Asymmetric Catalysis

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Gold(I)-Catalyzed Stereoconvergent, Intermolecular Enantioselective Hydroamination of Allenes**

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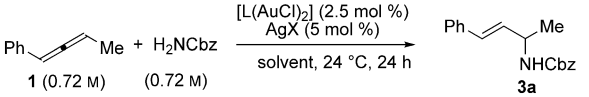
The intermolecular, enantioselective addition of the N–H bond of an amine or carboxamide derivative across a C–C multiple bond (hydroamination) represents an attractive, atom-economical approach to the synthesis of chiral, nonracemic amines and amine derivatives.[1] Within this family of transformations, the intermolecular enantioselective hydroamination (EHA) of allenes is of interest as a potentially expedient route to enantiomerically enriched α-chiral allylic amines, which are important chiral building blocks that are utilized in the synthesis of complex nitrogen-containing molecules.[2] However, despite considerable efforts in this area,[1] effective intermolecular EHA processes are scarce,[3] and the intermolecular EHA of allenes remains unknown.[4]

One of the challenges associated with the intermolecular EHA of allenes is the regioselectivity of extant hydroamination catalysts, which form predominantly achiral products from electronically unbiased monosubstituted allenes.[4,5] To circumvent this regiochemical bias, we envisioned the stereoconvergent, intermolecular EHA of chiral, racemic 1,3-disubstutited allenes catalyzed by chiral bis(gold) phosphine complexes. This approach builds upon our previous efforts in the area of gold-catalyzed allene hydroamination.[6,7] In particular, we have shown that achiral gold(I) N-heterocyclic carbene (NHC) complexes catalyze the regio- and diastereoselective hydroamination of chiral 1,3-disubstituted allenes with carbamates, and that allene racemization was rapid under reaction conditions.[6] Furthermore, both we[7] and Toste and co-workers[8] have demonstrated the enantioselective intramolecular hydroamination of allenes catalyzed by chiral bis(gold) phosphine complexes.[9] Herein we describe the stereoconvergent, enantioselective, intermolecular hydroamination of chiral, racemic 1,3-disubstituted allenes with carbamates catalyzed by chiral bis(gold) phosphine complexes.[10]

Initial experiments directed toward the intermolecular EHA of allenes were only modestly encouraging. The reaction of benzyl carbamate (0.72 M) with 1-phenyl-1,2-butadiene (**1**; 1 equiv) catalyzed by a 1:2 mixture of [{(*R*)-**2**}$(AuCl)_2$] ((*R*)-**2** = (*R*)-DTBM-MeOBIPHEP, see structure of (*S*)-**2** under Table 1) and AgOTf (OTf = trifluoromethanesulfonate) in dioxane at 24 °C for 24 h led to isolation of *N*-allylic carbamate (*R*)-**3a** in 35% yield as a single diastereomer (d.r. ≥ 25:1) with 50% *ee* (Table 1, entry 1).[11,12] Substitution of ligand (*R*)-**2** with the SEGPHOS ligand (*R*)-**4** led to deterioration in both the yield and enantioselectivity of hydroamination (Table 1, entry 2). Conversely, optimization with respect to silver salt revealed that the use of $AgBF_4$ instead of AgOTf led to marked improvement in both yield and enantioselectivity of gold-catalyzed allene hydroamination (Table 1, entry 7). The reaction yield was further improved through employment of a slight excess of allene relative to benzyl carbamate and, in an optimized procedure, treatment of benzyl carbamate (0.72 M) with **1** (1.5 equiv) and a catalytic 1:2 mixture of [{(*S*)-**2**}$(AuCl)_2$] and $AgBF_4$ in dioxane at 24 °C led to isolation of (*S*)-**3a** in 89% yield with 72% *ee* (Table 1, entry 10). A single recrystallization from warm hexanes increased the enantiopurity of (*S*)-**3a** to 96% *ee*.

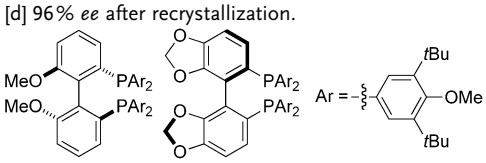
Table 1: Effect of supporting ligand, solvent, silver salt, and allene concentration on the gold(I)-catalyzed enantioselective hydroamination of **1** with benzyl carbamate.



