Recent advances in chiral phosphine–silver(I) complex-catalyzed asymmetric reactions

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Received (in Cambridge, UK) 5th November 2007, Accepted 21st December 2007
First published as an Advance Article on the web 24th January 2008
DOI: 10.1039/b717104h

Since the first report of silver(I)-catalyzed asymmetric aldol-type reaction of activated isocyanides with aldehydes using a chiral ferrocenylphosphine as a chiral phosphine ligand has been appeared in 1990, various chiral phosphine–silver(I) catalysts have been utilized in asymmetric transformations. This feature articles describes recent examples of chiral phosphine–silver(I) complex-catalyzed asymmetric reactions such as allylation, aldol reaction, Mannich-type reaction, hetero-Diels–Alder reaction, 1,3-dipolar cycloaddition and nitroso aldol reaction.

Introduction

Silver(I) salts possess moderate Lewis acidity and have been applied as catalysts and promoters to organic reactions. For instance, $AgNO_3$, $AgClO_4$, $AgBF_4$ and AgOTf are known to induce cycloadditions, rearrangements and glycosylation, which make use of their attractive interaction with halogen and sulfur functional groups, and carbon–carbon multiple bonds.[1] The first example of chiral silver(I)-catalyzed asymmetric reaction has been reported by Ito and co-workers who have found that chiral ferrocenylphosphine–silver(I) complexes behave as efficient chiral catalysts in asymmetric aldol-type reactions between isocyanoacetates or tosylmethyl isocyanide and aldehydes.[2] Since their findings, numerous chiral silver(I) complexes have been developed for chiral catalysts in asymmetric transformations. This feature article focuses on recent examples of carbon–carbon bond forming reactions catalyzed by chiral phosphine–silver(I) complexes. These catalysts are effective in promoting enantioselective allylation, aldol reaction, Mannich-type reaction, hetero-Diels–Alder reaction, 1,3-dipolar cycloaddition, nitroso aldol reaction and so on.

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Allylation reactions

Asymmetric allylation of carbonyl compounds is a useful method of preparing optically active homoallylic alcohols because the products are readily transformed into nonracemic β-hydroxy carbonyl compounds and other related chiral compounds.[3] In 1996 the BINAP·silver(I) complex-catalyzed asymmetric allylation of aldehydes with allylic stannanes was first reported by Yanagisawa, Yamamoto and their colleagues.[4] Since then, chiral phosphine–silver(I) complexes are frequently employed as chiral catalysts in the carbon–carbon bond forming reaction. Loh and Zhou have shown that a similar chiral silver(I) catalyst, (*S*)-Tol-BINAP·$AgNO_3$ promotes the enantioselective addition of allyltributyltin to aldehydes in an aqueous medium.[5] In contrast, Shi *et al.* have reported that a chiral bidentate diphenylthiophosphoramide prepared from (*R*)-1,1′-binaphthyl-2,2′-diamine is also an effective chiral ligand for the silver(I)-catalyzed asymmetric allylation of aldehydes.[6] Although these allylation reactions are able to yield the corresponding optically active products with high enantioselectivity, they have a demerit of requiring environmentally less benign organotin compounds. To

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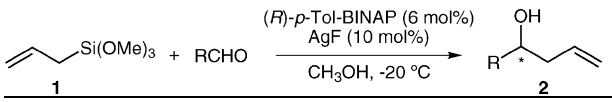
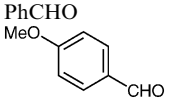
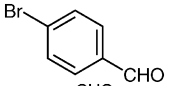
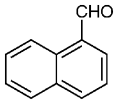
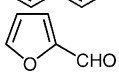
Takayoshi Arai

Takayoshi Arai graduated from Hokkaido University and received his PhD from the University of Tokyo. He became an Assistant Professor at the University of Tokyo in 1995 and moved to Osaka University (1997–2003). He is currently an Associate Professor of Chemistry in Chiba University since 2003. His research interests are focused on the development of new catalysts using combinatorial technologies directed toward the synthesis of biologically significant complex molecules.

Table 1 (*R*)-*p*-Tol-BINAP·AgF complex-catalyzed asymmetric addition of allyltrimethoxysilane (**1**) to various aldehydes[a]

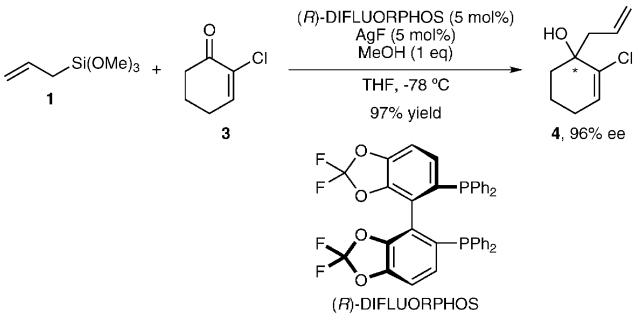


Entry	Aldehyde	Yield[b] (%)	ee[c] (%)
1[d]	PhCHO	80	94 (*R*)
2		67	93 (*R*)
3		90	93
4		81	92 (*R*)
5		70	83 (*R*)
6	(*E*)-PhCH=CHCHO	93	78 (*R*)

