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Chiral Brønsted Acid from a Cationic Gold(I) Complex: Catalytic Enantioselective Protonation of Silyl Enol Ethers of Ketones

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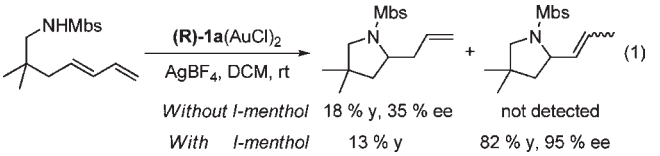
Supporting Information

ABSTRACT: A chiral Brønsted acid has been developed from a cationic gold(I) disphosphine complex in the presence of alcoholic solvent and applied to the enantioselective protonation reaction of silyl enol ethers of ketones. Various optically active cyclic ketones were obtained in excellent yields and high enantioselectivities, including cyclic ketones bearing aliphatic substrates at the α-position. Furthermore, the application of this Brønsted acid was extended to the first Brønsted acid-catalyzed enantioselective protonation reaction of silyl enol ethers of acyclic substrates, regardless of their *E*/*Z* ratio.

Over the past decade, gold catalysis has attracted significant attention from the synthetic community.[1] More recently, notable progress has been made in asymmetric catalysis using homogeneous gold(I) complexes. In general, enantioselective reactions have relied on the ability of cationic gold(I) complexes to activate π-donor ligands such as alkynes, allenes, and alkenes toward nucleophilic attack.[2−4] In contrast, similar σ complexes of cationic gold complexes with σ-donor ligands have been little explored in asymmetric catalysis, although there have been several reports of reactivity differences in gold catalysis in the presence of protic additives.[5] Very recently, we found that an alcoholic additive has a dramatic effect on the regio- and enantioselectivity in gold-catalyzed hydroamination of 1,3-dienes.[6] For example, in the absence of alcohol, 1,2-addition products were obtained as exclusive products with very poor enantioselectivity, whereas in the presence of an alcohol additive, 1,4-addition products were obtained in good yields with high enantioselectivity (eq 1).



We hypothesized that in the absence of alcohol, the cationic gold(I) complex directly activates the 1,3-diene toward nucleophilic attack, leading to the 1,2-addition products. On the other hand, in the presence of alcohol, cationic gold(I) forms a σ complex with the alcohol, generating a chiral Brønsted acid activated by complexation with gold, that is, a so-called Lewis acid-activated Brønsted acid (LBA).[7] On the basis of these observations, we envisioned that a new chiral Brønsted acid could be generated by complexation of alcohol with cationic gold, significantly enhancing the acidity of the original alcohol. Herein we describe the development of a chiral LBA derived from a cationic gold complex and its application to the enantioselective protonation reaction of silyl enol ethers of ketones.[8−11]

We began our investigation by examining the protonation reaction of silyl enol ether **4a** catalyzed by 3 mol % (*R*)-DTBM-SEGPHOS(AuCl)$_2$ activated by 3 mol % AgBF$_4$ in isopropyl alcohol as the solvent. Under these conditions, the desired protonation product **5a** was obtained in quantitative yield and 87% ee (Table 1, entry 1). Encouraged by this initial result, we examined other chiral diphosphine(bis)gold complexes as catalysts for the enantioselective protonation reaction (entries 2−6). Among the gold(I) complexes tested, the (*R*)-BINAP-derived complex proved to generate the most selective catalyst for the asymmetric protonation reaction (entry 5).

With BINAP as the diphosphine ligand on gold, we next examined the effect of the counterion on the protonation reaction (entries 4 and 7−11). Generation of the cationic gold(I) complex proved to be essential for the protonation reaction, as no protonation was observed without AgBF$_4$ (entry 12) or when a more coordinating counterion was used (entry 7). On the other hand, reactive catalysts were generated from noncoordinating anions (entries 4 and 8−11), with tetrafluoroborate providing the protonation adduct with highest enantioselectivity. Furthermore, the catalyst derived from the monocationic gold(I) complex proved to be more selective than the one from the dicationic gold complex (entries 5 and 13). We also investigated the possibility of protonation catalyzed by a Brønsted acid derived from the AgBF$_4$·BINAP complex; however, this silver-based Brønsted acid was not reactive enough to protonate silyl enol ether **4a** (entry 14).[12] Finally, the enantioselectivity could be further increased by changing the solvent from isopropyl alcohol to ethanol (entry 15).[13]

With these optimized conditions, we first investigated the scope of the gold-catalyzed enantioselective protonation reaction of silyl enol ethers of cyclic ketones (Table 2). Various silyl enol ethers from 2-aryl cyclic ketones could be employed in the enantioselective protonation reaction, and the corresponding ketones were obtained in excellent yields with high enantioselectivities (entries 1−5). The cationic gold(I)-derived LBA could be further applied to the protonation reaction of silyl enol ethers of 2-alkyl cyclic ketones (entries 6 and 7). Tetralone and indanone analogues bearing a methyl group at the 2-position were obtained in quantitative yield with excellent enantioselectivity. It is

