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Review

Stereoselective reactions involving hypervalent silicate complexes

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Contents

Abstract

In the last few years the possibility of effectively employing relatively simple organic molecules as enantioselective catalysts able to promote reactions with high levels of chemical efficiency and stereocontrol has been demonstrated. In this context chiral Lewis bases play an important role as promoters of a large variety of stereoselective reactions. In the field of silicon-based chemistry several, new metal-free compounds have recently been developed to efficiently catalyze different reactions where "hypervalent" silicates are involved as intermediates. The review will present the more recent achievements in silicate-mediated stereoselective reactions catalyzed by chiral Lewis bases.

Keywords: Hypervalent silicon center; Chiral Lewis bases; Stereoselective reactions; Organic catalysts; Silyl reagents

1. Introduction

The design and development of chiral catalysts able to promote stereoselective reactions with high chemical and stereochemical efficiency is of primary importance in modern synthetic chemistry. Demand for enantiomerically pure compounds is continuously increasing, not only for use as pharmaceuticals but also in other fields such as agrochemicals, food additives, flavor and aroma chemicals, and speciality materials [1]. The use of a catalyst generally allows to operate under mild reaction conditions; also the economic advantages of an efficient catalytic process are enormous since it is less capital intensive, has lower operating costs, produces higher purity products and fewer by-products. In addition, a sub-stoichiometric process provides important environmental benefits. In this framework the explosion of the so-called "organocatalysis" is specially significative since it can be regarded as a significant step towards the development of a truly green chemistry [2]. Indeed, the possibility of using catalytic amounts of an organic compound of relatively low molecular weight and simple structure to promote reactions that previously required costly and possibly toxic transition metals-based catalyst, has been clearly demonstrated [3]. The replacement, or the co-hexistence, of metal-based catalysts with equally efficient metal-free counterparts would be very attractive also in view of possible applications in the future of non-toxic, low cost, and more environmentally friendly promoters on industrial scale with obvious benefits from the environmental and economic point of view [4].

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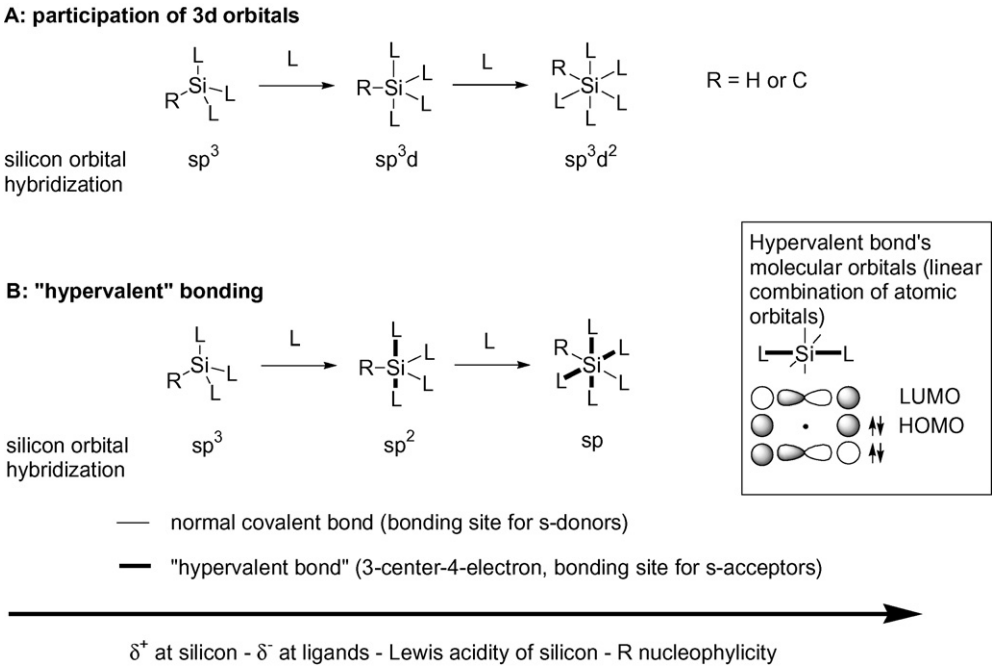


Fig. 1. Hypervalent silicon species.

In this context the chemistry of penta and/or hexavalent silicon compounds has recently attracted much attention because of the possibility to develop organocatalyzed enantioselective reactions in the presence of cheap, low toxic and environmental friendly species such as hypervalent silicates [5]. The discovery of silicon compounds with a coordination number greater than four dates back to the dawn of modern chemistry, the adduct $SiF_4{\cdot}2NH_3$ having been reported by Gay-Lussac as early as in 1809 [6]. Starting from the last decades of 20th century, the distinctive reactivity displayed by penta- and hexavalent silicon compounds has been increasingly studied, and organosilicon compounds have become more and more important intermediates in organic synthesis [7]. In the last few years stereoselective versions of several reactions promoted by silicon-based catalysts have been developed [8], specially promoted by hypervalent silicate intermediates used as chiral Lewis bases [9].

Contrary to carbon (its first row group 14-analogue), silicon displays the ability to form more bonds than the four necessary for fulfilling the octet rule: in the presence of donor molecules or ions it is possible the formation of five-, six- and even seven-coordinated silicon species, some of which have been isolated and/or characterized [7]. In order to explain this behavior, two main different theories have been formulated: the first invokes the participation of the silicon 3d orbitals in the expansion of the coordination sphere (Fig. 1A) [8,9], in the five-coordinated species the silicon orbitals would have a sp^3d hybridization (with trigonal–bipyramidal geometry), while in the six-coordinated species the hybridization would be sp^3d^2 (with octahedral geometry). The reduced s-character of the silicon orbitals in the hypercoordinated species would explain their increased Lewis acidity and the transfer of electron density to the ligands. The second theoretical approach (Fig. 1B) [10], in contrast, rules out the participation of the 3d orbitals in the bonding process and hypothesizes instead a so-called "hypervalent bonding": the formation of a penta- or hexa-coordinated silicon species would involve respectively one or two 3-center-4-electron molecular bonds, each formed by a silicon p-orbital and two p-orbitals of electronegative ligands featuring a relative *trans*-disposition. An important consequence is the non-equivalence of the ligand positions in five- and six-coordinated silicon species, the σ-acceptor ligands preferring "hypervalent" bonds and the σ-donors forming preferentially normal covalent bonds with the sp^2 (for pentacoordianted compounds) or sp (for hexacoordinated compounds) silicon orbitals. The presence of hypervalent bonds imposes some stereochemical constraints (like the *trans*-disposition of the most electronegative ligands) and it allows one to formulate predictions about the positions of the other ligands on the base of their electronic properties. Accordingly, the number of possible configurations of the silicon ligands to be considered in the elaboration of a stereoselection model is actually restricted, as shown in a recent paper by Denmark et al. [11].

Both theories prove to be helpful in the interpretation of the fundamental properties of hypervalent silicon species, that clearly distinguish their reactivity from that of four-coordinated compounds, such as the increased Lewis acidity of the silicon atom and the transfer of electronic density to the ligands, which confer to silicon-bound R groups (carbanion or hydride equivalent) marked nucleophilic properties. The hypervalent silicon species involved in synthetically useful processes are generally formed *in situ* by reaction between a four-coordinated species and a Lewis base in what is often called the "activation step" [7,8]. The so-formed five- or six-coordinated silicon species is able to promote the desired reaction in a catalytic process if the base can dissociate from silicon after the product is formed.

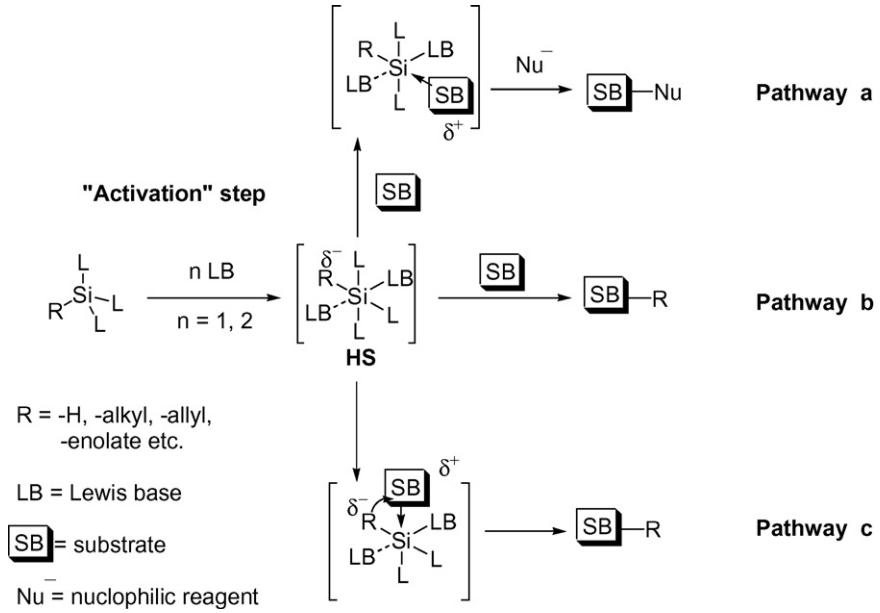


Fig. 2. Reaction mechanisms involving hypervalent silicon species.

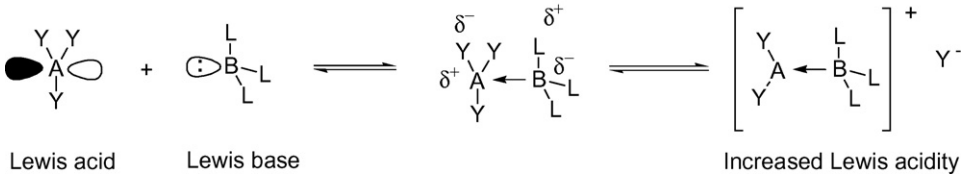


Fig. 3. Enhanced activity of Lewis acids.

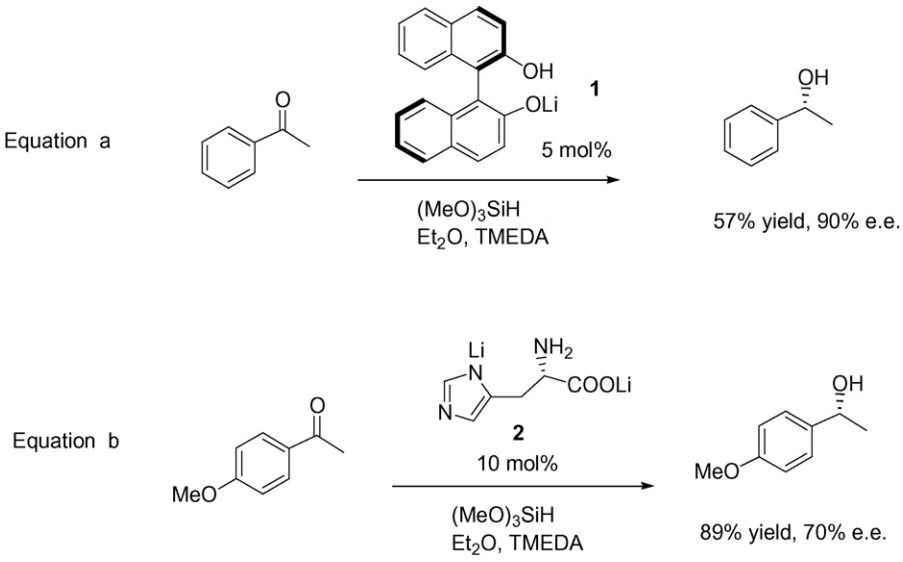
Three general kinds of reaction mechanism can be envisaged depending on the role played by the hypervalent species (Fig. 2): (i) the hypervalent species (**HS**) may act as a Lewis acid coordinating the substrate and activating it towards the attack of an external nucleophile (Fig. 2, pathway a); (ii) as in pathway b of Fig. 2, a nucleophilic silicon ligand is transferred to the substrate which is not coordinated by silicon; (iii) the hypervalent species coordinates the substrate transferring at the same time one of its ligands to it (Fig. 2, pathway c). In the last case both of the peculiar properties of hypervalent silicon species are so exploited at the same time. When a mechanism of type C is operating, the cyclic transition state allows an efficient control of the relative stereochemistry of the product. The mechanism operating through pathway a was explored in recent works by Denmark, where a basic ligand is employed to enhance the activity of Lewis acid (Fig. 3). The coordination of a Lewis base to the central atom of a Lewis acid makes it more electrophilic; since the ligand is ionized and a cationic species is generated, the result is a significantly increased Lewis acidity of the new adduct [11].