[a] Prepared from (*R*)-*p*-Tol-BINAP (6 mol%) and AgF (10 mol%). [b] Isolated yield. [c] Determined by HPLC analysis with chiral columns. [d] 3 mol% of (*R*)-*p*-Tol-BINAP and 5 mol% of AgF were used.

overcome the difficulty, Yanagisawa, Yamamoto and their colleagues have achieved a Tol-BINAP·AgF-catalyzed enantioselective Sakurai–Hosomi-type allylation of aldehydes employing allyltrimethoxysilane (**1**) as an allyl-donor.[7] Table 1 indicates the results given in the reaction of the allylsilane **1** with diverse aldehydes in the presence of 6 mol% of (*R*)-*p*-Tol-BINAP and 10 mol% of silver(I) fluoride in methanol at −20 °C. The reaction furnishes the corresponding optically active homoallylic alcohols **2** in moderate to high yields with significant enantioselectivity not only from aromatic aldehydes but also from an α,β-unsaturated aldehyde. The ratio of *p*-Tol-BINAP to the silver salt is a vital factor for obtaining high yield and enantioselectivity, because a reactive 1 : 1 complex of (*R*)-*p*-Tol-BINAP and AgF is generated accompanied with a considerable amount of an inactive 2 : 1 complex if the silver salt is mixed with an equimolar amount of (*R*)-*p*-Tol-BINAP. In case of an α,β-unsaturated aldehyde, 1,2-addition takes place completely (entry 6). Asymmetric allylation of aldehydes with crotyltrimethoxysilane are also achievable by this recipe.[7] Notable γ and *anti* selectivities are obtained in this reaction, regardless of the double bond geometry of the crotylsilane. The chiral silver(I)-catalyzed allylation protocol has been applied into the asymmetric synthesis of intermediates of fostriecin and 8-*epi*-fostriecin.[8,9]

Wadamoto and Yamamoto have reexamined the chiral silver catalyst system and attained catalytic asymmetric addition of allyltrimethoxysilane to ketones.[10] A variety of acyclic and cyclic ketones including α,β-unsaturated ketones are efficiently allylated with high enantioselectivity as well as exclusive 1,2-selectivity. In fact, the reaction of 2-chloro-2-cyclohexen-1-one (**3**) with 2 equiv. of **1** in the presence of 5 mol% of (*R*)-DIFLUORPHOS, 5 mol% of AgF and 1 equiv. of MeOH in THF at −78 °C for 12 h affords the corresponding tertiary homoallylic alcohol **4** in 97% yield with 96% ee (Scheme 1).



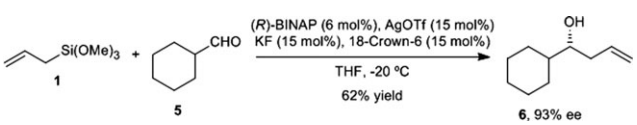
Scheme 1 Catalytic enantioselective addition of allyltrimethoxysilane to ketones.

Employment of γ-substituted allylic trimethoxysilanes results in selective formation of branched *syn* adducts with high enantioselectivity from both *E*- and *Z*-allylic silanes. In this reaction, allylic silver species are suggested to be involved.

Since AgF is not dissolved in less polar aprotic solvents, the above-mentioned catalytic asymmetric allylation reactions have to be carried out in MeOH or a mixture of THF and MeOH as solvent; however, MeOH often brings about unexpected protonation of an allylating agent if it is adequately reactive. Yamamoto and co-workers have therefore developed a new catalyst system comprised of KF·18-crown-6 ether and a BINAP·AgOTf complex in polar aprotic solvent.[11] A catalytic amount of KF·18-crown-6 complex, a soluble fluoride source is effective in activating the asymmetric Sakurai–Hosomi allylation. Noteworthy is the fact that even aliphatic aldehydes show remarkable reactivity under the reaction conditions. For instance, when cyclohexanecarbaldehyde (**5**) is treated with 3 equiv. of allyltrimethoxysilane (**1**) under the influence of (*R*)-BINAP (6 mol%), AgOTf (15 mol%), KF (15 mol%) and 18-crown-6 (15 mol%) in THF at −20 °C, the targeted (*R*)-enriched homoallylic alcohol **6** is formed in 62% yield with 93% ee (Scheme 2). Such an aliphatic aldehydes does not give the desired product under the influence of of BINAP·AgF catalyst in MeOH.[7] Applying this procedure, an enantioselective total synthesis of the antifungal agent (–)-pterocarpin has been accomplished.[12] Chiral phosphine–silver(I) complex catalysts have been further utilized in desymmetrization of cyclohexadienyltriisopropoxysilane choosing benzaldehyde as electrophile though $Cu(OTf)_2$ catalysis provided higher enantio- and diastereoselectivities.[13,14]