1 (0.72 M) (0.72 M) **3a**

Entry	L	AgX	Solvent	Yield [%][a]	*ee* [%]	Config.
1	(*R*)-**2**	AgOTf	dioxane	35	50	*R*
2	(*R*)-**4**	AgOTf	dioxane	15	44	*R*
3	(*S*)-**2**	$AgSbF_6$	dioxane	20	60	*S*
4	(*S*)-**2**	$AgPF_6$	dioxane	12	66	*S*
5	(*S*)-**2**	$AgClO_4$	dioxane	49	63	*S*
6	(*S*)-**2**	$AgNTf_2$	dioxane	20	45	*S*
7	(*S*)-**2**	$AgBF_4$	dioxane	71	72	*S*
8	(*S*)-**2**	$AgBF_4$	toluene	65	50	*S*
9[b]	(*S*)-**2**	$AgBF_4$	THF	36	61	*S*
10[c]	(*S*)-**2**	$AgBF_4$	dioxane	89	72[d]	*S*

[a] Yield of isolated product; d.r. ≥ 25:1. Cbz = benzyloxycarbonyl. [b] [**1**] = [H_2NCbz] = 0.4 M, 48 h, yield determined by GC. [c] [**1**] = 1.1 M. [d] 96% *ee* after recrystallization.



(*S*)-**2** (*R*)-**4**

In addition to benzyl carbamate, methyl carbamate; 9-fluorenylmethyl carbamate; and trichloroethyl carbamate

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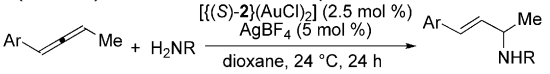
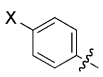
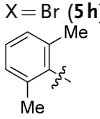
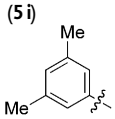
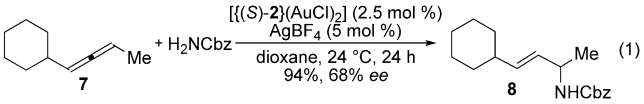
underwent gold-catalyzed reaction with **1** to form *N*-allylic carbamates **3b**–**3d** with enantiopurities comparable to that of **3a** (Table 2, entries 1–3).[13] Likewise, gold-catalyzed intermolecular EHA was effective for a number of 1-aryl-1,2-butadienes (Table 2, entries 4–13). For example, gold(I)-catalyzed reactions of benzyl carbamate with *p*-substituted 1-aryl-1,2-butadienes **5a**–**5d** led to isolation of *N*-allylic carbamates **6a**–**6d** in 82–99% yield with 60–76% *ee*, albeit without a clear relationship between the electron-donating or -withdrawing properties of the arenes and the enantioselectivity (Table 2, entries 4–7). Also worth noting is that the enantiopurity of **6d** increased from 69 to 99% *ee* after a single recrystallization from warm hexanes (Table 2, entry 7). In comparison, gold-catalyzed hydroamination of the *ortho*-substituted 1-aryl-1,2-butadienes **5e**–**5h** formed *N*-allylic carbamates **6e**–**6h** with 80–86% *ee* (Table 2, entries 8–11). Gold(I)-catalyzed intermolecular hydroamination of the more sterically hindered *o*,*o*-disubstituted 1-aryl-1,2-butadiene **5i** occurred with even higher enantioselectivity (92% *ee*) but with diminished yield (Table 2, entry 12). Gold-catalyzed intermolecular EHA was not restricted to 1-aryl-1,2-butadienes, and gold-catalyzed reaction of 1,3-dialkyl-substituted allene **7** with benzyl carbamate led to isolation of *N*-allylic carbamate **8** in 94% yield with 68% *ee* [Eq. (1)]. Conversely, gold-catalyzed intermolecular EHA was not effective for 1,3-disubstituted allenes lacking a methyl substituent.[14]

Table 2: Enantioselective hydroamination of allenes (1.1 M) with carbamates (0.71 M) catalyzed by a mixture of [{(*S*)-**2**}$(AuCl)_2$] (2.5 mol%) and $AgBF_4$ (5 mol%) in dioxane at room temperature.



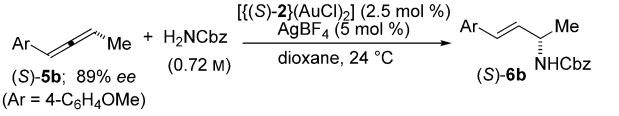
Entry	Ar	R[a]	Product	Yield [%][b]	*ee* [%][c]
1	Ph (**1**)	CO_2Me	**3b**	81	69
2	Ph (**1**)	Fmoc	**3c**	79	71
3	Ph (**1**)	Troc	**3d**	43	73
					
4	X = Me (**5a**)	Cbz	**6a**	97	72
5	X = OMe (**5b**)	Cbz	**6b**	85	60
6	X = CF_3 (**5c**)	Cbz	**6c**	82	75
7	X = Br (**5d**)	Cbz	**6d**	99	69[d]
					
8	X = Me (**5e**)	Cbz	**6e**	82	81
9[e]	X = *i*-Pr (**5f**)	Cbz	**6f**	80	81
10	X = Ph (**5g**)	Cbz	**6g**	86	86
11	X = Br (**5h**)	Cbz	**6h**	69	80
12[e]	 (**5i**)	Cbz	**6i**	42	92
13[e]	 (**5j**)	Cbz	**6j**	44	72

[a] Troc = 2,2,2-trichloroethoxycarbonyl, Fmoc = fluorenylmethyloxycarbonyl. [b] Yield of isolated product; d.r. ≥ 25:1. [c] Enantiomeric excess determined by HPLC analysis using chiral support. Absolute configuration assigned as *S* based on analogy to (*S*)-**3a**. [d] 99% *ee* after recrystallization. [e] Reaction run for 48 h.