This classification should be helpful for a more immediate comprehension of the mechanistic details that are discussed in the following sections. However it is not used as the criterion of organization of this paper, since the actual mechanism of several reactions is still a matter of discussion. Taking advantage of the publication of some excellent reviews on the topic [8,9]. The present review will report the more important contributions in the field of stereoselective reactions catalyzed by hypervalent silicate compounds generated by the addition of chiral Lewis bases, with a special focus on the most recent contributions to the area. The presentation is organized by type of stereoselective transformations promoted by hypervalent silicon species.

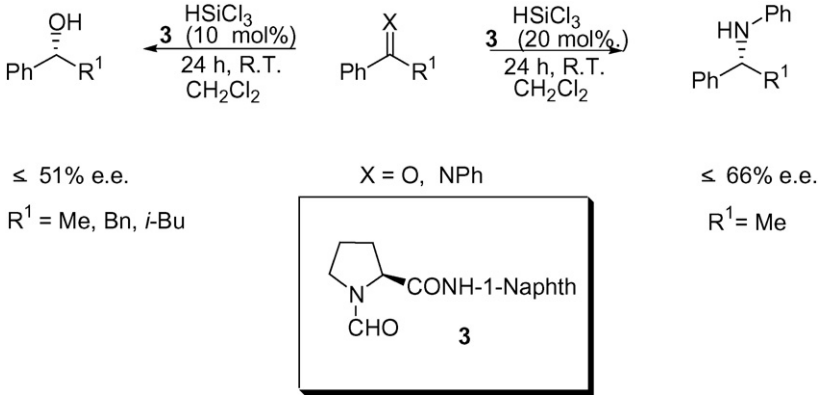
2. Stereoselective C–H bond formation

A variety of catalytic methods have been used for enantioselective reduction of ketones and ketimines: hydrogenation, hydroboration and hydrosilylation. Among others, trialcoxysilanes activated by coordination with different bases have been employed in the reduction of carbonyl compounds. After the seminal works by Hosomi in the 80s [7], in 1997 Kagan reported the use of a monolithium salt of (*R*)- binaphthol **1** as activator of trimethoxysilane for the reduction of ketones [12a]. Enantiomeric excesses up to 90% were obtained but only in the case of aromatic ketones (Scheme 1, eq. a) [12b]. A couple of years later a dilithium salt of histidine **2** was shown to catalyze the reduction of aromatic ketones with trimethoxysilane but in lower stereoselectivities (<70% e.e.) [13] (Scheme 1, eq. b).

Among the metal-free methodologies recently developed, the use of trichlorosilane as reducing agent is particularly attractive. This cheap reagent is a colorless liquid, easily prepared by the silicon industry, which has already been employed in large scale for transforming phosphine oxide to phosphine and *N*-acyliminium ion to *N*-acylamine. Trichlorosilane needs to be activated by coordination with Lewis bases, such as *N,N*-



Scheme 1.



Scheme 2.

dimethylformamide, acetonitrile, trialkylamines, to generate hexacoordinated hydridosilicate, the real active reducing agent that operates under mild conditions. In 1999 in a preliminary communication Matsumura reported the results obtained using *N*-formylproline derivatives such as compound **3** as organic catalysts in the reduction of aromatic ketones with $HSiCl_3$ (Scheme 2) [14]. Later the methodology was extended also to imines derived from aromatic carbonyl derivatives [15]. Both reactions proceed at room temperature in chlorinated solvents (CH_2Cl_2) with modest enantioselectivity and chemical yield.

The working hypothesis originally proposed to explain the stereoselectivity in the reduction of ketones is shown in Fig. 4. The coordination of the bidentate Lewis basic ligand **3** to the silicon atom causes the formation of a cationic active species that would be able to coordinate the carbonyl oxygen and transfer the proton [16].

In 2004 Malkov et al. developed a more successful methodology in which aminoacid-derived chiral formamides behaved as organocatalysts for the stereoselective reduction of imines [17]. In a preliminary communication L-valine-derived formamides were selected as more efficient systems. The choice of L-valine was the result of a screening of a series of aminoacids: a variation of the side-chain affected the sense of stereoselection rather than its entity (Scheme 3).

The reaction was carried out in non-polar solvents; toluene was chosen for its relatively low environmental impact. Different substituted *N*-aryl ketimines have been tested as substrates. A more complete survey about the *N*-methylvaline-derivatives has been recently published: the presence of bulkier groups in the

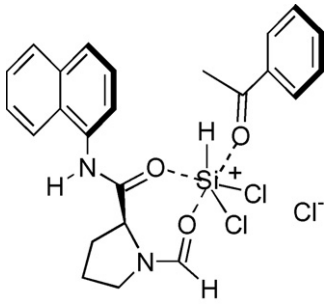
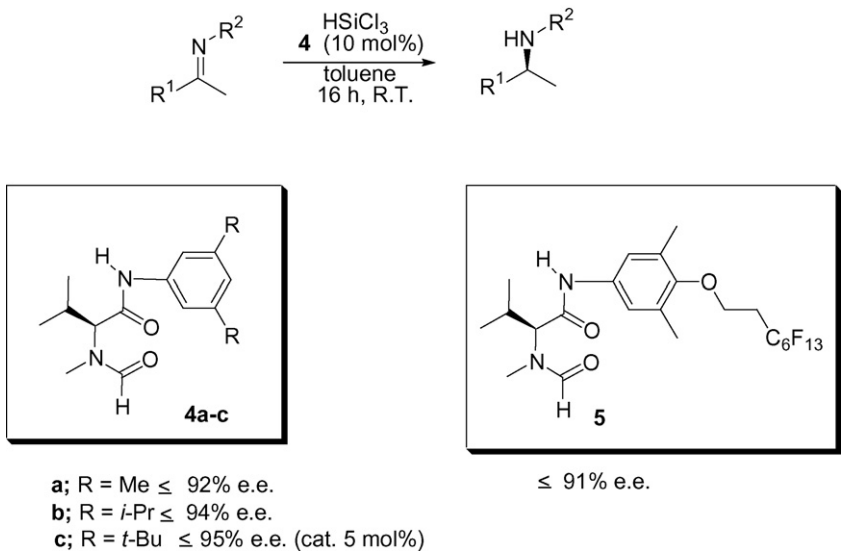


Fig. 4. Transition state proposed for catalyst **3**.



Scheme 3.

3,5-positions on the aryl ring (di-*iso*-propyl and di-*tert*-butyl) determine an increase of enantioselectivity in the reduction of aromatic and non-aromatic ketoimines [18].

Catalyst–substrate hydrogen bonding and coordination of the silicon atom by the two oxygen atoms of the amides seem to play a major role in determining the stereoselectivity of the catalyst. In the proposed transition state also the formation of hydrogen bond between the amide group of the catalyst and the substrate can be an additional element of stereocontrol (Fig. 5).

A recoverable version of this family of catalysts has also been realized [19]. The florous-tagged catalyst **5** was shown to be easily recoverable and recyclable: in addition the product isolation was easier and the high level of enantioselectivity preserved (Scheme 3). (*S*)-valine-derived formamide was employed also in the reduction of a α-chloro-imines generated in situ from α-chloro-acetophenones, to afford after cyclization the corresponding aziridine as final product with high enantioselectivity (up to 96% e.e.) and good yield [20].

A new *N*-formyl derivative catalyst has been recently described [21]; in the presence of a catalytic amount of *N*-formyl-α^{ε}-(2,4,6-triethylphenyl)-(*S*)-proline secondary alcohols were obtained with high enantioselectivity (up to 97%) (Scheme 4). The selection of catalyst **6** is the result of the screening of a series of α′-arylproline derivatives. This outcome suggests the importance of both a carbonyl group at the α-position and a 2,4,6-triethylphenyl group at the 5–position in the proline ring of catalyst **6**.

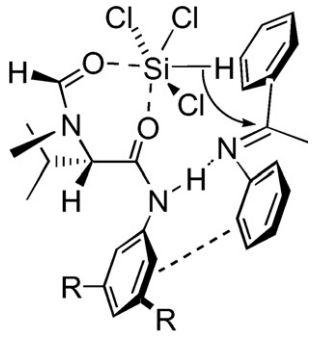
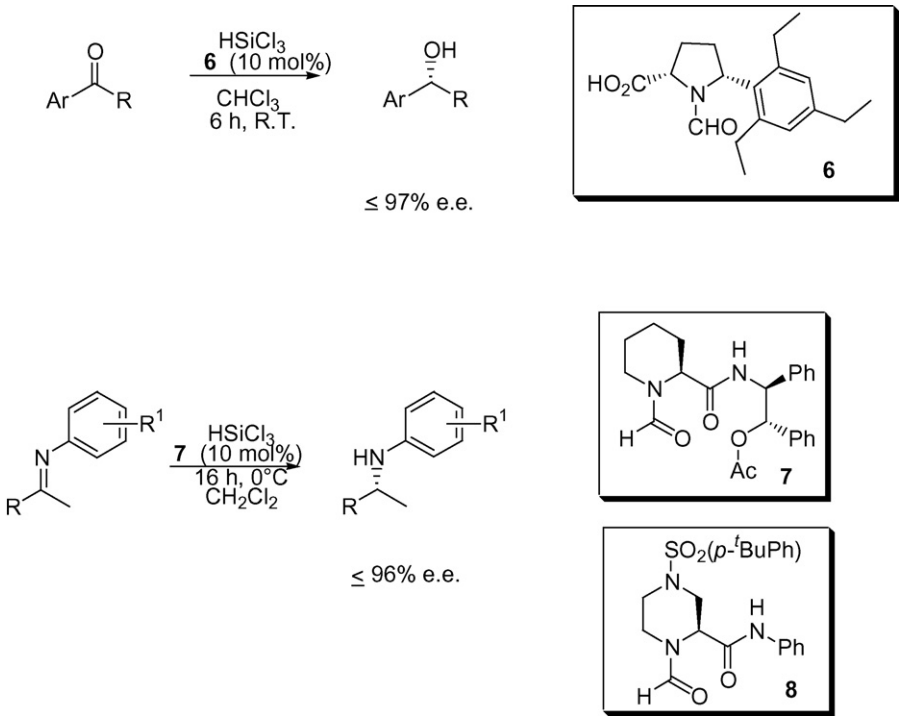


Fig. 5. Transition state proposed for catalyst **4**.