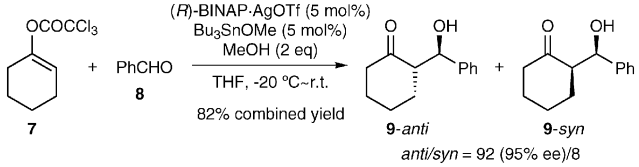
Aldol reactions

The first example of BINAP·silver(I)-catalyzed asymmetric aldol reaction has been realized using tributyltin enolates as nucleophiles by Yanagisawa, Yamamoto and co-workers in 1997.[15] The reaction occurs at low temperature and provides high enantioselectivity as well as diastereoselectivity which is dependent on the enolate's geometry; however, it has an



Scheme 2 Catalytic enantioselective addition of allyltrimethoxysilane to cyclohexanecarbaldehyde.

essential problem of employing a stoichiometric amount of toxic organostannane compounds. In order to improve this point, they have attained an alternative BINAP·silver(I)-catalyzed asymmetric aldol reaction using a catalytic amount of organotin compound.[16,17] A typical example is shown in Scheme 3. When the alkenyl trichloroacetate **7** derived from cyclohexanone is reacted with benzaldehyde (**8**) in the presence of 5 mol% of (*R*)-BINAP, 5 mol% of Bu_3SnOMe and 2 equiv. of MeOH at −20 °C to room temperature in THF, the nonracemic aldol adduct **9** is obtained with an *anti* : *syn* ratio of 92 : 8. The *anti* isomer indicated 95% ee. The catalytic mechanism is shown in Fig. 1. The accelerator of the catalytic cycle is suggested to be MeOH as an additive. First of all, alkenyl trichloroacetate **A** reacts with R_3SnOMe to form trialkytin enolate **B** and methyl trichloroacetate. Successively, the tin enolate **B** undergoes addition reaction to an aldehyde by assistance of a BINAP·AgOTf catalyst to produce a tin alkoxide of nonracemic aldol adduct **C**. Finally, protonolysis of the alkoxide **C** by MeOH gives the



Scheme 3 BINAP·silver(I) catalyzed asymmetric aldol reaction using a catalytic amount of tin compound.

product **D** and regenerates the tin methoxide.

The Mukaiyama aldol reaction is a more ideal route to β-hydroxy carbonyl compounds with respect to environmental friendliness since the method employs less toxic silyl enolates compared to organotin enolates.[18,19] Yamagishi and co-workers have extensively studied a BINAP·Ag(I)-catalyzed asymmetric Mukaiyama aldol reaction of trimethylsilyl enolates and have found that BINAP·$AgPF_6$ accelerates the reaction in DMF containing a small amount of water to yield the aldol adduct with significant enantioselectivity (Scheme 4).[20] They have proposed that a silver enolate species is generated from a silyl enolate under the influence of water.[20a] A crystal structure of a BINAP·Ag(I) complex has been also reported.[20b]

In contrast, Yanagisawa, Yamamoto and co-workers have examined various combinations of BINAP·silver(I) catalysts

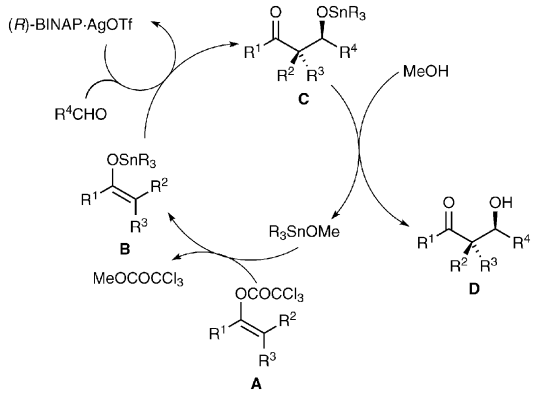
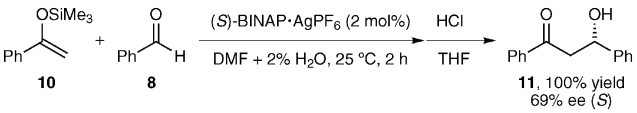


Fig. 1 Suggested catalytic cycle of asymmetric aldol reaction catalyzed by (*R*)-BINAP·AgOTf and tin methoxide.

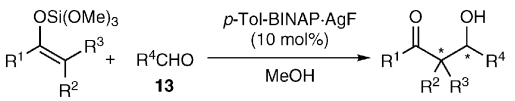


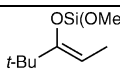
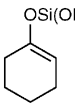
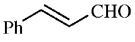
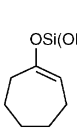
Scheme 4 BINAP·$AgPF_6$ catalyzed asymmetric Mukaiyama aldol reaction with trimethylsilyl enolates.

and silyl enolates and found that high levels of asymmetric induction occur in the *p*-Tol-BINAP·AgF-catalyzed aldol reaction of trimethoxysilyl enolates **12** with aldehydes **13** in methanol (Table 2).[21] The results obtained for the reaction of (*E*)- and (*Z*)-silyl enolates with various aldehydes are summarized in Table 2. *Syn*-aldol adducts **14** are obtained almost exclusively with high enantioselectivity up to 97% ee when (*Z*)-trimethoxysilyl enolate of *tert*-butyl ethyl ketone is treated with benzaldehyde and its derivatives in the presence of 10 mol% of the silver complex at −78 to −20 °C (entries 1–4). In addition, cycloalkanone-derived (*E*)-silyl enolates also give enantiomerically enriched *syn* products diastereoselectively (entries 5–9). In the reaction with an α,β-unsaturated aldehyde, 1,2-adducts are obtained exclusively (entries 4 and 8).

