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Synergistic Effect: Hydroalkoxylation of Allenes through Combination of Enantiopure BIPHEP-Gold Complexes and Chiral Anions

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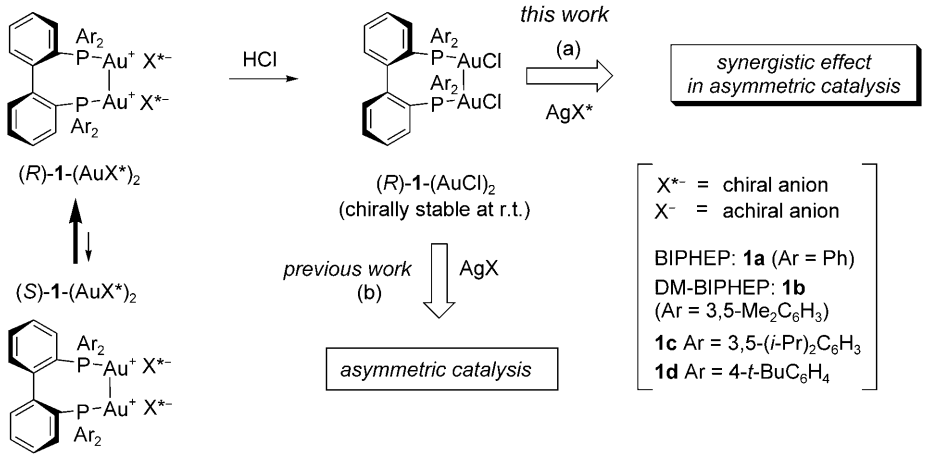
Abstract: A synergistic effect is observed for the combination of a neutral dinuclear gold complex with a chiral silver phosphate in the intramolecular hyroalkoxylation of allenes to give furan derivatives in high yields and enantioselectivities. The monocationic dinuclear gold complex affords higher catalytic activity and enantioselectivity than the neutral or dicationic digold complexes. The synergistic effect is thus highly promising to provide a guiding principle in designing an efficient chiral environment for creating an asymmetric catalyst.

Keywords: asymmetric activation; chiral anion; chirality control; gold catalyst; hydroalkoxylation; synergistic effect

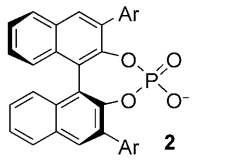
Regarding new frontiers of asymmetric catalyst systems, a variety of highly efficient chiral ligands have been developed that dramatically increase the catalytic activity and enantioselectivity.[1] An asymmetric catalyst is usually constructed by a proper combination of chiral ligand and central metal. An asymmetric catalyst can be further evolved into a more activated catalyst to give higher catalytic activity and enantioselectivity with a chiral activator as an additional chiral source; for this process, we have previously coined the term 'asymmetric activation'.[2] A synergistic effect has been observed where the matched pair with the additional chiral source (*R* or *S*) can lead to higher catalytic activity and enantioselectivity than the mismatched one (*S* or *R*).

Recently, highly efficient asymmetric catalyst systems based on chiral anions,[3] especially those with a binaphthyl backbone, have been reported to induce high levels of enantioselectivity.[4,5,6] List defined the concept as 'asymmetric counteranion-directed catalysis (ACDC)' in a general strategy for asymmetric catalysis.[5] The catalytic systems through the combination of chiral or achiral amines and chiral phosphate anions have been developed in transfer hydrogenation,[5a,b] allylation,[5c] and epoxidation[5d–f] with high-to-excellent yield and enantioselectivity. As another important breakthrough, Toste and co-workers have also developed the chiral anion strategy for asymmetric transition metal catalysis for highly enantioselective hydroamination,[6] hydroalkoxylation,[6] and hydrocarboxylation[6a] reactions of allenic fragments by a gold catalyst bearing both chiral or achiral diphosphine ligand and chiral phosphate anion.

On the other hand, we have found that the axial chirality of gold complexes bearing *tropos* BIPHEP ligands [BIPHEP = bis(phosphanyl)biphenyl],[7] which are highly modular, versatile, and easy to synthesize without enantiomer resolution, could be controlled by the phosphate and the corresponding *N*-triflyl phosphoramide as chiral anions (Scheme 1).[8] The axial chirality of BIPHEP-$(AuCl)_2$ complexes could also be memorized due to the Au–Au contact even after the dissociation of chiral anions. Treatment of the enantiopure BIPHEP-$(AuCl)_2$ complexes with two equivalents of Ag salt thus facilitated the intramolecular hydroamination of allenes as an *atropos* asymmetric catalyst with high enantioselectivity [Scheme 1, previous work (b)]. Herein, we report a synergistic effect through the combination of the enantiopure BIPHEP-$(AuCl)_2$ complexes and chiral phosphate anions as a matched pair, which affords the high level of enantioselectivity in an intramolecular hydroalkoxylation [Scheme 1, this work (a)]. Since gold complexes possess not only a two-coordinate linear geometry but also have the chiral ligands far from the reactive site, the development of the highly catalytic enantiselective reactions is still a challenging subject.[9] Therefore, we believe that the synergistic effect is



