 min. The suspension was passed through short Celite plug, and the filtrate was evaporated in vacuo. Then, ethyl vinyl ether and the substrate were added to the residue to carry out the reaction.
[f] $AuClPPh_3$: 2 mol %, AgOAc: 1 mol %.
[g] Butyl vinyl ether was used instead of ethyl vinyl ether. Reaction carried out at 80 °C.
[h] Reaction carried out at 30 °C.
[i] NEt_3: 0.5 equiv.
[j] Complex mixture.

Table 2
$AuClPPh_3/AgOAc$-catalyzed vinylation of alcohols[a]



Entry	Substrate	Time (h)	Yield[b] (%)
1		10	74
2	$^{n}C_{12}H_{25}OH$	8	93
3		5	93
4		8	90
5		12	71[c]
6		20	78
7		45	90
8		22	90
9		20	64[d]
10[e,f]		40	26
11[e,g]		50	0[h]
12[e,g,i]	Ph_3SiOH	16	0[j]
13[e,i]	PhOH	48	20

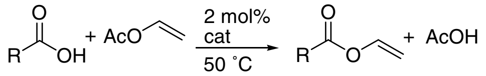
[a] A mixture of $AuClPPh_3$ (2 mol %), AgOAc (2 mol %), ethyl vinyl ether (1 ml), and alcohols (1 mmol) was stirred at 50 °C.
[b] GC yield.
[c] Yield of divinyl ether.
[d] Diastereomer mixture.
[e] 2 mol % of AgTFA was used instead of AgOAc.
[f] 1 equiv of NEt_3 and 2 ml (20 equiv) of ethyl vinyl ether were used.
[g] 0.5 equiv of NEt_3 was added.
[h] No reaction.
[i] Vinyl acetate was used instead of ethyl vinyl ether.
[j] The desired vinyl ether was not obtained. GC and GC–MS analysis suggested the formation of dehydrated dimer of silanol ($Ph_3SiOSiPh_3$).

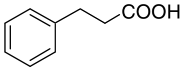
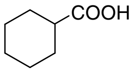
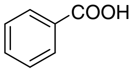
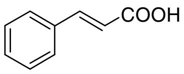
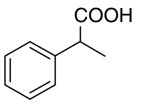
product yield was not increased with prolonged reaction time (75% at 20 h). The additive (AgOAc) itself did not catalyze the reaction at all (entry 3), which indicate that the addition of the additive generate an active Au species by exchange of the counter anion.[15] In entry 4, a solid seems to be AgCl that was filtrated, and the filtrate showed comparable activity. When the half amount of AgOAc was used for the reaction, slightly decreased activity was observed (62% at 10 h, entry 5), and the reaction reached equilibrium at 20 h (74% at 20 h). When butyl vinyl ether was used as vinylating reagent, slightly decreased yield (69%) was observed despite higher temperature (80 °C, entry 6). Lower temperature (30 °C) decreased the reaction rate, thus 55% yield was obtained (entry 7). When the additive was changed to AgTFA, ($TFA = CF_3COO^-$), increased catalytic activity was attained so that the reaction reached equilibrium in 5 h (74% yield, cf. 75% yield at 10 h, entry 8). However, simultaneous formation of acetals was observed. This was suppressed by the addition of 0.5 equiv of NEt_3, but the reaction rate was decreased (70% yield, entry 9). The reaction gave a complex mixture with AgOTf ($OTf = CF_3SOO^-$) as an additive, maybe due to too strong Lewis acidity of Au complex or the generation of TfOH (entry 10).