The BINAP/AgOTf/KF/18-crown-6 catalyst system, which is effective in promoting asymmetric allylation of aldehydes with allylic trimethoxysilanes, has been further applied to the Mukaiyama-type aldol reaction of trimethoxysilyl enolates.[11] The catalytic aldol reaction is performable in an aprotic polar solvent such as THF and provides *syn* selectivity regardless of the double-bond geometry (*E* or *Z*) of the silyl enolate

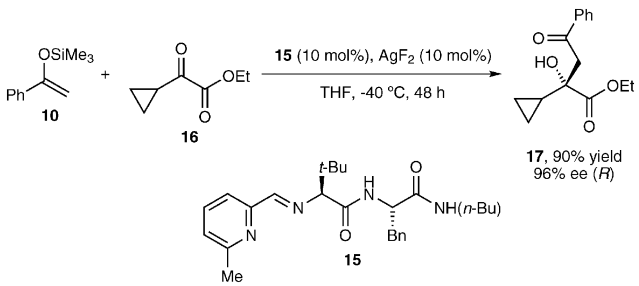
Table 2 Diastereo- and enantioselective aldol reaction of trimethoxysilyl enolates **12** with aldehydes **13** catalyzed by a (*R*)-*p*-Tol-BINAP·AgF complex



Entry	Silyl enolate	Aldehyde	Yield[a] (%)	*Syn* : *anti*[b]	ee[c] (%)
1[d]		PhCHO	84	>99 : 1	97
2[d]		4-$MeOC_6H_4CHO$	76	>99 : 1	96
3[d]		1-Naphthyl-CHO	63	94 : 6	95
4[d]			56	>99 : 1	85
5[e]		PhCHO	78	84 : 16	87
6[e]		4-$MeOC_6H_4CHO$	86	75 : 25	92
7[e]		4-BrC_6H_4CHO	87	76 : 24	90
8[e]			81	81 : 19	68
9[e]		PhCHO	67	81 : 19	78

[a] Isolated yield. [b] Determined by ^1H NMR analysis. [c] The value corresponds to the major diastereomer. Determined by HPLC analysis with chiral columns. [d] The reaction was performed at −78 °C for 2 h, then at −40 °C for 2 h and finally at −20 °C for 2 h. [e] The reaction was performed at −78 °C for 4 h.

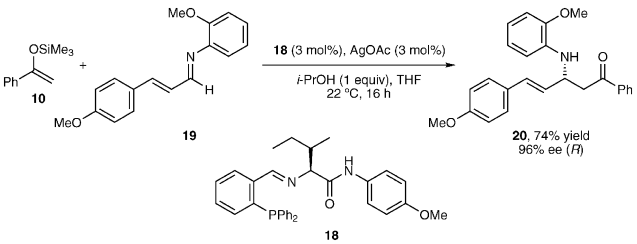
employed. This stereochemical feature is similar to that shown by *p*-Tol-BINAP·AgF catalyst.[21] By adopting the bifunctional catalyst system: BINAP·AgOTf complex and a fluoride source, enantioselective hydroxymethylation of trimethoxysilyl enolates has been also accomplished using an aqueous solution of formalin.[22] Doyle and co-workers have applied the BINAP/AgOTf/KF/18-crown-6 mixed catalyst into an asymmetric Mukaiyama-type aldol reaction of 3-(trimethylsilyloxy)vinyldiazoacetate with aldehydes.[23] In contrast, Hoveyda and his colleagues have described that a silver complex generated from a 1 : 1 mixture of AgF_2 and chiral amino acid-based ligand **15** catalyzes asymmetric Mukaiyama aldol reaction of silyl enolates with α-ketoesters.[24] Among the electrophiles tested, the ones which possess sterically hindered alkyl substituents are effective in obtaining high enantioselectivity, for example, under the influence of 10 mol% of the catalyst, silyl enolate **10** is allowed to add to α-ketoester **16** in THF at −40 °C to give nonracemic tertiary alcohol **17** in 90% yield with 96% ee (Scheme 5).



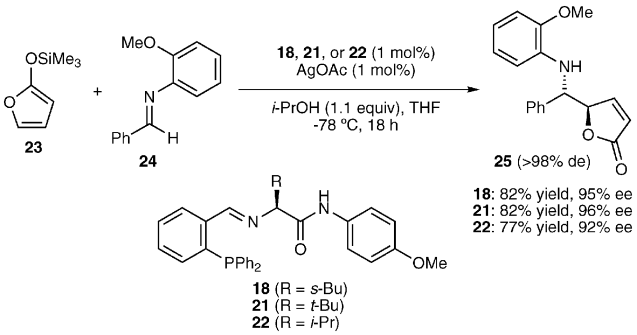
Scheme 5 AgF_2 catalyzed enantioselective Mukaiyama aldol reaction employing chiral amino acid-based ligand **15**.