Scheme 1. This work (a): Synergistic effect by the combination of chirally stable enantiopure (*R*)-**1**-$(AuCl)_2$ and chiral AgX* salt. Previous work[8] (b): Asymmetric catalysis using chirally stable enantiopure (*R*)-**1**-$(AuCl)_2$ and an achiral AgX salt.



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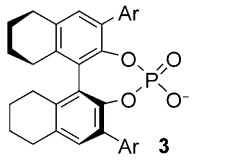
a: Ar = 4-phenylC$_6$H$_4$
b: Ar = 3,4-(CF$_3$)$_2$C$_6$H$_3$
c: Ar = Ph
d: Ar = 4-*t*-BuC$_6$H$_4$
e: Ar = 4-(2-naphthyl)C$_6$H$_4$
f: Ar = 4-(4-*t*-BuC$_6$H$_4$)C$_6$H$_4$
g: Ar = 2,4,6-(*i*-Pr)$_3$C$_6$H$_2$



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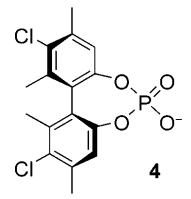
Ar = 4-(4-*t*-BuC$_6$H$_4$)C$_6$H$_4$



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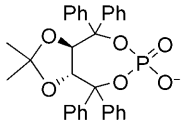

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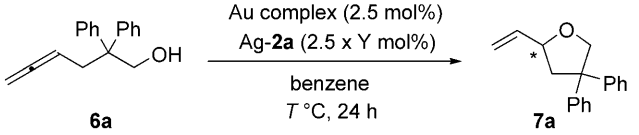
highly promising to gain a new insight in designing an efficient asymmetric gold catalyst.[10]

To demonstrate the effectiveness of the synergistic effect on the Au catalyst system,[11] we focused our attention on enantioselective intramolecular hydroalkoxylation.[6a,12] As initial experiments, the reaction of allene **6a** was examined using cationic Au complexes bearing chiral phosphate anions **2a**, which are immediately generated by the combination of enantiopure (*S*)- or (*R*)-**1**-$(AuCl)_2$ with Ag-**2a** in benzene at room temperature (Table 1). When the reaction did not finish even after 24 h, we attempted the work-up regardless of the remaining substrate **6a** (entries 1–7, 10–15). Treatment of (*S*)- or (*R*)-**1a**-$(AuCl)_2$ with Ag-**2a** promoted the reaction in moderate yields, but the conspicuous synergistic effect (matched and mismatched pairing with the *S*-chiral anion) was not observed in the enantioselectivity (entries 1 *vs.* 2). However, the use of **1b**-$(AuCl)_2$ was found to show the synergistic effect more clearly; in sharp contrast to (*S*)-**1b**-$(AuCl)_2$ as a mismatched pair (6% *ee*, *S*), (*R*)-

Table 1. Synergistic asymmetric hydroalkoxylation using various Au complexes and chiral anion **2a**.[a]



Entry	Au complex	Y	*T* [°C]	Yield [%][e]	*ee* [%][f]
1	(*S*)-**1a**-$(AuCl)_2$	2.0	r.t.	65	30 (*S*)
2	(*R*)-**1a**-$(AuCl)_2$	2.0	r.t.	63	50 (*R*)
3	(*S*)-**1b**-$(AuCl)_2$	2.0	r.t.	88	6 (*S*)
4	(*R*)-**1b**-$(AuCl)_2$	2.0	r.t.	88	74 (*R*)
5	(*R*)-**1c**-$(AuCl)_2$	2.0	10	52	47 (*R*)
6	(*R*)-**1d**-$(AuCl)_2$	2.0	10	66	60 (*R*)
7	(*R*)-**1b**-$(AuCl)_2$	2.0	10	75	75 (*R*)
8[b]	(*R*)-**1b**-$(AuCl)_2$	1.5	10	82	82 (*R*)
9[c]	(*R*)-**1b**-$(AuCl)_2$	1.0	10	86	83 (*R*)
10	(*R*)-**1b**-$(AuCl)_2$	0.5	10	82	83 (*R*)
11	(*S*)-**1b**-$(AuCl)_2$	1.0	10	33	42 (*S*)
12	(*R*)-DM-BINAP-$(AuCl)_2$	2.0	10	45	39 (*R*)
13	dppm-$(AuCl)_2$	2.0	10	58	18 (*S*)
14	dppm-$(AuCl)_2$	1.0	10	69	13 (*S*)
15[d]	dppm-$(AuCl)_2$	2.0	10	42	18 (*S*)