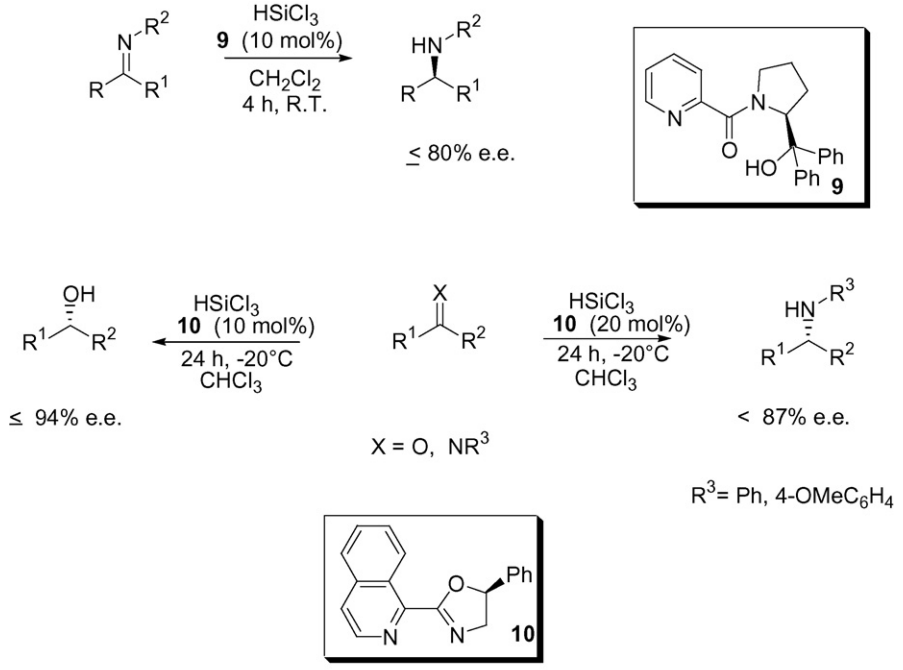
In 2006 Sun and co-workers [22] developed new Lewis basic organocatalysts that promoted the reduction of *N*-aryl ketimines with trichlorosilane with high yields and excellent enantioselectivities. These compounds were prepared starting from (*S*)-pipecolinic acid and enantiopure 2-amino-1,2-diphenylethanol, both commercially available derivatives. The evaluation of different parameters led to the selection of catalyst **7** and of the optimal reaction conditions (Scheme 4). Later Sun and co-workers have designed the catalyst **8** featuring a piperazinyl backbone [23] instead of a piperidinyl one. The amino group on the 4-position should allow the introduction of different elements providing also different catalytic properties. The arenesulfonyl group has been shown to be essential for getting high enantiocontrol (Scheme 4). Catalyst **8** has a simple structure and it is able to promote the reduction of both methyl ketimines and ketimines having bulky R [1] with excellent yields and enantioselectivities.

N-picolinoylpyrrolidine derivatives activate trichlorosilane in the reduction of aromatic imines, showing that *N*-formyl group is not always essential for catalytic activity [24]. *N*-picolinoyl-(2*S*)-(diphenylhydroxymethyl)pyrrolidine **9** led to the best results suggesting that both the nitrogen atom of picolinoyl group and the carbonyl oxygen play a fundamental role in the coordination of silicon atom. The hydrogen of the hydroxy group is probably involved in a hydrogen bond with the nitrogen atom of the imine (Scheme 5).

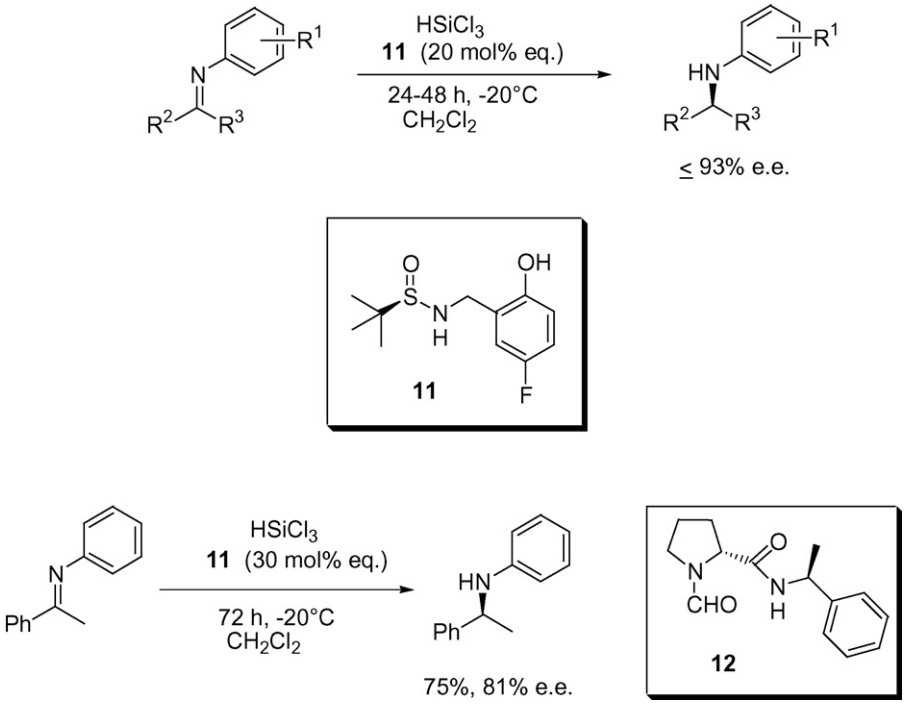
Malkov et al. have demonstrated that also quinoline, isoquinoline and pyridine-derived chiral oxazolines may be efficient promoters for the addition of trichlorosilane to ketones and imines (Scheme 5) [25]. The most efficient catalyst, **10**, promotes the reduction of both ketones and ketimines with a good level of enantioselectivity. According to the authors, coordination of the trichlorosilane by the catalyst generates a



Scheme 4.



Scheme 5.



Scheme 6.

chiral hexacoordinated silicon species that is the actual reducing species (pathway b of Fig. 2). When a ketone is the substrate, a further activation would be provided by coordination of a molecule of trichlorosilane by the carbonyl oxygen (Scheme 5).

Very recently, a new family of organocatalysts able to activate trichlorosilane has been published [26]. The stereoselective reduction of a broad range of *N*-aryl ketimines was catalyzed in the presence of sulfinamide **11**, that contains a stereogenic sulfur atom (Scheme 6).

Finally, it must be mentioned that Tsogoeva's research group has studied new *N*-formylproline derivatives able to catalyze reduction of imines; among other catalysts compound **12** showed good chemical and stereochemical efficiency [27]. The yield and enantioselectivity can be increased employing both HMPA or *p*-nitro benzoic acid as additives, the former being more effective (Scheme 6).

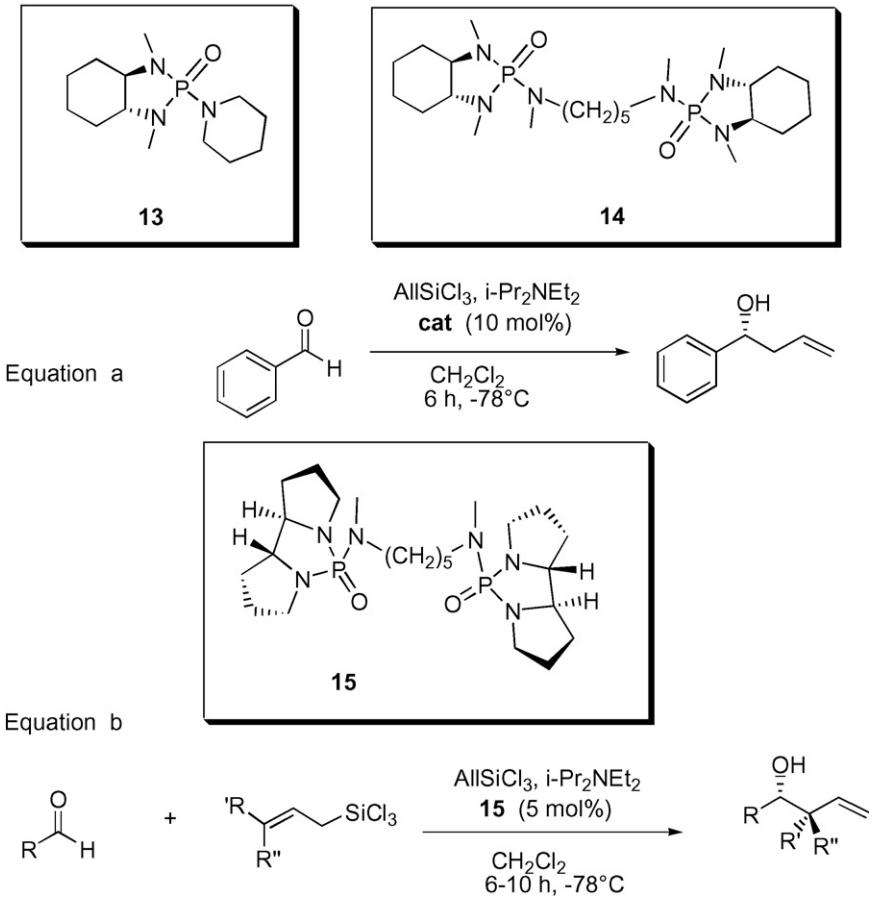
3. Stereoselective C–C bond formation

As already shown in Scheme 1, the coordination of a Lewis base to a tetracoordinated silicon atom leads to hypervalent silicate species of increased Lewis acidity at silicon centre. As consequence, such extracoordinated organosilicon compounds become very reactive carbon nucleophiles or hydride donors with a strong electrophilic character at silicon and an enhanced capability to transfer a formally negative charged group to an acceptor. One might say that when a hypervalent silicon atom is involved as the reactive site in a transformation carbon–carbon as well as carbon–heteroatom bond formation can occur. On the contrary, when a tetracoordinated silicon atom is exclusively involved in the reaction mechanism a carbon–silicon as well as heteroatom–silicon bond formation may occur but not a carbon–carbon formation. Along these lines several asymmetric catalytic systems have been explored in order to develop new stereoselective substoichiometric methodologies for carbon–carbon bond construction.

3.1. Allylation of C=O group

The catalytic enantioselective allylation of aldehydes provides a paradigmatic example of how an organometallic catalyst can be effectively replaced by a metal-free one. Previously promoted by chiral Lewis acids, this reaction that may lead to the formation of two new stereocenters can currently be carried out in the presence of a variety of organic Lewis bases as catalysts [8,9]. Since a few reviews have recently covered the topic [8,9,28], in the present section the most important contributions in the field will be discussed as representative examples of different classes of developed catalysts; in addition the more recent achievements in the allylation reaction of carbonyl compounds will be included.

Following preliminary studies by Hosomi [7] and Kobayashi [29] in 1994 Denmark reported the first enantioselective, non-catalytic, addition of allyltrichlorosilane to aldehydes promoted by the chiral phosphorotriamide **13** (Scheme 7) [30]. A series of detailed studies demonstrated that two pathways were possible; one involving an octahedral cationic silicon atom, coordinated by two Lewis bases molecules leading to a good selectivity [31a], and another less selective one where only one phosphoroamide was bound to a pentacoordinated silicon centre [31b]. In view of these mechanistic considerations several chiral bidentate phosphoroamides were prepared and studied in the test allylation of benzaldehyde; a catalyst loading as low as 5 mol% of compound **14** was found to promote the reaction affording the product in



Scheme 7.

high yield and enantioselectivity up to 72% (Scheme 7, eq. a) [32].

Based on these results, that clearly indicated the beneficial effect of combining two phosphoramide units through a diamminoalkyl chain, new bidentate catalysts derived from 2,2′-bispyrrolidine and 2,2′-bis piperidine units were investigated. Compound **15** was found to be a really efficient promoter for the allylation reaction and by addition of allyltrichlorosilane to benzaldehyde afforded the homoallylic alcohol in 85% yield and 87% e.e. [33]. Various γ-substituted allyltrichlorosilanes were employed leading to the products in high yields and up to 96% e.e., showing a good correlation between the configuration of the C=C double bond in the reagent and the *syn/anti* diastereoisomeric ratio of the products (Scheme 7, eq. b) [32].