Mannich-type reactions

Asymmetric Mannich-type reaction is a favorable method for the synthesis of nonracemic β-amino carbonyl compounds, which can be further converted into β-lactams or related compounds.[25] Lectka and co-workers have demonstrated that a BINAP·silver(I) complex behaves as a promising asymmetric catalyst in the reaction of α-imino esters for the first time in 1998.[26] The chiral silver(I) catalyst has been also utilized in asymmetric ene reactions of α-imino esters.[27,28] In contrast, Hoveyda and co-workers have found a chiral silver(I) catalyst bearing iso-Leu-derived phosphine **18** as a chiral ligand, which promotes asymmetric Mannich reaction of silyl enolates of ketones with aldimines.[29] For instance, in the presence of 3 mol% of **18**·AgOAc and 1 equiv. of *i*-PrOH, the reaction of silyl enolate **10** with alkenyl imine **19** proceeds at 22 °C to give the targeted product **20** in 74% yield with 96% ee (Scheme 6). In addition to α,β-unsaturated imines, aromatic and aliphatic imines are also enantioselectively transformed into the corresponding β-amino ketones by this process. This reaction can be performed even in undistilled THF under air. This procedure is also applicable to a combination of ketene silyl acetals and alkynyl imines which provides an optically active β-alkynyl-β-amino esters.[30] Asymmetric vinylogous Mannich reaction using siloxyfurans has been accomplished by similar chiral silver(I) catalysts **18**, **21** or **22** (Scheme 7).[31] According to this protocol, γ-butenolide **25** can be obtained highly diastereo- and enantioselectively. This reaction is achievable on a multigram scale with 1 mol% catalyst loading.



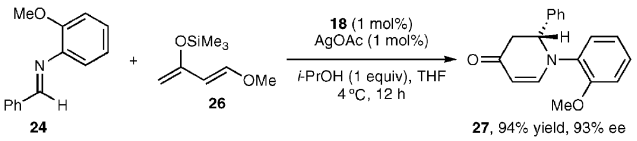
Scheme 6 Chiral silver(I) catalyzed asymmetric Mannich reaction of silyl enolates of ketones with aldimines.



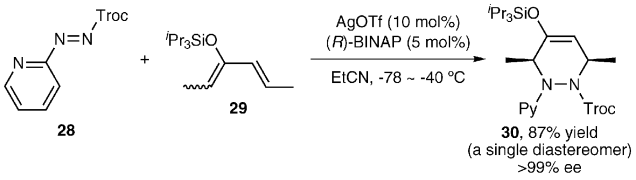
Scheme 7 Chiral silver(I) catalyzed asymmetric vinylogous Mannich reaction of siloxyfurans.

Hetero-Diels–Alder reactions

Catalytic asymmetric hetero-Diels–Alder reaction is one of the convenient routes to nonracemic *N*-containing heterocycles.[32] In 1998, the first paper on chiral silver(I)-catalyzed hetero-Diels–Alder reaction of α-imino carbonyl compounds with Danishefsky's dienes has been reported by Jørgensen and his colleagues.[33] Since then, several achiral and chiral silver(I)·phosphine catalysts have been used in the cycloaddition reaction. Silver(I)·phosphine complexes partnered with carborane anions $[1\text{-}closo\text{-}CB_{11}H_{12}]^-$ and $[1\text{-}closo\text{-}CB_{11}H_6Br_6]^-$ have been shown to be highly active achiral Lewis acid catalysts in the hetero-Diels–Alder reaction of *N*-benzylideneaniline with Danishefsky's diene by Frost, Weller and their co-workers.[34] In contrast, silver(I) acetate complexed with iso-Leu-derived phosphine **18**, which is an efficient chiral catalyst for asymmetric Mannich-type reaction,[29] has been also found to catalyze enantioselective hetero-Diels–Alder reaction between arylimine **24** and Danishefsky's diene **26** providing enantioenriched cyclic amine **27** (Scheme 8).[35] Yamamoto and Kawasaki have achieved a BINAP·AgOTf-catalyzed asymmetric azo hetero-Diels–Alder reaction.[36] When 2-azopyridine **28** was treated with acyclic siloxydiene **29** under the influence of 10 mol% of silver triflate and 5 mol% of (*R*)-BINAP in EtCN at low temperature,



Scheme 8 Chiral silver(I) catalyzed asymmetric hetero-Diels–Alder reaction between arylimine **24** and Danishefsky's diene **26**.

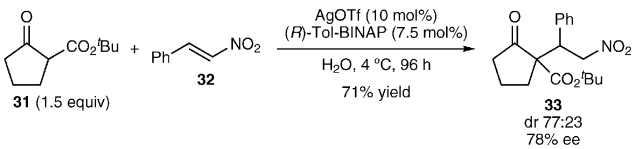


Scheme 9 BINAP·AgOTf-catalyzed asymmetric azo hetero-Diels–Alder reaction.

nonracemic cycloadduct **30** was formed in 87% yield with >99% ee (Scheme 9). The product **30** can be further converted into the corresponding protected 1,4-diaminoalcohol.