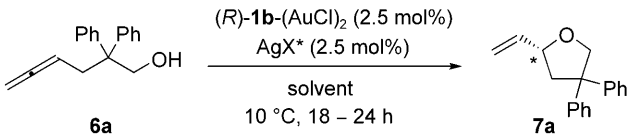
[a] Au catalysts were produced *in situ* by treatment of the Au complex (2.5 mol%) and Ag-**2a** (2.5 × Y mol%) in benzene at 10 °C for 30 min.
[b] Reaction time was 22 h.
[c] Reaction time was 20 h.
[d] Ag-**2g** as a chiral silver phosphate was used instead of Ag-**2a**.
[e] Isolated yield.
[f] Enantiomeric excess was determined by chiral HPLC analysis.

1b-$(AuCl)_2$ as a matched pair afforded the desired product **7a** to increase the enantioselectivity (74% *ee*, *R*) (entries 3 *vs.* 4). As the steric effect of the BIPHEP moiety, (*R*)-**1c**- and −**1d**-$(AuCl)_2$ decreased the enantioselectivities even at lower temperature (60 and 47% *ee*) (entries 5 and 6). Precatalyst **1b**-$(AuCl)_2$ is a dinuclear complex, the amount of Ag-**2a** is thus controlled (entries 7–10). Significantly, the decrease of Ag-**2a** (less than 2.0 equivalents) was found to increase both catalytic activity and enantioselectivity. The reaction finished within 20 h by the addition of one equivalent of Ag-**2a**; the best result was obtained to give the highest catalytic activity and enantioselectivity (86%, 83% *ee*) (entry 9). Even with one equivalent of Ag-**2a**, a mismatched pair (*S*)-**1b**-$(AuCl)_2$ led to extremely low yield and enantioselectivity (33%, 42% *ee*) (entry 11). Compared to the catalyst bearing DM-BIPHEP **1b**,[13] (*R*)-DM-BINAP-$(AuX^*)_2$ counterpart gave lower catalytic activity and enantioselectivity probably due to the significant difference in structure without any intramolecular Au−Au contact (entry 12).[9b,14] In addition, the employment of achiral dppm-$(AuCl)_2$ complex and chiral silver phosphate, which was developed by Toste,[6] gave the adduct in moderate yield but lower enantioselectivity regardless of the chiral anion **2** (entries 13–15).

Since the additional amount of Ag-**2a** reflected the enantioselectivity, we investigated the generation of monocationic (*R*)-**1b**-AuClX* by ^{31}P NMR analyses (Scheme 2).[15] The combination of (*R*)-**1b**-$(AuCl)_2$ and one equivalent of Ag-**2a** in benzene-d_6 at room temperature produced an (*R*)-**1b**-$(AuCl)_2$/(*R*)-**1b**-AuClX*/(*R*)-**1b**-$(AuX^*)_2$ mixture in a 0.5/1.0/0.3 ratio. In addition, two equivalents of Ag-**2a** led only to (*R*)-**1b**-$(AuX^*)_2$ quantitatively. It was demonstrated that the monocationic (*R*)-**1b**-AuClX* afforded not only higher catalytic activity but also better enantioselectivity, because (*R*)-**1b**-$(AuCl)_2$ was inactive in this reaction and an addition of two equivalents of Ag-**2a** gave the lower catalytic activity and enantioselectivity (Table 1, entries 7 *vs.* 8–10). Therefore, another Au-Cl portion of (*R*)-**1b**-AuClX* should take an important role in not only the catalytic activity but also the steric effect to induce a higher enantioselectivity by the catalyst system.