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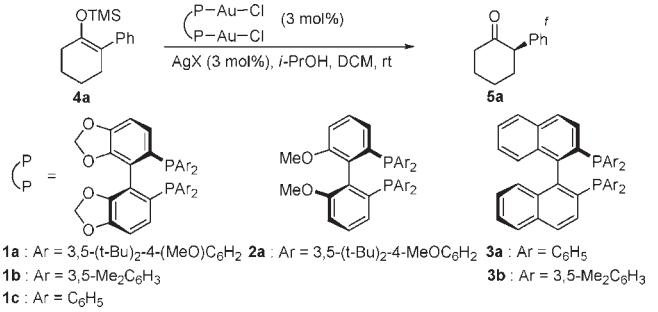
Table 1. Optimization of the Reaction Conditions



1a : Ar = 3,5-(t-Bu)$_2$-4-(MeO)C$_6$H$_2$ **2a** : Ar = 3,5-(t-Bu)$_2$-4-MeOC$_6$H$_2$ **3a** : Ar = C$_6$H$_5$
1b : Ar = 3,5-Me$_2$C$_6$H$_3$ **3b** : Ar = 3,5-Me$_2$C$_6$H$_3$
1c : Ar = C$_6$H$_5$

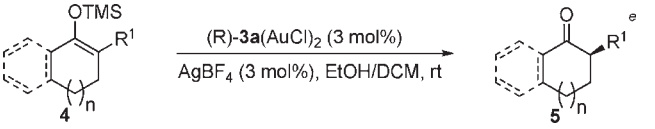
entry	P P	AgX	conversion (%)[a]	ee (%)[b]
1	**1a**	$AgBF_4$	100	87
2	**1b**	$AgBF_4$	70	87
3	**1c**	$AgBF_4$	100	83
4	**2a**	$AgBF_4$	100	36
5	**3a**	$AgBF_4$	100	88
6	**3b**	$AgBF_4$	100	70
7	**3a**	AgOBz	N. R.	N. D.
8	**3a**	$AgNTf_2$	100	86
9	**3a**	AgOTf	100	86
10	**3a**	$AgClO_4$	100	84
11	**3a**	$AgSbF_6$	100	82
12	**3a**	-	N.R.	N. D.
13[c]	**3a**	$AgBF_4$	100	83
14[d]	**3a**	$AgBF_4$	N.R.	N. D.
15[e]	**3a**	$AgBF_4$	100	93

[a] Conversion was determined by ^{1}H NMR analysis. [b] Enantiomeric excess (ee) was determined by HPLC using a chiral IC column. [c] 6 mol % $AgBF_4$ was used. [d] The reaction was carried out in the absence of gold. [e] EtOH was used as the solvent. [f] The absolute stereochemistry was determined by comparison of optical rotation.[13]

noteworthy that the ring size of the cyclic ketone had little effect on the reactivity, and high levels of enantioselectivity were obtained regardless of ring size (entry 1 vs 5 and entry 6 vs 7).

Although several examples of Brønsted acid-catalyzed enantioselective protonation reactions of silyl enol ethers of cyclic ketones have been reported,[9−11] to the best of our knowledge, *there have been no reports of Brønsted acid-catalyzed enantioselective protonation reactions of silyl enol ethers of acyclic ketones.*[14,15] Therefore, we next examined the use of our gold(I)-based catalytic system for the enantioselective protonation of these more challenging substrates. The first anticipated challenge with acyclic substrates is the stereochemistry of the starting silyl enol ether. In contrast to cyclic ketones having only one isomer of the silyl enol ether, acyclic ketones can generate both (*E*)- and (*Z*)-silyl enol ethers. Since the transition states for the protonations of these diastereomeric silyl enol ethers are different, we anticipated that it might be important to generate the silyl enol ethers diastereoselectively.[8e] Furthermore, the acyclic substrates generally have more conformational flexibility than the corresponding cyclic ones, which can also lead to lower asymmetric induction.