The solid-state structure of the complex formed by catalyst **15** with $SnCl_4$ was determined. On the basis of these studies and of a computational analysis of the coordination geometries in hypervalent silicon species [34] a rationalization of the behavior of catalyst **15** was also proposed (Fig. 6). In the chairlike, cyclic TS A the aldehyde ring is located in an unfavorable position occupied by a forward-pointing pyrrolidine ring, creating destabilizing steric interactions. In the diastereoisomeric chairlike arrangement of TS B the aldehyde ring does not have any unfavorable interaction with the reward-pointing pyrrolidine unit, leading to the experimentally observed product of *S*-configuration.

Recently, the first example of chiral phosphoramides supported on a polymeric matrix has been reported [35]. Polystyrene-anchored catalysts **16a–c** of different active site contents were used as catalysts (10 mol%) to promote the allylation of benzaldehyde with allyl trichlorosilane in the presence of excess diisopropylethylamine (DCM, −78 °C, 6 h), affording the product in 82–84% yield and 62–63% e.e.. Remarkably, the supported catalysts proved to be more efficient than the corresponding non-supported derivatives featuring a benzyl group instead of the polymer residue both in terms of yield and of stereoselectivity. Since it has been shown that bis-phosphoramides are more efficient than mono-phosphoramides in promoting the allylation reaction, the better results obtained with **16a–c** were regarded as suggestive that two phosphoramide groups of the supported catalysts could bind the hypervalent octahedrally coordinated silicon atom believed to be involved in the transition structure of the reaction. In other words, the polymer backbone apparently forces two catalyst's sites in such a close proximity that they can behave as bis-phosphoramides. Neither the recycling of **16a–c** nor the extension of their use to the allylation of aldehydes different from benzaldehyde has been described (Scheme 8).

Among Lewis basic catalysts, another class of compounds that deserves a special attention are amine *N*-oxides [28]. The use of pyridine-derived *N*-oxides was summarized recently [36], and the present review provides an opportunity for an update on the

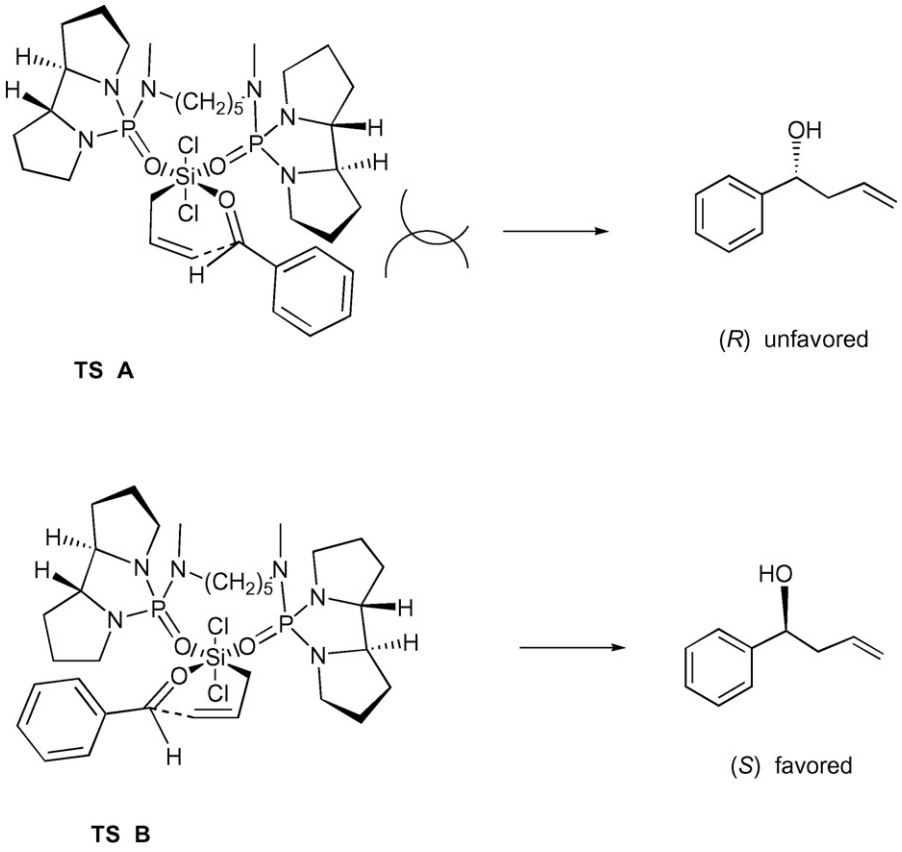
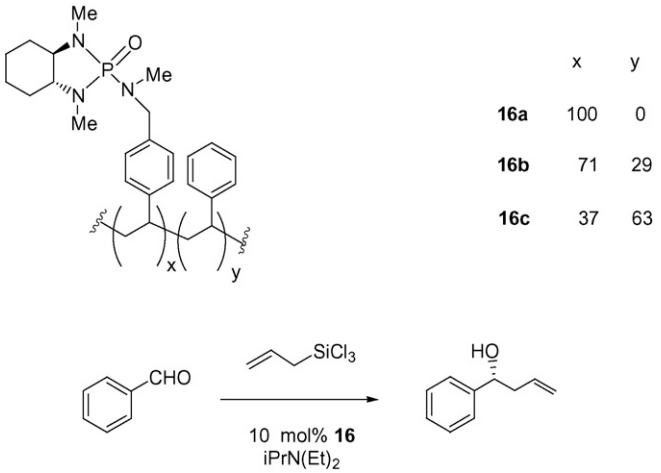


Fig. 6. Transition state proposed for catalyst **15**.

latest developments in the application of chiral *N*-oxides derived from tertiary amines and pyridines in asymmetric catalysis.

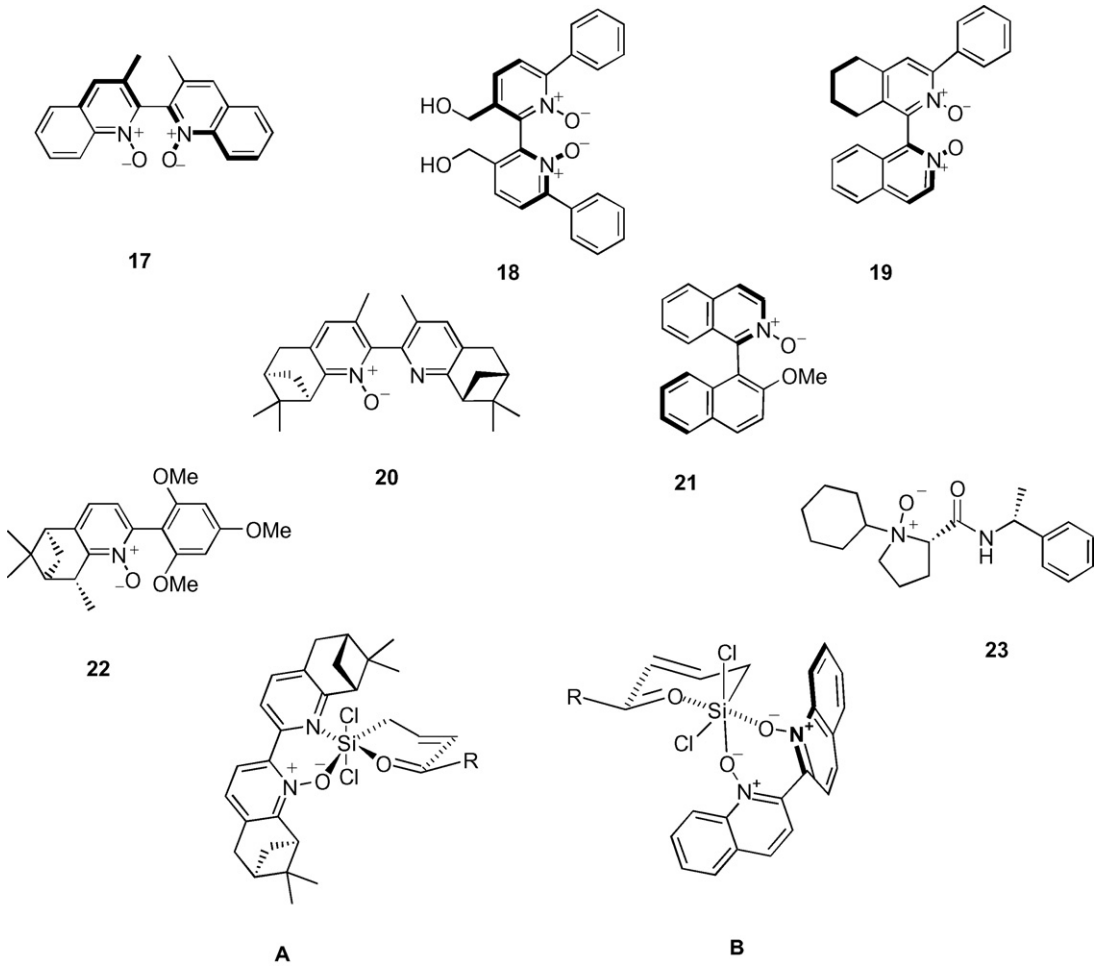
The high nucleophilicity of the oxygen in *N*-oxides, coupled with a high affinity of silicon for oxygen represents ideal properties for the development of synthetic methodology based on nucleophilic activation of organosilicon reagents. The first asymmetric addition of trichlorosilane to aldehyde catalyzed by biquinoline *N,N′*-dioxides **17** was reported in 1998 by Nakajima et al. [37]. The reaction was accelerated by the addition of diisopropylethylamine and afforded the products in high yields and enantioselectivities (up to 92%) with aromatic and heteroaromatic aldehydes, but lower yields and stereocontrol were observed with non-conjugated aldehydes (Scheme 9).



Scheme 8.

Later another chiral catalyst with a stereogenic axis as key element of stereocontrol was developed by Hayashi and coworkers [38]; this catalyst led to enantioselection similar to that obtained with **17** (56–98% e.e.). Remarkably the Hayashi's catalyst was found to be effective at the 0.1 mol% level (−40 °C, acetonitrile) and retains moderate activity even at 0.01 mol% loading, which makes this organocatalyst the most reactive one reported to date. Very recently, a simple synthesis of unsymmetric atropoisomeric bipyridine *N,N′*-dioxides in three steps from commercially available material was reported [39]. The key step of this reaction sequence is cobalt-catalyzed heterocyclotrimerization of 1-pyridyl-1,7-octadiynes with nitriles to provide unsymmetrical bipyridines, followed by oxidation and resolution into enantiomers. Catalyst **19** promoted the addition of allyltrichlorosilane to aromatic aldehydes in up to 80% e.e. (Scheme 9).