Under these optimized conditions using (*R*)-**1b**-$(AuCl)_2$ as a precatalyst, we investigated the effects of various solvents and chiral anions (Table 2). CH_2Cl_2, AcOEt, and THF instead of benzene gave lower enantioselectivities (entries 2–4). The best results were obtained in toluene (97%, 83% *ee*) (entry 5). The use of achiral anions could not increase the enantioselectivities; the reactions with AgOTf or AgOTs maintained a high reactivity but led to lower enantioselectivity (entries 6 and 7). AgOPNB with either (*R*)-**1b**-$(AuCl)_2$ or (*R*)-DM-BINAP-$(AuCl)_2$ extremely

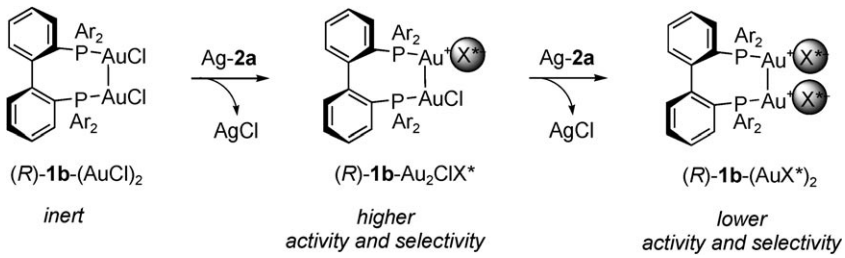
Table 2. Effects of solvent and chiral anions on catalytic asymmetric hydroalkoxylation.



6a **7a**

Entry	AgX*	Solvent	Yield [%][d]	*ee* [%][e]
1	Ag-**2a**	benzene	86	83
2	Ag-**2a**	CH_2Cl_2	84	15
3	Ag-**2a**	AcOEt	74	57
4	Ag-**2a**	THF	12	61
5	Ag-**2a**	toluene	97	83
6[a]	AgOTf	toluene	71	34
7	AgOTs	toluene	89	46
8	AgOPNB[c]	toluene	27	57
9[b]	AgOPNB[c]	toluene	trace	-
10	Ag-**2b**	toluene	76	40
11	Ag-**2c**	toluene	81	57
12	Ag-**2d**	toluene	85	84
13	Ag-**2e**	toluene	83	80
14	Ag-**2f**	toluene	94	87
15	Ag-**2g**	toluene	14	41
16	Ag-**3**	toluene	88	65
17	Ag-**4**	toluene	73	21
18	Ag-**5**	toluene	38	53

[a] Reaction was examined at 10 °C for 2 h.
[b] (*R*)-DM-BINAP-$(AuCl)_2$ (2.5 mol%) was used instead of (*R*)-**1b**-$(AuCl)_2$.
[c] OPNB = *p*-nitrobenzoate.
[d] Isolated yield.
[e] Enantiomeric excess was determined by chiral HPLC analysis.

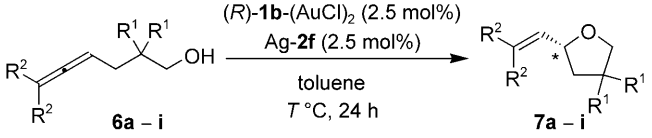


Scheme 2. Dinuclear neutral and cationic Au complexes.

decreased the activity (entries 8 and 9). The chiral silver phosphates could allow us to introduce a variety of different substituents on the 3,3′-positions of the 1,1′-binaphthyl backbone. Indeed, the chiral anion **2f** bearing a *p*-substituted biphenyl ring attained the highest yield and enantioselectivity (94%, 87% *ee*) (entry 14); it was confirmed by taking ^{31}P NMR analysis that the epimerization of DM-BIPHEP **1b** portion did not take place during the course of reaction even at room temperature. In contrast, **2g** which has often been used as an efficient chiral anion in asymmetric catalyses,[5,6] led to a much lower yield and enantioselectivity because of stronger steric hindrance (entry 15). The use of chiral anions bearing a biphenyl or taddole[16] backbone resulted in lower enantioselectivities (entries 16–18).

The scope of allene substrates was examined utilizing the optimized reaction conditions (Table 3). The reaction of **6b**, **c** with *p*-methoxyphenyl or *p*-chlorophenyl groups in the tether smoothly proceeded to

Table 3. Asymmetric catalytic hydroalkoxylation with various allenes.



Entry	R^1, R^2	*T* [°C]	Yield [%][b]	*ee* [%][c]
1[a]	Ph, H (**6a**)	10	94	87
2	*p*-$MeOC_6H_4$, H (**6b**)	0	85	95
3	*p*-ClC_6H_4, H (**6c**)	0	75	77
4	H, Me (**6d**)	−20	97	93
5	H, Et (**6e**)	−20	89	95
6	H, -C_4H_8- (**6f**)	−20	97	90
7	H, -C_5H_{10}- (**6g**)	−20	98	95
8	Ph, Me (**6h**)	10	75	70
9	Ph, -C_5H_{10}- (**6i**)	10	92	75

[a] Reaction time was 20 h.
[b] Isolated yield.
[c] Enantiomeric excess was determined by chiral HPLC or GC analysis.

give moderate-to-good yield and enantioselectivity (85%, 95% *ee* and 75%, 77% *ee*) (entries 2 and 3). The reaction could also be extended to allenes even without substituent in the tether. Allenes **6d–g** were also reactive at −20 °C to provide good-to-excellent yields and enantioselectivities (89–98%, 90–95% *ee*) (entries 4–7). The use of **6h**, **i** provided good yields but decreased enantioselectivities (75%, 70% *ee* and 92%, 75% *ee*) (entries 8 and 9).