Michael addition reactions

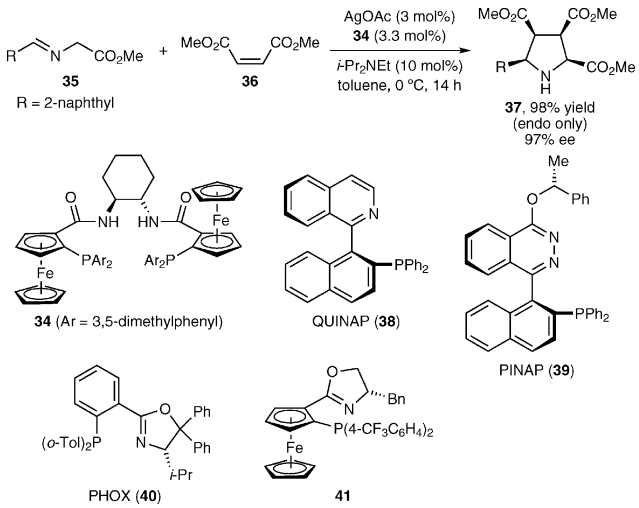
Phosphine·AgOTf complexes are known to catalyze Michael addition reactions.[37] Kobayashi and Shirakawa have reported enantioselective conjugate addition of a β-ketoester to nitroalkenes catalyzed by (*R*)-Tol-BINAP·AgOTf in water.[38] When cyclopentanone-2-carboxylic acid *tert*-butyl ester (**31**) and *trans*-β-nitrostyrene (**32**) were employed as substrates, the Michael addition product **33** was obtained in 71% yield as a 77 : 23 mixture of two diastereomers. The major diastereomer indicated 78% ee (Scheme 10).



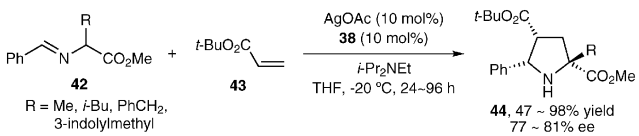
Scheme 10 Tol-BINAP·AgOTf-catalyzed enantioselective conjugate addition of β-ketoester **31** to nitroalkene **32**.

1,3-Dipolar cycloaddition reactions

Azomethine ylides are versatile reactive 1,3-dipoles, which undergo cycloaddition reactions with electron-deficient alkenes. Diverse chiral Lewis acids have been exploited as chiral catalysts in asymmetric version of the reaction furnishing nonracemic proline derivatives.[39] Concerning chiral silver(I) Lewis acids, Grigg have first described that a chiral AgOTf complex mediates asymmetric 1,3-dipolar cycloaddition reactions of ester stabilized azomethine ylides with chiral dipolarophiles.[40] A truly catalytic enantioselective [3 + 2] cycloaddition of azomethine ylides by chiral silver(I) catalysts have been realized by Zhang and co-workers in 2002. They examined numerous chiral phosphine ligands and concluded that bisferrocenyl amide phosphine **34** is the ligand of choice in getting high enantioselectivity in the chiral phosphine·AgOAc-catalyzed cycloaddition of α-iminoesters **35** to dimethylmaleate (**36**) giving the endo products **37**.[41] The highest enantiomeric excess (97% ee) has been achieved in the reaction of α-(2-naphthylimino)ester **35** (*R* = 2-naphthyl) in the presence of 3 mol% of the silver(I) complex (Scheme 11). In addition to the chiral bisphosphine ligand **38**, chiral P,N ligands **38–41** have been also reported to undertake high level of asymmetric induction in combination with silver(I) salts in the enantioselective 1,3-dipolar cycloaddition reactions.[42–45] Schreiber and co-workers have shown that a AgOAc–QUINAP (**38**) complex enables the enantioselective introduction of quaternary stereo-

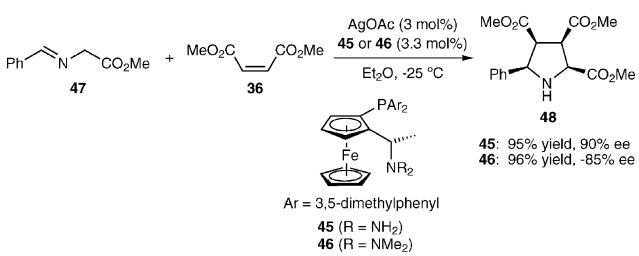


Scheme 11 Catalytic asymmetric [3 + 2] cycloaddition of azomethine ylides employing chiral silver(I) catalysts.