Another class of catalysts was actively studied by Malkov et al., which have shown that the terpene-derived bipyridine *N*-monoxides, Me_2PINDOX, **20** (cat. 10 mol%, −78 °C, CH_2Cl_2) was extremely enantioselective (up to 98% e.e.), although the reaction was somehow slow [40]. Compound **20** combines the effects of both stereoelement, stereogenic centers and axis, since the rotation about the bond connecting the two pyridine moi-



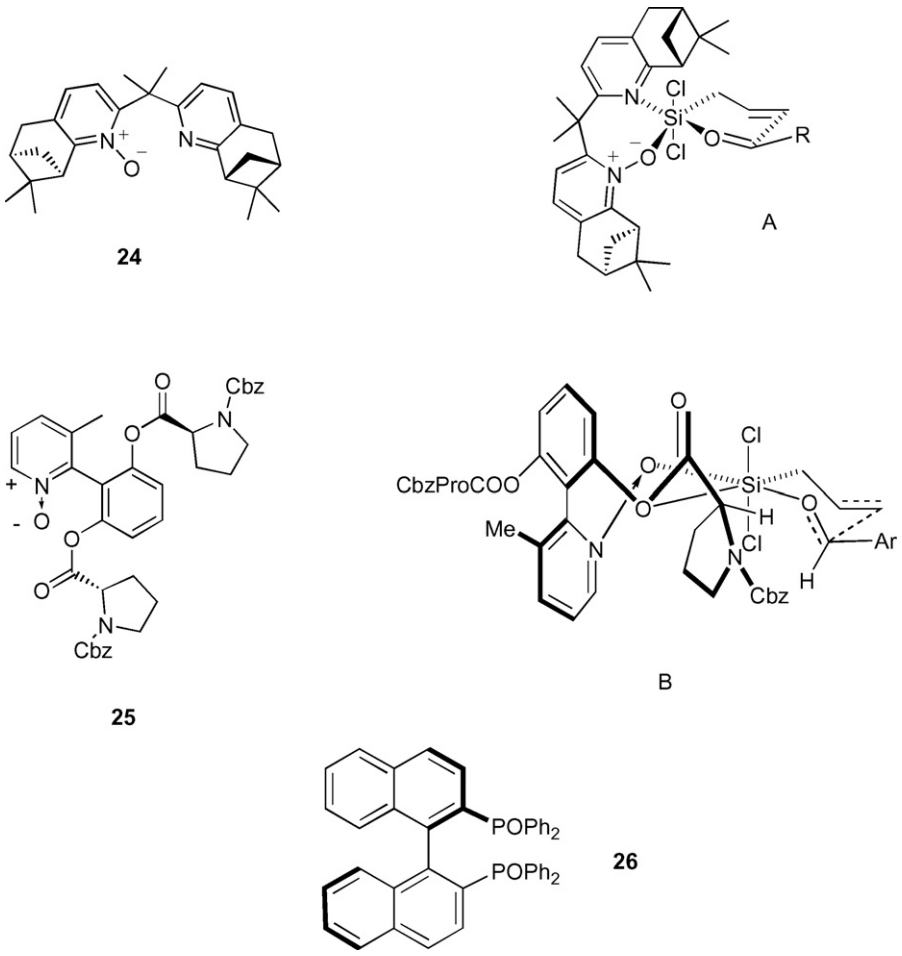
Scheme 9.

eties is restricted by the two methyl groups and the N–O group. However, the barrier to rotation is rather low, and the molecule isomerizes within 2 weeks to a 1:2 mixture of **20** and its atropoisomer. In analogy to the chelation model proposed for **17**, chelation of the silicon in allyltrochlorosilane by O and N was proposed for **20** (Scheme 9).

In another important contribution Malkov et al. showed that two *N*-oxide groups are not necessary, but one *N*-oxide and a second coordination element are enough to guarantee high levels of stereocontrol, such as in **20** and in the new developed catalyst **21** [41]. The proposed transition structure for the mono-*N*-oxide derivatives **A** is very similar to that proposed for bis-*N*-oxide compounds, **B** (Scheme 9). In catalyst **22** arene–arene interactions between the catalyst and the substrate have been suggested to account for the high reactivity and selectivity. Furthermore, the case of METHOX (**22**) shows clearly that the axial stereogenicity, whether predetermined or induced during the reaction is not an absolute prerequisite for attaining high enantioselectivity in the allylation reaction [42]. As further demonstration of these considerations, Hoveyda developed the *N*-oxide **23**, the only representative of aliphatic tertiary amine *N*-oxides so far reported in this series, that presents a stereogenic center at the nitrogen [43]. The catalysts **22** and **23** secure high enantioselectivity even at room temperature.

Based on these studies recently other systems characterized by the absence of stereogenic axis were developed [44]. For example new chiral dipyridine *N*-monoxides and *N*,*N*′-dioxides, which possess an isopropylidene backbone between two pyridine rings, have been prepared from naturally occurring monoterpenes, the more efficiently being compound **24** [45] (Scheme 10). Its utility as organocatalysts has been demonstrated in the enantioselective addition of allyltrichlorosilane to aldehydes, where enantioselectivities up to 85% e.e. have been obtained.

A series of structurally simple pyridine *N*-oxides have readily been assembled from inexpensive aminoacids and tested as organocatalysts in the allylation of aldehydes with allyltrichlorosilane to afford homoallylic alcohols [46]. (*S*)-Proline-based catalyst **25** afforded the products derived from aromatic aldehydes in fair to good yields and up to 84% e.e. By implementing the results of conformational analysis with those of a few control experiments, transition structure shown in Scheme 10 can be proposed to tentatively explain the stereochemical result of the allylation reaction promoted by catalyst **25**. In this model, the hypervalent silicon atom is co-ordinated by the pyridine *N*-oxide oxygen and the phenolic oxygen of one side arm. The bulky proline residue effectively blocks one side of the adduct and accommodates the aldehyde bet-



Scheme 10.

ter than the sterically more requiring allyl residue as its *cis* substituent.

Other organocatalysts have been investigated with less success in the allylation of carbonyl compounds, such as sulfoxides that however were used in non-catalytic amounts, or phosphine oxides. Catalyst **26** showed a good chemical and stereochemical efficiency, and it promoted the addition of several β-substituted allyl-trichlorosilanes to aldehydes in the presence of tetrabutylammonium iodide as additive with enantioselectivities up to 79% e.e. [47] (Scheme 10).

3.2. Allylation of C=N group

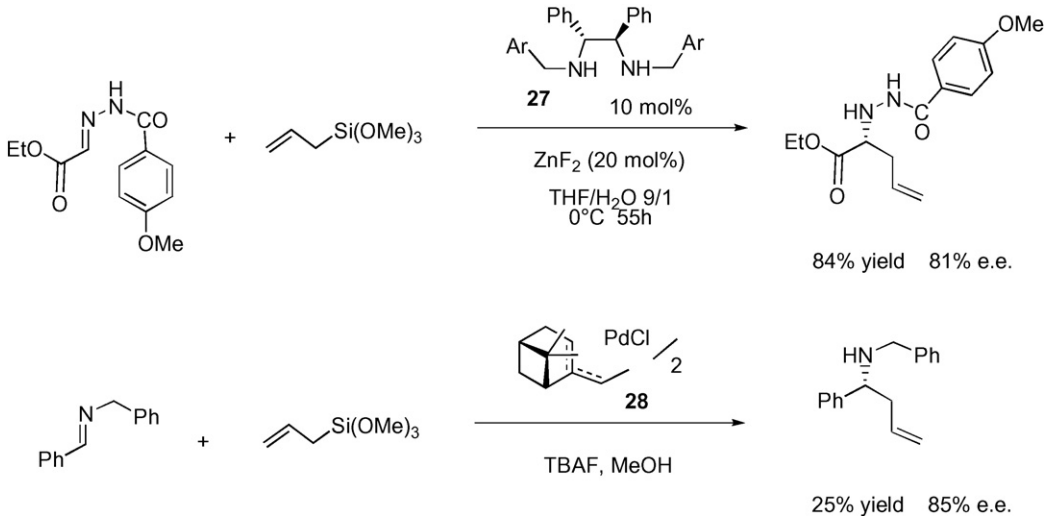
The synthesis of enantiomerically enriched homoallylic amines is a topic of paramount importance since they represent useful synthetic intermediates that may be converted in different functional groups. However while the catalytic enantioselective allyl addition to carbonyl compounds is well developed, few examples of the analogous reaction with imines and imino esters are known, despite their utility in organic synthesis [48]. Recently, Kobayashi developed a zinc fluoride catalyzed addition of allyltrimethoxy silane [49] to acylhydrazono esters, in the presence of a chiral diamine ligand **27** (Scheme 11) [50]. In the reaction water plays a determinant role in affording the product of reaction that suffers anyway from substrate limitations. Recently, Fernandes and Yamamoto have reported the addition of allyltrimethoxysilane to simple imines mediated by a dual activation/promotion process that involves the use of TBAF and a chiral complex of palladium **28**; the product is isolated in 84% e.e. but very low yields (Scheme 11) [51].

Kobayashi reported also the first example of an enantioselective allylation to imine-type compounds promoted by a stoichiometric amount of a non-organometallic system [52]. The sulfoxide (*R*)-**29** (3 eq., Scheme 12) promoted the adddition of allyltrichlorosilane to *N*-acylhydrazones with high enantioselectivity (up to 96% e.e.). In this case the use of *E*-crotylsilanes affords the *syn* product while the use of *Z*-crotylsilanes affords the *anti* adduct, as shown in Scheme 12.

Finally, it was reported that also 2 equivalents of phosphine oxide **26** may be employed to obtain in high yields and enantioselectivity the $AllylSiCl_3$ addition to acylhydrazono esters [53], but once again it must be noted that an efficient catalytic enantioselective organocatalyzed version of this reaction is missing.

3.3. Aldol reaction

Since the structure and the reaction mode of allylsilane may recall that of silyl enol ether (C–Si bond cleavage *vs*. O–Si bond

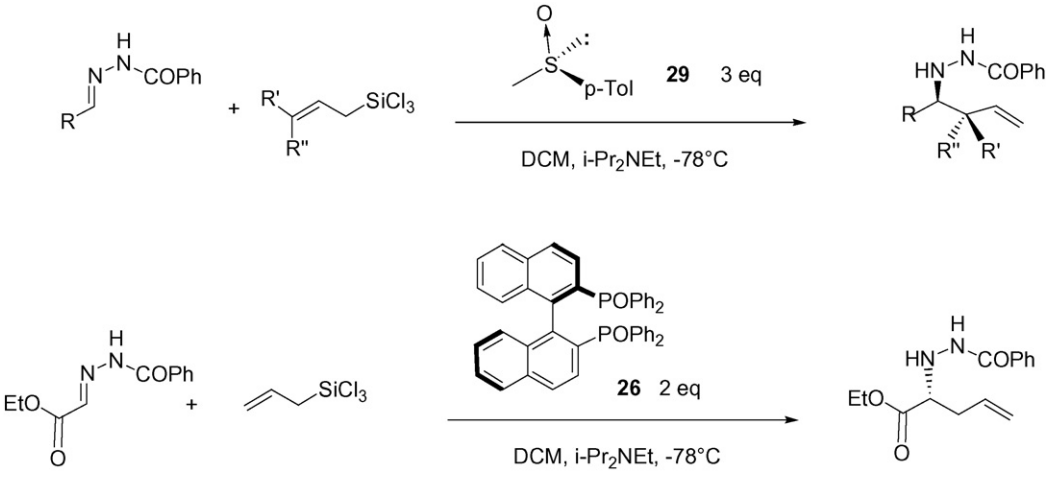


Scheme 11.