Substrate generality was examined with the optimized catalytic system. Various kinds of primary, secondary, and tertiary alcohols were tested (Table 2). For primary and secondary alcohols, the catalyst system of entry 2 in Table 1 ($AuClPPh_3/AgOAc$) was found to be suitable. Simple primary alcohols reacted smoothly to give the products in 90–93% yield (entries 2–4). Hexane-1,6-diol was converted into vinyl ethers almost completely which afforded 71% of divinyl ether and the rest was monovinyl ether (entry 5). Secondary alcohols showed somewhat lower reactivity so that required longer times compared to primary alcohols to give corresponding vinyl ethers in 64–90% yield (entries 1 and 6–9). In entry 9, the substrate alcohol was diastereomer mixture, and the produced vinyl ether found to have a similar diastereomer ratio (~1:1) to the substrate. Further lower reactivities were observed with tertiary alcohols (entries 10 and 11). In entry 10, the catalyst system of entry 8 in Table 1 (AuClPPh$_3$/AgTFA) with 20 equiv of ethyl vinyl ether exhibited better yield but resulted in 26% at 40 h. Linalool remained intact under the condition of entry 11. Actually, this compound is known as one of the most difficult substrate for vinylation. Both Pd and Ir catalysts failed in obtaining the product.[11d] Recently, Ishii et al. reported that silanol derivatives were vinylated using Ir catalysts with vinyl acetate.[16] However, our catalyst did not afford desired vinylated product of triphenylsilanol (entry 12). GC and GC–MS analysis suggested the formation of dehydrated dimer of silanol (Ph$_3$SiOSiPh$_3$). In entry 13, transfer vinylation of phenol was tested. When ethyl vinyl ether was used as vinylating reagent, no product formation was observed but vinyl acetate as vinylating reagent gave the product in 20% yield. Addition of NEt$_3$ caused the formation of phenyl acetate.

Table 3 shows the result of transfer vinylation of carboxylic acids. The optimized catalyst system (AuClPPh$_3$/AgOAc) with vinyl acetate as vinylating reagent was found to be effective for this transformation. The product vinyl esters of both aliphatic and aromatic carboxylic acids were attained in 78–96% yield (entries 1–5).

Table 3
AuClPPh$_3$/AgOAc-catalyzed vinylation of carboxylic acids[a]



Entry	Substrate	Time (h)	Yield[b] (%)
1		22	89
2		44	78
3		52	96
4		40	81
5		51	83

[a] A mixture of AuClPPh$_3$ (2 mol %), AgOAc (2 mol %), vinyl acetate (1 ml), and carboxylic acids (1 mmol) was stirred at 50 °C.

[b] GC yield.

Although detailed mechanism of the present Au(I)-catalyzed vinyl transfer reaction is unclear, a similar function of Au(I) and Pd(II) metal centers is expected. Thus, oxygen nucleophiles attack the α-position of the coordinated vinyl group, which is followed by rotation and β-alkoxy elimination. Since the known Pd(II)-catalysts for this transformation employ nitrogen ligands rather than phosphine ligands, the Au(I) catalysts may present an opportunity for further optimization by modifying the phosphine ligand used. It is reported that Pd(II) was deactivated to a considerable extent when phosphines were used as a ligand.[11b] Other features of the present reaction compared to the Ir(I)-catalyzed reactions are a milder condition (50 °C cf. 100 °C for Ir) and nonnecessity of an inert-gas atmosphere. In conclusion, we have developed the first example of Au-catalyzed transfer vinylation of alcohols and carboxylic acids.

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14. *Typical procedure for Au-catalyzed transfer vinylation of alcohols*: To a screw cap tube containing AuClPPh$_3$ (9.9 mg, 2 mol %) and silver salt (2 mol %), 1 ml of ethyl vinyl ether (10 equiv) was added under air.

The mixture was stirred at room temperature for 10 min. After the addition of tridecane (internal standard, 46.1 mg, 0.25 mmol) and alcohol (1 mmol), the mixture was stirred at 50 °C. Yield of the product was determined by GC analysis. Calibration curves for GC analysis for each sample were made with isolated product of the present reactions. Product isolation was carried out by silicagel column chromatography (Kanto Silica Gel 60N, particle size 40–100 μm, pretreated with 0.1% triethylamine containg eluent).

15. Similar methods to generate an active Au species by the addition of Ag salts have been reported, for example, see Ref. 13b.
16. Ishii, Y.; Nakano, T.; Iwahama, T. Japan Patent Application No. JP 2006-66531.