Scheme 12 Construction of quaternary stereogenic centers at the 2-position of pyrrolidines by chiral silver(I)-catalyzed asymmetric 1,3-dipolar cycloaddition reaction.

genic centers at the 2-position of pyrrolidines (Scheme 12).[42] PINAP (**39**) developed by Carreira has been disclosed to possess similar ability as a chiral ligand to that of QUINAP.[43] In a base-free intramolecular [3 + 2] cycloaddition of azomethine ylides catalyzed by AgOAc–PHOX (**40**) complex, almost perfect diastereoselectivity and enantiomeric excesses up to 99% have been attained by Pfaltz and his colleagues.[44] Zhou has also described that AgOAc-catalyzed enantioselective 1,3-dipolar cycloaddition reaction employing ferrocenyloxazoline-derived chiral P,N ligand **41** does not require extra base.[45] In both cases, acetate ion is considered to behave as a base. Zhou and co-workers have further observed a hydrogen bond-directed reversal of enantioselectivity in the cycloaddition of azomethine ylides employing similar chiral P,N ligand–AgOAc complexes **45** and **46** as catalysts (Scheme 13).[46] Chiral ferrocene derived P,S ligands are also promising alternative for the AgOAc catalyzed asymmetric [3 + 2] cycloaddition of azomethine ylides.[47] In contrast, Nájera *et al.* have reported that (*R*)- or (*S*)-BINAP–$AgClO_4$ complex indicates remarkable catalytic activity in the asymmetric 1,3-dipolar cycloaddition reaction

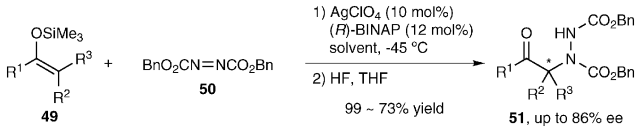


Scheme 13 A reversal of enantioselectivity in AgOAc-catalyzed [3 + 2] cycloaddition of iminoester **47**.

between azomethine ylides and *N*-methylmaleimide, giving the corresponding bicyclic products with high *endo* diastereoselectivity and enantioselectivity.[48] The silver(I) complex can be recovered and reused without any further purification. Besides chiral phosphine ligands, hydrocinchonine is known to act as a chiral ligand in the silver(I)-catalyzed [3 + 2] cycloaddition. Jørgensen has fixed AgF for the best silver(I) salt to generate a suitable catalyst with the cinchona alkaloid for the asymmetric reaction of azomethine ylides with acrylates.[49,50]

α-Amination reactions

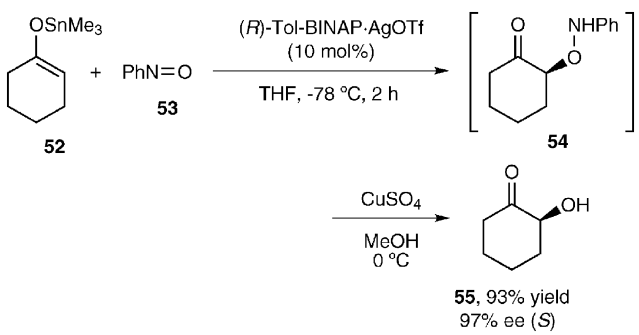
α-Amination of carbonyl compounds is recognized to be a beneficial way to α-amino acid derivatives.[53] Kobayashi and coworkers have reported that silver triflate as well as copper(II) triflate catalyzes amination of silyl enolates with azo diester compounds.[54] Asymmetric version of this reaction has been achieved by the same group using BINAP as a chiral ligand.[55] When silyl enolates **49** are exposed to dibenzyl azodicarboxylate (**50**) under the influence of a catalytic amount of (*R*)-BINAP·$AgClO_4$ complex, the corresponding enantiomerically enriched α-amino carbonyl compounds **51** are yielded with up to 86% ee (Scheme 14). However, the chiral silver complex is less effective in catalyzing the asymmetric amination of enecarbamates.[56]



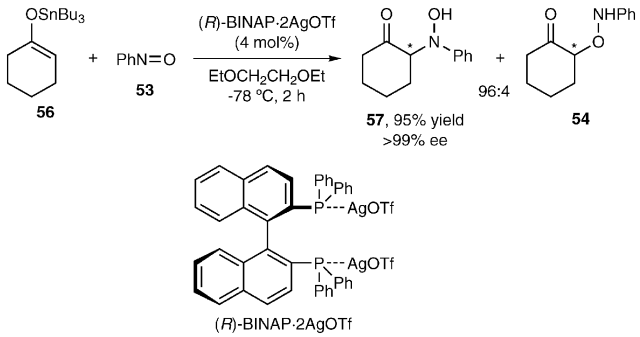
Scheme 14 BINAP·$AgClO_4$-catalyzed enantioselective α-amination of silyl enolates with dibenzyl azodicarboxylate.

Nitroso aldol reactions

Nitroso compounds are also versatile aminating agents for carbonyl compounds and are gradually becoming popular electrophiles in organic synthesis.[57] Yamamoto and Momiyama have found novel nitroso aldol reactions in which either an *O*-adduct (aminooxy ketone) or a *N*-adduct (hydroxyamino ketone) is formed selectively by adopting appropriate catalysts and nucleophiles.[58,59] They have thereafter introduced BINAP·silver(I) catalysts into these reaction systems and attained highly enantioselective nitroso aldol reactions. For instance, addition of 10 mol% of (*R*)-Tol-BINAP·AgOTf to a mixture of



Scheme 15 Tol-BINAP·AgOTf-catalyzed enantioselective *O*-nitroso aldol reaction of trimethyltin enolate **52** with nitrosobenzene (**53**).