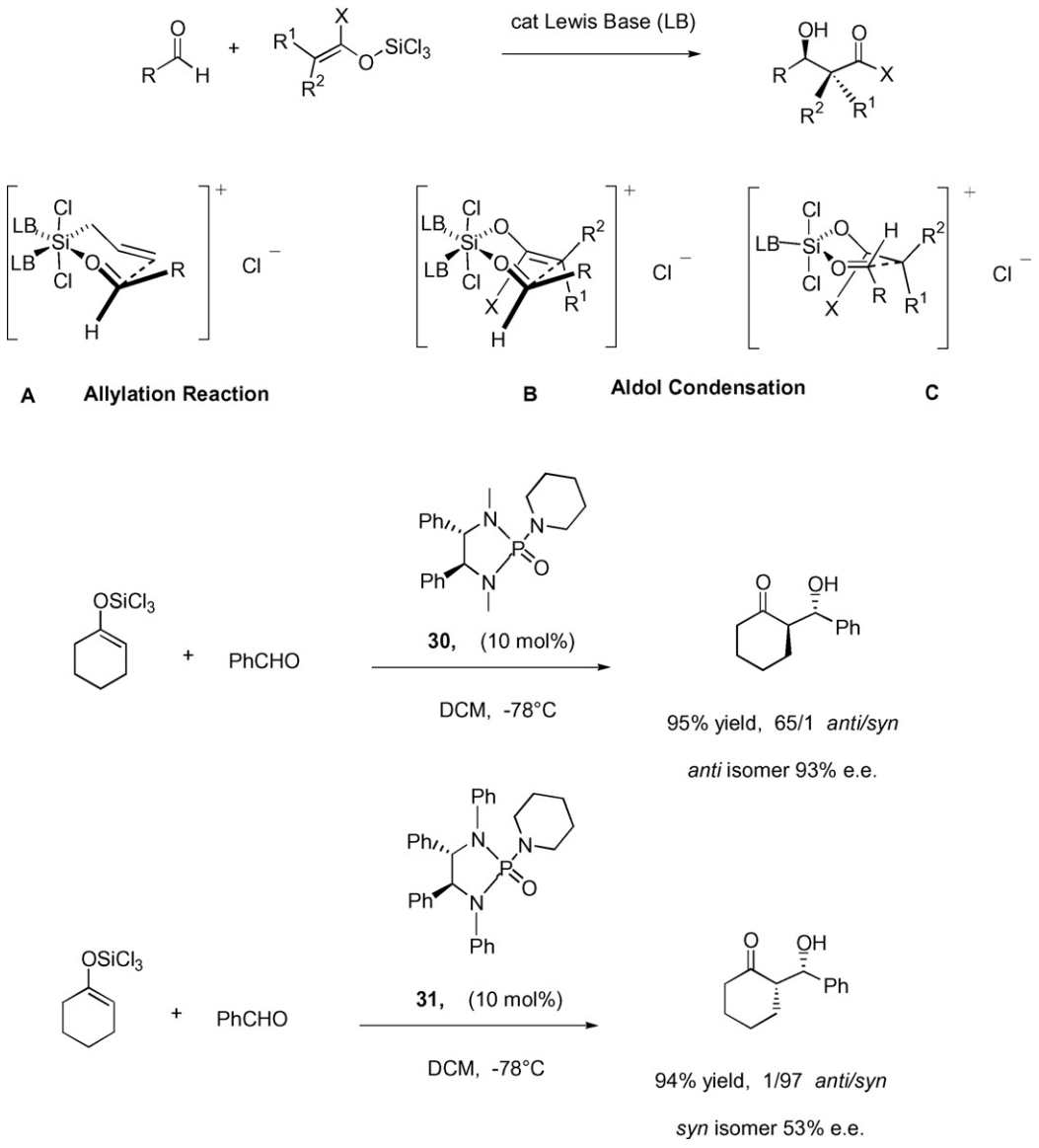
cleavage), the addition of trichlorosilyl enol ethers to carbonyl derivatives catalyzed by Lewis bases was studied. However since silyl enol ethers have a higher nucleophilicity compared to the corresponding allylsilanes, the aldol addition of trichlorosilyl enol ethers to aldehydes proceeds readily at room temperature without a catalyst and it exhibits simple first-order kinetics in each component. Nevertheless, the reaction is substantially accelerated by Lewis bases, which set the scene for the development of an asymmetric variant. Denmark introduced a range of efficient chiral phosphoramides as nucleophilic activators for enantioselective C–C bond aldol formation and also carried out a detailed mechanistic investigation [54]. In 1996 the first example of aldol condensation of trichlorosilyl enol ethers was reported [55]. The chiral phosphoroamide **30** derived from 1,2-diphenylethylendiamine successfully promoted in 10 mol% the addition of the trichlorosilyl enol ether of cyclohexanone to benzaldehyde in 95% yield, 65:1 *syn*/*anti* ratio and 93% e.e. (Scheme 13).

However it was demonstrated that the diastereoselectivity was largely dependent on the structure of the chiral catalyst. After carrying out a detailed mechanistic study bidentate and smaller monodentate catalysts were shown to react through a cationic chair-like transition state **B**, similar to **A**, usually proposed for the allylation reaction, with octahedral extracoordinate silicon (Scheme 13). According to this scheme, (*Z*)-enol ethers produced *syn* adducts, whereas (*E*) derivatives furnished *anti* diastereoisomers. In the case of a bulky monodentate activator, in which coordination of the second catalyst molecule is precluded by steric factors, the diastereoselectivity of the reaction was reversed. Here, the reaction presumably proceeds via the cationic boat-like TS **C**, in which the silicon is pentacoordinate. According to this scheme, the cyclohexanone-derived enol ether with a fixed (*E*) configuration of the double bond gave rise to the *syn* product with sterically demanding catalyst **31** through transition state **C**, and to the *anti* isomer with catalyst **30** via intermediate **B** [56].

Denmark was able to show that also pyridine *N*-oxides may work as catalyst in the aldol reaction. In the absence of an activator, addition of trichlorosilyl ketene acetal to acetophenone slowly takes place at 0 °C, but it can be accelerated by a Lewis base (Scheme 14). Bis-*N*-oxide **32** emerged as the most promis-



Scheme 12.



Scheme 13.

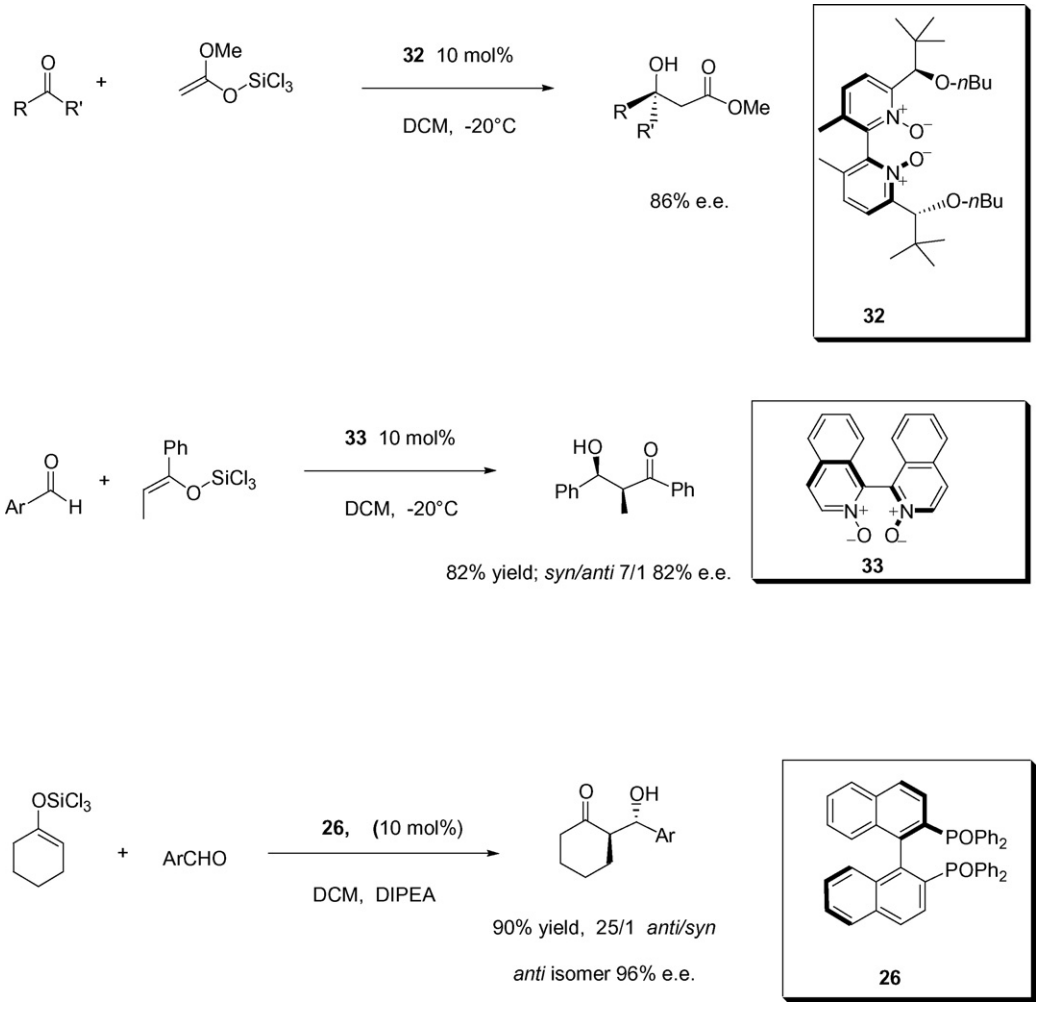
ing in terms of reactivity and enantioselectivity (cat. 10 mol%, −20 °C, CH_2Cl_2), affording the β-hydroxy ester, with a tertiary stereocenter in 94% yield and 84% e.e. [57]. A new procedure for the synthesis of atropoisomeric bis-*N*-oxide has also been developed. An X-ray crystal structure of the complex between a catalyst and silicon tetrachloride has been obtained. Extensive computational analysis was conducted to propose a stereochemical rationale for the observed trends in enantioselectivities.

Other chiral *N*-oxides were employed, but with less success; for example Nakajima et al. reported that catalyst **33** promoted the addition of trichlorosilyl enol ethers to aromatic aldehydes in decent diastereoselectivity and enantioselection up to 82% [58] (Scheme 14). Also phosphine oxide **26**, already employed in allylation reaction, was shown to be able to catalyze the addition of cyclohexanone-derived silyl enol ether with activated aromatic aldehydes in high stereoselectivity, indicating that the reaction probably proceeds via a chair-like transition state [59].

More recently, Denmark explored the possibility to develop chiral hypervalent silicates to be used as Lewis acid, according to the mode of activation described in Fig. 3 [11]. A highly efficient enantioselective aldol reaction of silyl enol ethers catalyzed by a Lewis base activated with tetrachlorosilane was reported [11]. Catalytic amounts of phosphoramide **34** (1 mol%) in the presence of stoichiometric amount of tetrachlorosilane promoted the addition of silyl ketene acetals to aromatic aldehydes in high enantioselectivities (Scheme 15, eq. a).

By exploiting the same concept, and always by using catalyst **34** other reactions were performed, such as the addition of silyl enol ethers (in the presence of tetrabutyl ammonium salt), allylation with allyltributylstannane and vinylogous aldol reactions [60] (Scheme 15, eqs. b–d respectively). Recently, the vinylogous aldol addition of conjugated *N*,*O*-silyl ketene acetals to aldehydes was also described [61] (Scheme 15, eq. e).

The proposed catalytic cycle involves the formation of a highly electrophilic Lewis base-bound silyl cation as an inter-



Scheme 14.

mediate. These are not Lewis acid-catalyzed reactions; the fact that the aldol products are trichlorosilyl ethers, as demonstrated by NMR, is a clear evidence that each molecule of tetrachlorosilane participating in the catalytic cycle is incorporated into the product. Therefore it is appropriate to define these as phosphoroamide-catalyzed and $SiCl_4$-mediated reactions (Scheme 16).

In the proposed catalytic cycle the chiral trichlorosilyl cation **A** binds the aldehyde to give adduct **B**; this is attacked by the silyl ketene acetal to afford the intermediate **C** that after dissociation from the catalyst leads to the product as trichlorosilyl ether. Not only the reaction is *anti* selective, but is also diastereoconvergent, affording the same stereoisomer independently from the geometry of the starting enolate. The behavior was tentatively rationalized by proposing that the decisive factor responsible for the observed trend in diastereoselectivity is the interaction between the α-substituent and the bound silyl cation complex in an open, acyclic transition structure (Scheme 16). Analysis to explain the sense of the enantioselectivity of the process was less conclusive, but it was shown that the catalyst pocket is quite congested and the stereo and enantiocontrol was possibly dominated by steric factors.