Table 2. Substrate Scope for Cyclic Ketones



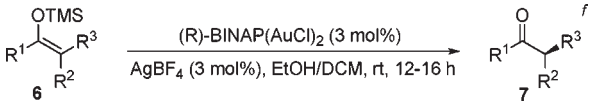
entry		n	R^1	yield (%)[a]	ee (%)[b]
1		1	Ph (**4a**)	96	93
2[c]	OTMS	1	4-MeOPh (**4b**)	98	90
3[c]	R^1	1	4-MePh (**4c**)	95	91
4	n	1	2-naphthyl (**4d**)	94	94
5[d]		2	Ph (**4e**)	95	94
6	OTMS	1	Me (**4f**)	96	93
7	R^1 n	0	Me (**4g**)	97	94

[a] Isolated yields. [b] Determined by chiral HPLC. [c] The reaction was conducted at −24 °C. [d] The reaction was carried out in EtOH without CH_2Cl_2. [e] The absolute stereochemistry was established by comparison of the optical rotations of the known compounds **4a** and **4f**. The absolute stereochemistries of the remaining compounds were assigned by analogy.[13]

With these challenges in mind, we examined the LBA-catalyzed asymmetric protonation reactions of silyl enol ethers of acyclic substrates (Table 3). First, we attempted to synthesize the stereochemically pure silyl enol ether of 2-phenylpropiophenone (**6a**), but after several unsuccessful attempts at this,[16] we decided to apply a mixture of (*E*) and (*Z*) silyl enol ethers to the enantioselective protonation reaction under the standard conditions developed for protonation reaction of cyclic substrates. To our surprise, the protonation product was obtained in nearly quantitative yield with 92% ee despite a 2:1 isomeric ratio of the silyl enol ether substrate (Table 3, entry 1).

With this rather unexpected result in hand, we moved our attention to other acyclic substrates under the same reaction conditions. Several other silyl enol ethers obtained from 2-aryl propiophenones were prepared were prepared as mixtures of *E* and *Z* isomers. Protonation products, however, were obtained in excellent yields and high enantioselectivities regardless of the *E*/*Z* ratio in the mixture of starting silyl enol ethers (entries 2−8). Electronic effects had little impact on the enantioselectivity (entries 1−4), although electron-withdrawing substituents required somewhat longer reaction times (entry 4). The reaction tolerated cyclic ketones bearing bulky aryl groups at the α-position, such as an *ortho*-substituted aryl group, albeit with slightly lower enantioselectivities (entries 6−8). We further examined the effect of substituents on the aromatic ring of 2-phenyl propiophenene (entries 1 and 9−11). Substituents on the phenyl ring had little effect on the enantioselectivity (entries 1 and 9−10), although the silyl enol ether with an electron-withdrawing substituent reacted more slowly in the protonation reaction (entry 11). Furthermore, alkyl-substituted silyl enol ether **6l** could also be employed in the gold-catalyzed protonation reaction with only slightly lower enantioselectivity (entry 12). The catalyst system was also effective for the protonation of the silyl enol ether of 2-phenyl butyrophenone

Table 3. Substrate Scope for Acyclic Ketones



entry	silyl enol ether		E/Z [c]	yield (%) [a]	ee (%) [b]
1		R^3 = Ph (**6a**)	2:1	97	92
2 [e]		R^3 = 4-MeOPh (**6b**)	5:1	98	95
3		R^3 = 4-MePh (**6c**)	2:1	95	95
4 [d]	OTMS, Ph, R^3, Me	R^3 = 4-CF_3Ph (**6d**)	1:1	92	92
5		R^3 = 2-naphthyl (**6e**)	2:1	95	94
6		R^3 = 1-naphthyl (**6f**)	3:1	91	86
7 [e]		R^3 = 2-MeOPh (**6g**)	3:1	94	90
8		R^3 = 2-MePh (**6h**)	2:1	93	85
9		R^1 = 4-MeOPh (**6i**)	3:1	94	89
10	OTMS, R^1, Ph, Me	R^1 = 4-MePh (**6j**)	3:1	95	90
11 [d]		R^1 = 4-CF_3Ph (**6k**)	3:1	82	88
12		R^1 = *t*-Bu (**6l**)	1:1	89	84
13	OTMS, Ph, R^2, Et	R^2 = Ph (**6m**)	1:1	91	85
14		R^2 = Me (**6n**)	4:1	94	17

[a] Isolated yields. [b] Determined by chiral HPLC. [c] Ratio of the major silyl enol ether to the minor silyl enol ether. [d] The reaction was carried out in EtOH without CH_2Cl_2. [e] The reaction time was 24 h. [f] The absolute stereochemistry was determined by comparison of the optical rotation of known compound **6a**, and the absolute stereochemistries of the remaining compounds were assigned by analogy.[13]

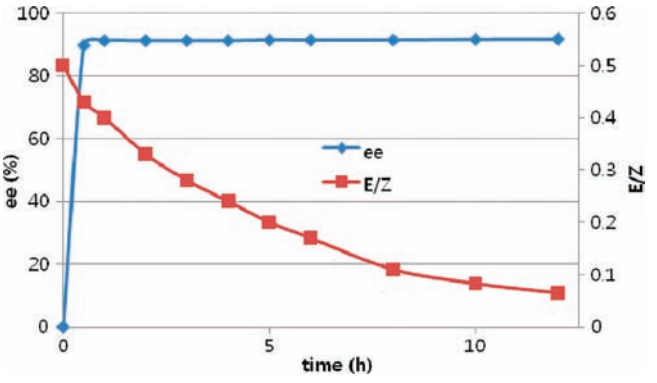
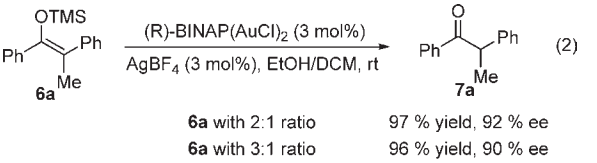


Figure 1. Enantioselectivity and *E*/*Z* ratio during protonation of **6a** with the LBA.