In summary, we have described an asymmetric synergy effect through the combination of a dinuclear gold complex and a chiral phosphate on the intramolecular hyroalkoxylation of allenes to give the corresponding products in high yields and enantioselectivites. It has also been clarified that the monocationic dinuclear gold complex affords higher catalytic activity and enantioselectivity. This synergistic effect on asymmetric catalyst systems is thus highly promising to gain a new insight in designing a chiral environment for producing an efficient asymmetric catalyst. Further mechanistic studies and applications of asymmetric activation/asymmetric synergy effect to other asymmetric catalysis are in progress.

Experimental Section

Isolation of Enantiopure (*R*)-1b-$(AuCl)_2$

To a mixture of *rac*-**1b**-$(AuCl)_2$ (44.0 mg, 0.04 mmol) and (*R*)-Ag-**2f** (69.7 mg, 0.08 mmol) was added acetone (8.0 mL), and the reaction mixture was stirred at 100 °C for 14 h. After the addition of CH_2Cl_2 (8.0 mL), the reaction mixture was filtered through celite and concentrated under reduced pressure. The yellow solid was dissolved in the minimum amount of dichloromethane and precipitated by dropwise addition of pentane. The complex was washed three times with pentane, and then dried under vacuum. The single diastereomer (*R*)-**1b**-Au/[(*R*)-**2f**]$_2$, which was confirmed by ^{31}P NMR analysis, was obtained quantitatively.

To a solution of the single diastereomer (*R*)-**1b**-Au/[(*R*)-**2f**]$_2$ (102.3 mg, 0.04 mmol) in CH_2Cl_2 (10 mL) was added 2 drops of concentrated HCl at 0 °C, and stirred at 10 °C for 3 h. The reaction mixture was washed with saturated $NaHCO_3$ solution and water. The resultant organic layer was dried over Na_2SO_4, and then concentrated under vacuum. Purification by column chromatography on silicagel (CH_2Cl_2 only) to give enantiopure (*R*)-**1b**-$(AuCl)_2$ (quantitatively). (*R*)-**2f** was recovered by column chromatography on silica gel (acetone only) as (*R*)-H-**2f** quantitatively.

Typical Experimental procedure (Table 2, entry 14)

To a solution of (*R*)-**1b**-$(AuCl)_2$ (4.4 mg, 0.004 mmol) in toluene (0.6 mL) was added (*S*)-Ag-**2f** (3.5 mg, 0.004 mmol) at 10 °C under an argon atmosphere. After the mixture had been stirred at 10 °C for 30 min, a solution of **6a** (40 mg, 0.16 mmol) in toluene (0.7 mL) was added at that temperature. After stirring at 10 °C for 20 h, the reaction mixture was directly loaded on to a silica gel column and eluted with hexane/ethyl acetate to give **7a**; yield: 94%. The enantiomeric excess was determined by chiral HPLC analysis (87% *ee*).

Acknowledgements

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[13] Crystal data for (*R*)-**1b**-$(AuCl)_2$: $C_{44}H_{44}Au_2Cl_2P_2$, orthorhombic, space group $P2_12_12_1$, $a=11.5398(10)$ Å, $b=17.523(15)$ Å, $c=20.837(17)$ Å, $V=4213(5)$ Å^3, $Z=4$, $D_{calc}=1.733$ g cm^{-3}, and $\mu = 72.116$ cm^{-1}. All measurements were made on a Rigaku Mercury375R/M CCD (XtaLAB mini) diffractometer with graphite monochromated Mo-Kα radiation at 193 K. Of the 44180 reflections that were collected, 9638 were unique ($R_{int}=0.0998$). $R_1=0.0566$, $wR_2=0.1377$, goodness of fit = 1.134, Flack parameter = −0.018(10), shift/error = 0.001. CCDC 782222 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

[14] M. A. Tarselli, A. R. Chianese, S. J. Lee, M. R. Gagné, *Angew. Chem.* **2007**, *119*, 6790; *Angew. Chem. Int. Ed.* **2007**, *46*, 6670.

[15] For details, see the Supporting Information.

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