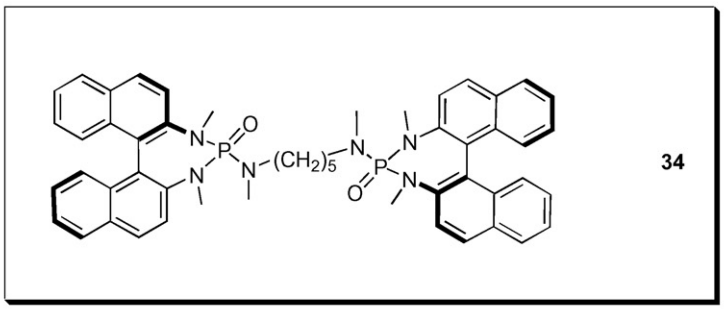
3.4. Allenylation and propargylation reactions

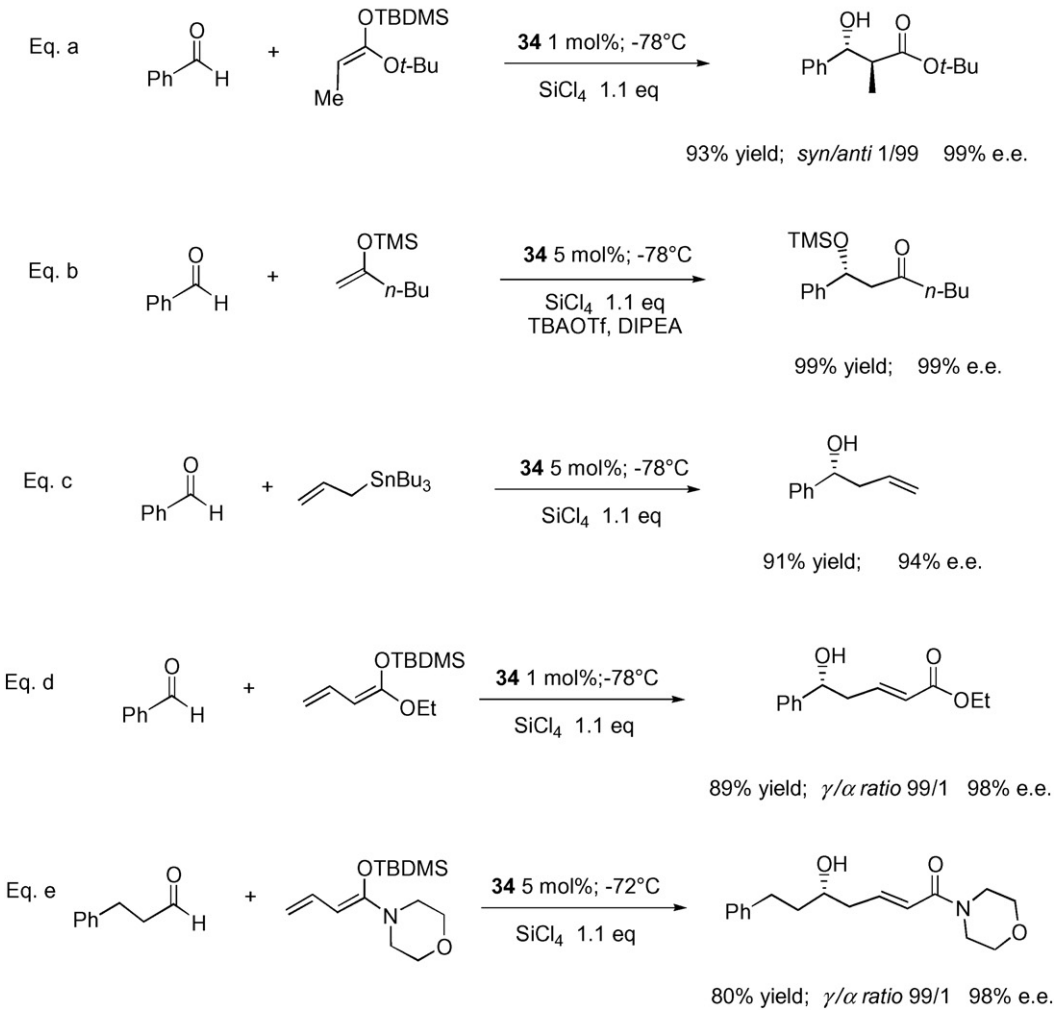
Propargyl trichlorosilane is prepared by CuCl-catalyzed reaction between propargyl chloride and $HSiCl_3$; analogous reaction in the presence of $(acac)_2Ni$ produced allenyl trichlorosilane. These two reagents were shown to react with aromatic aldehydes under activation of a Lewis base, similarly to the addition of allyltrichlorosilane to carbonyl compounds [62]. The addition of propargyl trichlorosilane to aldehydes leads to allenyl alcohols (Scheme 17, eq. a), while the reaction of allenyl trichlorosilane affords the corresponding homopropargyl alcohol (Scheme 17, eq. b).

An asymmetric version has been reported by Nakajima et al. [63], who employed the chiral biquinoline bis-*N*-oxide **17** as catalyst (10 mol%) but the enantioselectivities observed were rather modest (40–62% e.e.).

3.5. Trimethylsilyl cyanide addition

Recently, a few reactions involving trimethylsilyl derivative (including trimethylsilyl enol ether) and catalyzed by Lewis bases have been reported [64]. However, it is still under debate

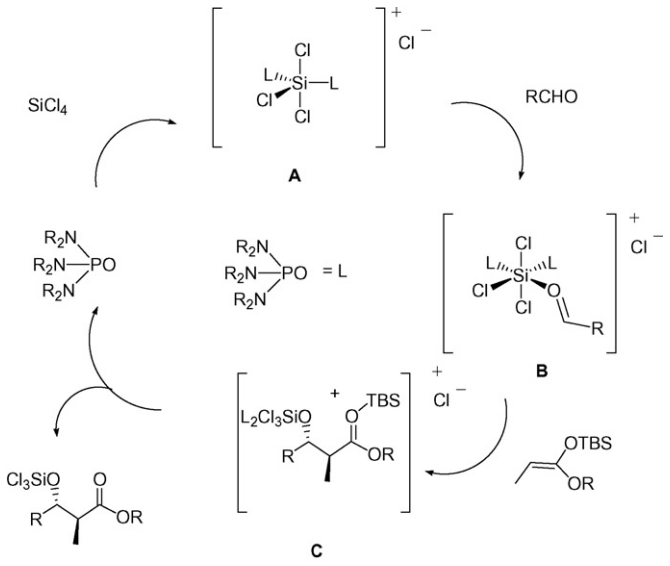




Scheme 15.

if all of these reactions actually involve a hyperconjugated silicate species; among these reactions addition of silyl cyanide to carbonyl and imine derivatives has been studied in more detail and an enantioselective version of this transformation has been described. The addition of cyanide anione to imines affords α-amino nitriles, key intermediates for the synthesis of α-amino acids. Feng and co-workers have studied the use of chiral *N*,*N*′-dioxides in the enantioselective Strecker reaction of aldimines and trimethylsilyl cyanide [65]. The Lewis base promoters are in this case employed in stoichiometric quantity. The most efficient *N*,*N*′-dioxide promotes the reaction of a broad range of aromatic *N*-benzhydrylimines in high yield and with moderate to excellent enantioselectivity (up to 95% e.e.) under mild conditions (Scheme 18, eq. a).

In 2005 Feng's group presented a family of new proline-based *N*,*N*′-dioxides of general formula **35** shown in Scheme 18, employed in the enantioselective cyanosililation of aldehydes [66]. This novel class of derivatives has been prepared starting from cheap materials: (*S*)-proline and a pool of primary amines. Examination of different parameters has allowed to identify



Scheme 16.

the best catalyst and optimal reaction conditions (Scheme 18, eq. b). The yield depends on substrate concentration and catalyst loading. The cyanosilylation of aromatic aldehydes gives the best results, especially when the substrate features a *meta*-substituent.

More recently, Feng and co-workers [67] have employed bifunctional *N*,*N*′-dioxides **36** in extending the reaction to α-α′-dialkoxy ketones (Scheme 18, eq. c). In this case the catalyst is generated in situ from *N*-alkyl prolinamides and *meta*-chloroperbenzoic acid, in order to avoid problems due to the presence of moisture. Having established the optimal conditions, the reaction was applied to several different substrates. The studies on the mechanism indicate that the *N*,*N*′-dioxide is a bifunctional catalyst where the *N*-oxide moiety activates the trimethylsilyl cyanide (as a Lewis base) and the amide hydrogen activates the carbonyl group of the substrate (as a Bronsted acid).

In 2003 Deng's group reported the first example of highly enantioselective cyanosilylation of ketones using a chiral Lewis base [68]. A modified cinchona alkaloid catalyses the reaction of acetal ketones and trimethylsilyl cyanide. The loading of derivative **37** required for obtaining high performance is only 2 mol% (Scheme 19).

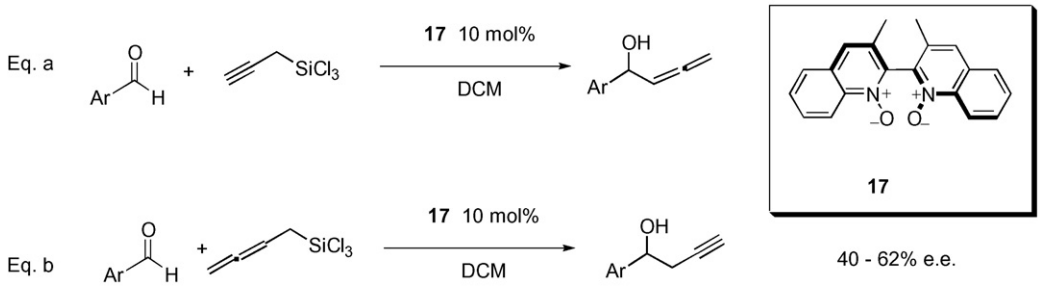
Ishihara and co-workers employed the catalytic system **1** based on chiral lithium binaphtholates in the presence of water and alcohol as of co-activators [69]. These derivatives have been employed in the asymmetric cyanation of aromatic aldehydes using a catalytic amount of additives. Several aldehydes with different features have been tested and the products have been obtained with high yield and enantioselectivity (Scheme 20).

Feng and co-workers [70] showed that asymmetric cyanosilylation can be promoted by a chiral *N*-oxide–titanium complex (Scheme 20). Ligand **38** employed in the reaction has been prepared from (*S*)-proline. The use of a titanium species has resulted from a screening of different metals; the best ligand/Ti(O*i*Pr)$_4$ ratio has been found to be 1:1.2. This ratio influences the enantioselectivity of the process. Several aromatic ketones have been tested and the results highlight that the selectivity and reactivity strongly depend on the nature of the substrate. Preliminary mechanistic studies indicate that there is a dual activation of ketones by the titanium ion and the hypervalent silicon species formed by coordination of **38** with trimethylsilyl cyanide.