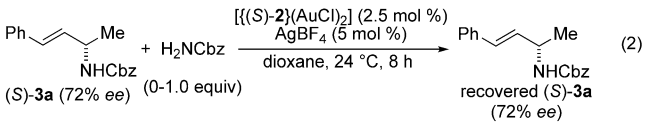
Congruent with our expectations, allene racemization occurred rapidly under reaction conditions. For example, a solution of enantiomerically enriched (*S*)-**5b** (89% *ee*), benzyl carbamate, and a catalytic mixture of [{(*S*)-**2**}$(AuCl)_2$] and $AgBF_4$ was periodically analyzed by HPLC using a chiral stationary phase; the analysis revealed complete racemization of (*S*)-**5b** prior to any detectable formation of **6b** (≤ 5 min; Table 3). Interestingly, continued analysis of the reaction mixture showed that the enantiopurity of **6b** decreased from 69% *ee* at 21% conversion to a terminal value of 59% *ee* at ≥ 74% conversion (Table 3). This phenomenon was not restricted to the formation of **6b**, and the enantiopurity of **3a** formed in the gold-catalyzed reaction of **1** with benzyl carbamate likewise decreased from 78% *ee* at 22% conversion to a terminal value of 72% *ee* at ≥ 83% conversion.

Table 3: Enantiopurity of allene and *N*-allylic carbamate as a function of conversion for the gold-catalyzed hydroamination of (*S*)-**5b** (89% *ee*).

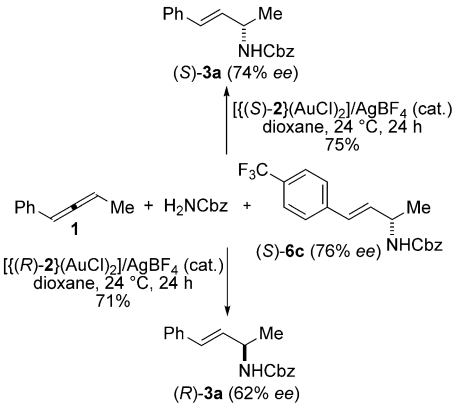


t [h]	Conv. [%]	**5b** *ee* [%]	**6b** *ee* [%]
≤ 0.08	≤ 2	≤ 2	–
1.0	21	≤ 2	69
1.5	39	≤ 2	65
2.0	44	≤ 2	63
4.0	74	≤ 2	59
5.0	81	≤ 2	58
6.0	> 90	≤ 2	59

Although we initially considered that racemization of **3a** or **6b** under the reaction conditions was responsible for the conversion-dependent enantioselectivity displayed by the gold-catalyzed intermolecular EHA of **1** or **5b**, respectively, this possibility was excluded. For example, stirring a solution of (*S*)-**3a** (72% *ee*) and a catalytic 1:2 mixture of [{(*S*)-**2**}$(AuCl)_2$] and $AgBF_4$ at room temperature for eight hours either in the presence (1 equiv) or absence of benzyl carbamate led to no detectable decrease in the enantiopurity of (*S*)-**3a** [Eq. (2)]. Rather, a pair of experiments pointed to the potentially deleterious effect of the *N*-allylic carbamate product on the enantioselectivity of intermolecular EHA. For example, treatment of a 1.5:1:1 mixture of **1**, benzyl carbamate, and (*S*)-**6c** with a catalytic mixture of [{(*S*)-**2**}$(AuCl)_2$]/$AgBF_4$ at 24 °C for 24 h led to isolation of (*S*)-**3a** in 75% yield



with 74% *ee* (Scheme 1), which is a nominally higher enantioselectivity than was realized in the absence of (*S*)-**6c** (Table 1, entry 10). However, the corresponding reaction of **1**, benzyl carbamate, and (*S*)-**6c** catalyzed by [{(*R*)-**2**}$(AuCl)_2$]/$AgBF_4$ led to isolation of (*R*)-**3a** in 71% yield with 62% *ee* (Scheme 1), which is a considerably lower enantioselectivity than was observed in the absence of (*S*)-**6c**.



Scheme 1. Effect of *N*-allylic carbamate (*S*)-**6c** on the hydroamination of **1** with benzyl carbamate.