Scheme 16 Enantioselective *N*-nitroso aldol reaction of tributyltin enolate **56** with nitrosobenzene (**53**) catalyzed by a 1 : 2 BINAP–silver(I) complex.

trimethyltin enolate **52** and nitrosobenzene (**53**) in THF at −78 °C followed by treatment with $CuSO_4$ in MeOH gives nonracemic α-hydroxy ketone **55** with 97% ee *via* α-aminooxy ketone **54** (Scheme 15).[60–63] In contrast, when a 1 : 2 complex of BINAP and AgOTf is selected as a chiral catalyst instead in a similar reaction system, asymmetric *N*-nitroso aldol reaction proceeds predominantly.[61,64] Ethylene glycol diethyl ether is the best solvent and nearly enantiomerically pure *N*-adduct **57** is obtained in high yield from tributyltin enolate **56** and nitrosobenzene (**53**) employing the solvent (Scheme 16).

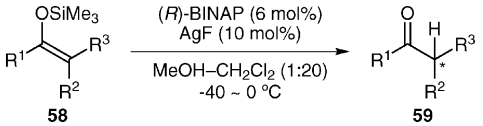
Protonation reactions

Catalytic asymmetric protonation of prochiral ketone enolates or enols is a convenient route to optically active carbonyl compounds bearing a tertiary stereogenic center at the α-position.[65] In the asymmetric protonation of trimethylsilyl enolates with methanol, BINAP·AgF has been reported to behave as a chiral catalyst,[66,67] which is also known to cause high level of asymmetric induction in allylation of aldehydes with allylic trimethoxysilanes[7] as well as aldol reaction with trimethoxysilyl enolates.[21] This protonation can be most effectively carried out employing 10 mol% of AgF and 6 mol% of BINAP as catalysts in a 1 : 20 mixture of methanol and dichloromethane at low temperatures. Table 3 indicates representative examples of the protonation of silyl enolates **58** furnishing the corresponding enantiomerically enriched ketones **59**. Moderate asymmetric induction is seen with the silyl enolates of 2-methyl-1-tetralone and its 2-ethyl derivative (entries 1 and 2). Use of 2,2,6-trimethylcyclohexanone-derived silyl enolate results in unexpectedly high enantioselectivity of more than 85% ee (entry 3). 2-Arylcycloalkanones are most suitable substrates for the protonation and in fact, quite high enantiomeric excesses are observed for the products of silyl enolates of 2-phenylcyclohexanone and 2-phenylcycloheptanone (entries 4–6). Concerning the substrates possessing a 2-naphthyl or *p*-methoxyphenyl group, nearly perfect enantioface discrimination has been attained (entries 7 and 8).

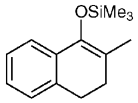
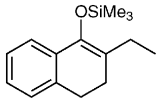
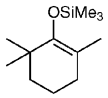
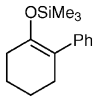
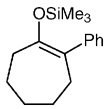
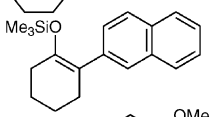
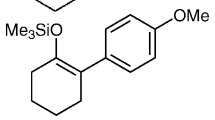
Conclusions

Described herein are recent examples of asymmetric transformations catalyzed by chiral silver(I) complexes. Among them, BINAP·silver(I) catalysts have realized various important carbon–carbon bond forming reactions such as allylation of

Table 3 Catalytic asymmetric protonation of trimethylsilyl enolates **58** using methanol and (*R*)-BINAP·AgF complex



58 59

Entry	Trimethylsilyl enolate	Yield[a] (%)	ee[b] (%) (config.)
1		72	62 (*S*)
2		75	64 (*S*)
3		82	87[c] (*S*)
4		96	98 (*R*)
5[d]		75	99 (*R*)
6		95	97 (*R*)
7		89	>99 (*R*)
8		93	>99 (*R*)

[a] Isolated yield. [b] Determined by HPLC analysis with a chiral column. [c] Determined by GLC analysis with a chiral column. [d] (*R*)-*p*-Tol-BINAP was used.

aldehydes and aldol reaction with high levels of enantio- and diastereoselectivities. The chiral silver catalysts have been further widely utilized in Mannich-type reactions, hetero-Diels–Alder reactions, Michael additions, 1,3-dipolar cycloadditions, α-aminations, nitroso aldol reactions and protonation. Many of these transformations can be performed in the presence of an alcohol or water (*cf*. Tables 1–3 and Schemes 1, 3, 4, 6–8 and 10), which shows Ag has a unique property of being stable to air and protic solvents. The above-mentioned reactions unambiguously point out that chiral silver(I) compounds have much potentiality as asymmetric Lewis acid catalysts and in the near future, additional unprecedented reactions catalyzed by these metal complexes will appear.

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