(**6m**), providing the desired ketone in 91% yield with 85% ee (entry 13). However, the silyl enol ether possessing two alkyl groups at the α-position provided the protonation product with poor enantioselectivity (entry 14).[17]

Several experiments were conducted in order to gain insight into the reaction mechanism. First, we tested the possibility that the reaction proceeds by protonation of a gold enolate[18,19] to generate transmetalation of the silyl enol ether; however, silyl enol ether **6a** remained intact and we could not detect any gold enolate formation upon treatment with the cationic gold complex in the absence of alcohol. A second possible scenario would be selective protonation of a rapidly equilibrating mixture of silyl enol ether isomers, in which the isomerization is catalyzed by either protonation or the cationic gold complex.[20] However, we did not observe any isomerization between silyl enol ethers by either LBA or the cationic gold complex, and the ratio of *E* and *Z* isomers did not remain constant during the protonation reaction (Figure 1). The third scenario would be that the gold-derived LBA discriminates between the two isomers and approaches both silyl enol ethers from the same prochiral face, which results in very high enantioselectivity regardless of the *E*/*Z* ratio. This scenario is consistent with the observation that the enantioselectivity of the reaction remains constant, despite changes in the ratio of olefin isomers (Figure 1). Similarly, protonation of the silyl enol ether of 2-phenyl propiophenone with different *E*/*Z* ratios produced ketone **7a** with comparable yields and enantioselectivities (eq 2).



In conclusion, we have developed the first gold-catalyzed enantioselective protonation reaction. The chiral Brønsted acids derived from cationic gold complexes and an alcohol were applied to the enantioselective protonation reaction of silyl enol ethers of ketones. Various silyl enol ethers from cyclic ketones could be applied to this catalytic system, and the desired protonation products were obtained in excellent yields with high enantioselectivities. Furthermore, the catalytic system could be extended to the first enantioselective protonation reactions of silyl enol ethers of acyclic ketones. The silyl enol ethers of acyclic ketones afforded the corresponding ketones with high enantioselectivities even when mixtures of the *E* and *Z* isomers of the silyl enol ethers were used. Mechanistic studies suggested that a gold-derived LBA selectively protonates the silyl enol ethers from the same prochiral face regardless of their stereochemistry.

■ ASSOCIATED CONTENT

Supporting Information. Experimental procedures and compound characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENT

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(12) We investigated the possibility that the protonation reaction was catalyzed by an LBA generated from $AgBF_4$ and alcohol in the absence of the chiral phosphine ligand. However, under these conditions, the silver-derived LBA did not catalyze the protonation reaction.

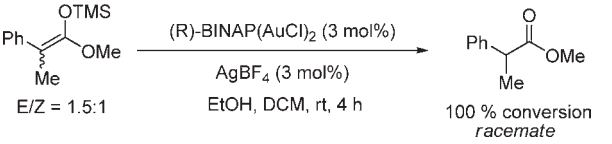
(13) See the Supporting Information for additional details.

(14) An enantioselective protonation reaction of acyclic substrates was reported by Yamamoto; however, the substrates employed could be only single-isomer silyl enol ethers, such as bis(trimethylsilyl)ketene acetals. See ref 9d.

(15) Fu has reported an alternative method for the synthesis of acyclic α-aryl ketones via enantioselective α-arylation of acyclic ketones. See: (a) Lou, S.; Fu, G. C. *J. Am. Chem. Soc.* **2010**, *132*, 1264. (b) Lundin, P. M.; Esquivias, J.; Fu, G. C. *Angew. Chem., Int. Ed.* **2009**, *48*, 154.

(16) The silyl enol ether of 2-phenyl propiophenone was obtained in different *E*/*Z* ratios depending on the reaction conditions. Soft enolization (TMSOTf, NEt_3) gave the silyl enol ether in a 1:3 ratio, whereas hard enolization (LDA/TMSCl) gave the silyl enol ether with a 1:2 ratio. For details, see the Supporting Information.

(17) Under the standard conditions, the gold-catalyzed protonation reaction of the silyl ketene acetal of methyl 2-phenylpropionate gave racemic product:



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