Rapid allene racemization precluded stereochemical analysis of the gold-catalyzed intermolecular EHA of (*S*)-**5b** (Table 3). However, we have previously established the *anti* stereochemistry of gold(I)-catalyzed intramolecular enantioselective allene hydrofunctionalization,[7,15] which is consistent with the outer-sphere addition of the nucleophile to a gold(I) π-allene complex. Although such a mechanism requires that one of the two gold centers of a bis(gold) catalyst participates in the allene activation/C–N bond formation process, there is no firm evidence that supports the direct participation of the second gold center in these steps.[10,16] There is, however, evidence that the ligation state of this spectator gold center can affect the enantioselectivity of gold-catalyzed hydrofunctionalization.[8] Given the noncoordinating nature of the BF_4^- counterion employed in the gold-catalyzed intermolecular EHA of allenes, the spectator gold center is presumably ligated with an allene, benzyl carbamate, or either enantiomer of the *N*-allylic carbamate product.[17] Therefore, the decreasing enantioselectivity of the gold-catalyzed intermolecular EHA of allenes with increasing conversion presumably reflects the increasing concentration of a less selective *N*-allylic carbamate ligated catalyst species.

In summary, we have developed a gold(I)-catalyzed protocol for the stereoconvergent, intermolecular enantioselective hydroamination of chiral, racemic 1,3-disubstituted allenes with *N*-unsubstituted carbamates. Furthermore, the observed decrease in enantioselectivity with increasing conversion of intermolecular EHA coupled with independent analysis of the effect of *N*-allylic carbamate on the enantioselectivity of these transformations suggests that the nature of the catalytically active species changes with increasing concentration of *N*-allylic carbamate. We continue to work toward the identification of more selective and more general catalytic systems for intermolecular EHA and toward the development of ligand-modulated enantioselective gold catalysis.

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[11] a) The absolute configuration of (*S*)-**3a** was determined by optical rotation {$[\alpha]_D^{25} = -39.4$ ($c = 0.19$, CH_2Cl_2); lit. [for (*S*)-**3a**] $[\alpha]_D^{23} = -55.4$ ($c = 1.10$, CH_2Cl_2)}.[11b] The absolute configurations of all remaining *N*-allylic carbamates were assigned by analogy; b) J. C. A. Hunt, P. Laurent, C. J. Moody, *J. Chem. Soc. Perkin Trans. 1* **2002**, 2378 – 2389.

[12] a) Allenes depicted in Tables 1 and 2 were synthesized in two steps from 3-butyne-2-ol in 26–51% yield employing the procedures of Knochel and co-workers[12c] and Myers and Zheng,[12b] with the exception of **1**, which was synthesized in one step from 4-phenyl-3-butyn-2-ol; b) A. G. Myers, B. Zheng, *J. Am. Chem. Soc.* **1996**, *118*, 4492 – 4493; c) N. Harrington-Frost, H. Leuser, M. I. Calaza, F. F. Kneisel, P. Knochel, *Org. Lett.* **2003**, *5*, 2111 – 2114.

[13] Sulfonamides were less effective than were carbamates. For example, gold-catalyzed reaction of **1** with *p*-toluenesulfonamide at room temperature for 48 h formed (*E*)-4-methyl-*N*-(4-phenyl-but-3-en-2-yl)benzenesulfonamide in 57% yield with 28% *ee*.

[14] For example, gold-catalyzed reaction of 1-phenyl-1,2-pentadiene with benzyl carbamate at room temperature for 48 h formed (*E*)-benzyl (1-phenylpent-1-en-3-yl)carbamate in 13% yield with 23% *ee*.

[15] Z. Zhang, R. A. Widenhoefer, *Angew. Chem.* **2007**, *119*, 287 – 289; *Angew. Chem. Int. Ed.* **2007**, *46*, 283 – 285.

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Communications

Asymmetric Catalysis

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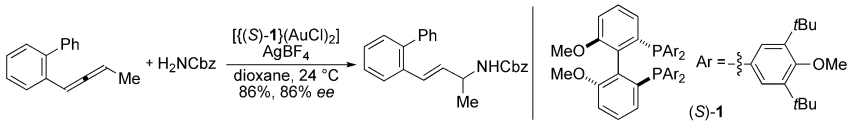
Gold(I)-Catalyzed Stereoconvergent, Intermolecular Enantioselective Hydroamination of Allenes



Gold and silver: A 1:2 mixture of [{(*S*)-**1**}$(AuCl)_2$] and $AgBF_4$ catalyzes the enantioselective hydroamination of chiral, racemic 1,3-disubstituted allenes with N-unsubstituted carbamates to form *N*-allylic carbamates in good yield, with high regio- and diastereoselectivity, and up to 92% *ee* (see scheme, Cbz = benzyloxycarbonyl).