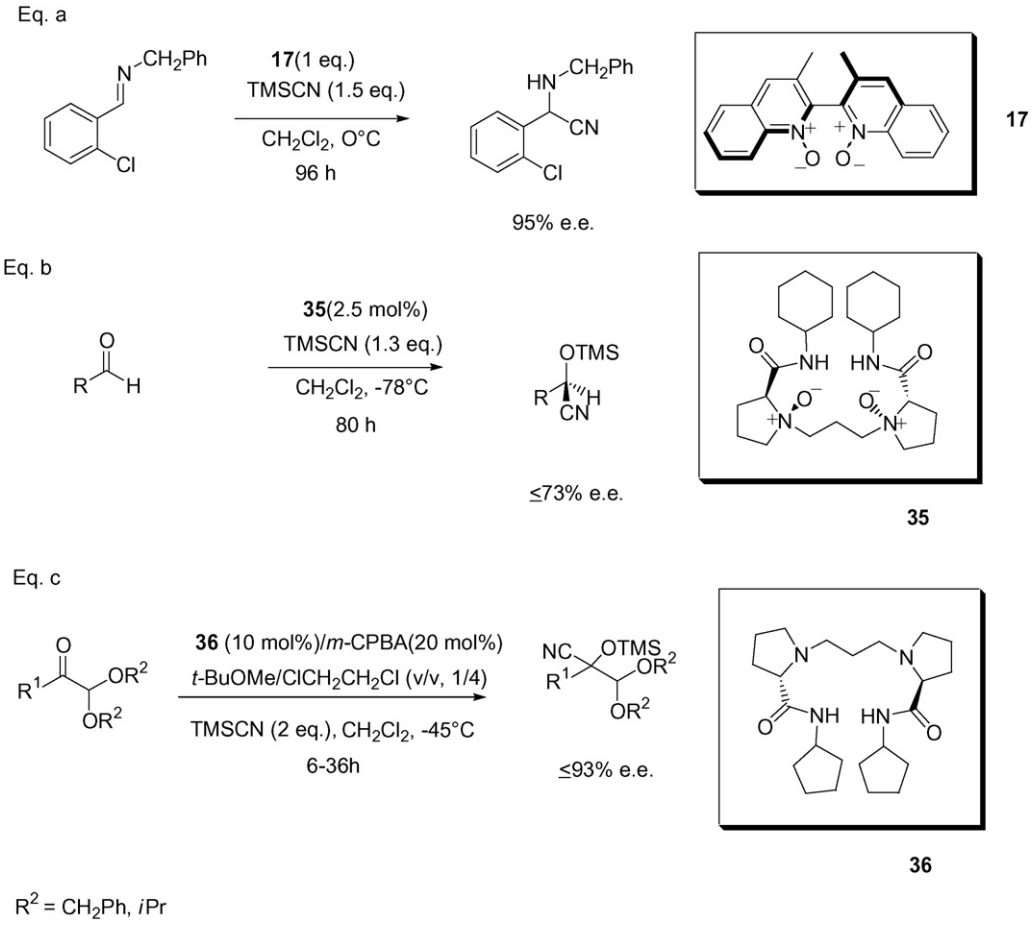
In this context, of particular interest are the communications of Shibasaki. In this case the oxygen atom of the phosphine oxide coordinates to the silicon atom of trimethylsilyl cyanide to activate it. In 2000 Shibasaki and co-workers [71] reported the activity of the new bifunctional catalyst based on a titanium complex generated in situ from the phosphine-oxide **39** and titaniumtetraisopropoxide (Scheme 21). The products of cyanosylilation of ketones are obtained with high enantioselectivity.

In 2001 Shibasaki's group [72] developed a novel catalyst whose ligand **40** differs from **39** for the presence of a benzoyl group at the catechol moiety. The benzoyl substituent has a positive effect in terms of enantioselectivity and yield, probably due to steric and electronic factors (Scheme 21). Since the benzoyl group can enhance the acidity of the phenol hydroxy group, these results seem to point to an involvement of this group in the catalytic cycle. With aryl ketones ligand **40** has been used with a loading of 1 mol%, while in the case of aliphatic ketones a loading of 2.5 mol% is required. In both conditions the cyanohydrines have been obtained in high yield and with excellent enantioselectivity. The authors have proposed the transition state showed in Fig. 7: the titanium atom acts as a Lewis acid on the ketone, while the phosphine-oxide oxygen coordinates the silicon atom of TMSCN generating a pentacoordinated silicon species and thus increasing the nucleophilicity of the cyanide group.

In 2001 the new bifunctional catalyst **41** was published and characterized by the simultaneous presence of one Lewis-acidic

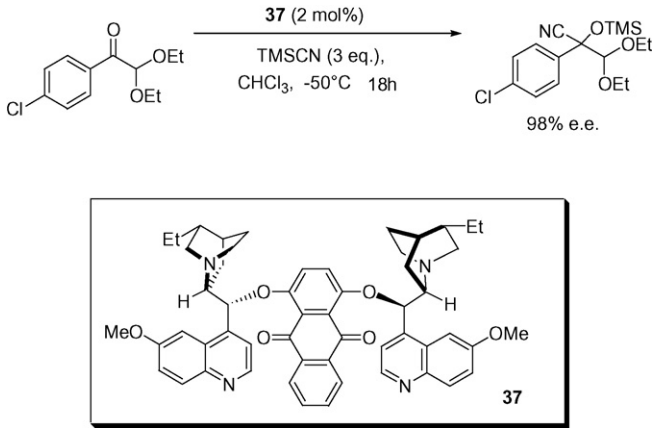


Scheme 17.



Scheme 18.

site (the metal) and two Lewis-basic sites (the phosphine-oxide oxygen atoms) [73]. In this case the stereoselective cyanosylilation of aldehydes is promoted *via* a dual activation: the aldehyde is activated by coordination with the metal, while the silicon reagent (trimethylsilyl cyanide), that in this process acts just as a nucleophilic species is activated by the Lewis bases centers, the phosphine oxides. Quite inexplicably the best results have been obtained using an additive: $Bu_3P(O)$ for aliphatic and α-β-unsaturated aldehydes and $MeP(O)Ph_2$ for aromatic aldehydes (Scheme 22).



Scheme 19.

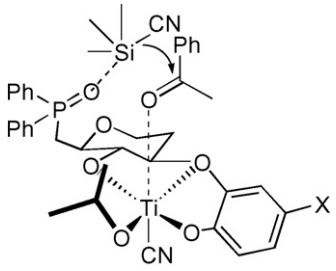
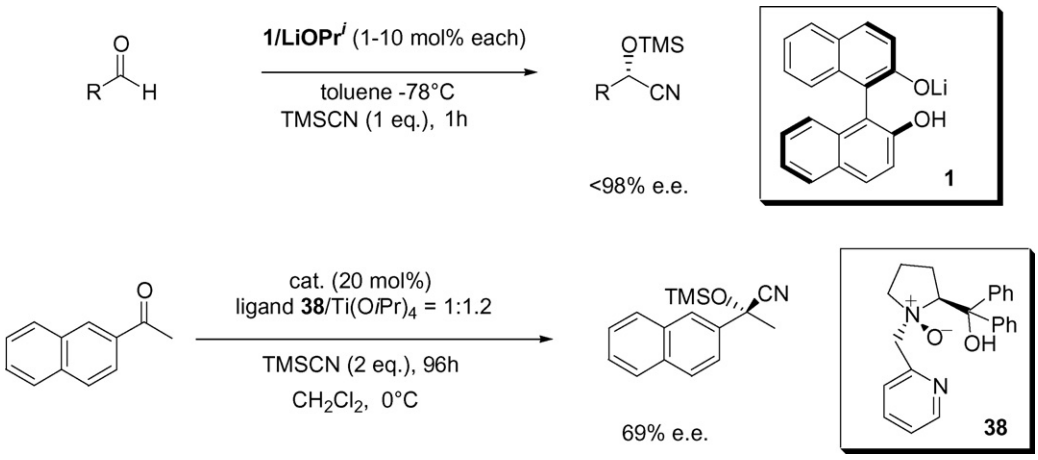


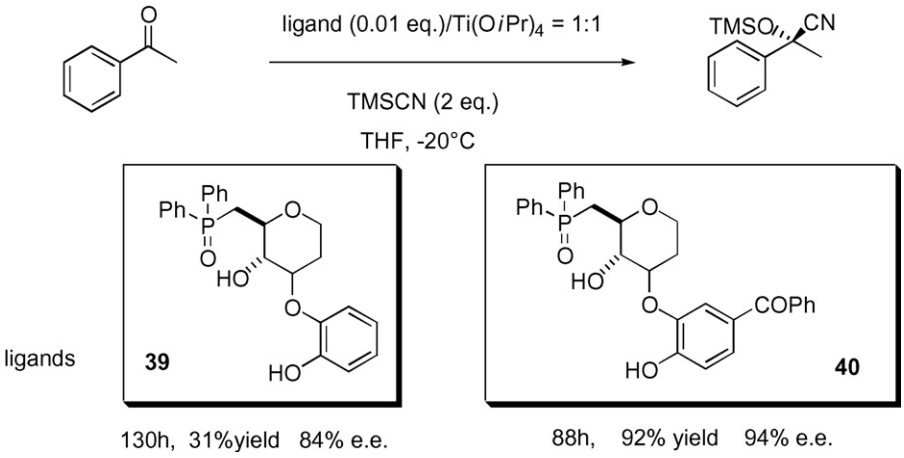
Fig. 7. Transition state proposed for catalyst **40**.

4. Ring opening reaction of epoxides

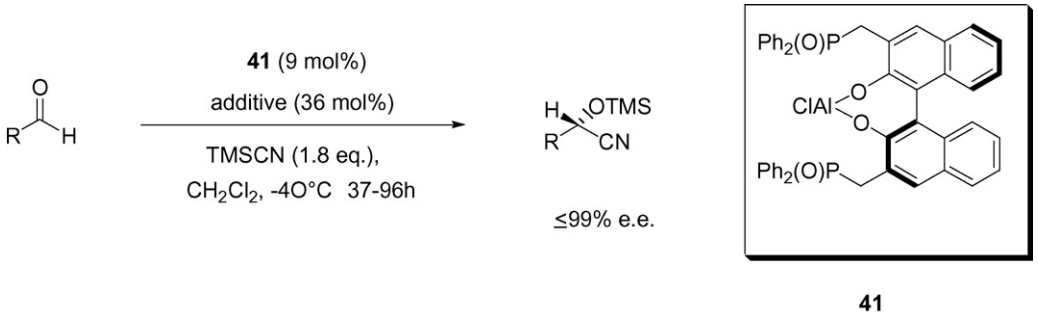
A variety of nucleophiles can be employed in the opening reactions of epoxides, and for this reason these compounds are versatile intermediates for organic synthesis. Denmark et al. [74] reported the first catalytic enantioselective opening of *meso*-epoxides with tetrachlorosilane in the presence of the chiral phosphoramide **42** as a Lewis base (Scheme 23). The mechanistic hypothesis is that the Lewis base reacts with tetrachlorosilane forming a pentacoordinate silicate complex which coordinates



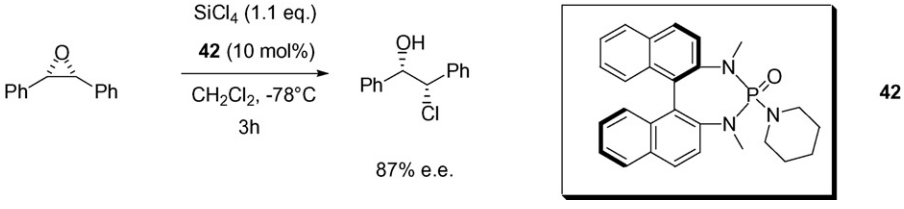
Scheme 20.



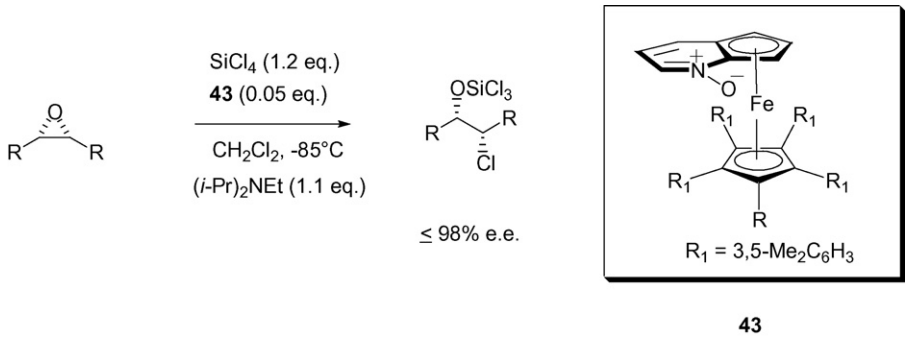
Scheme 21.



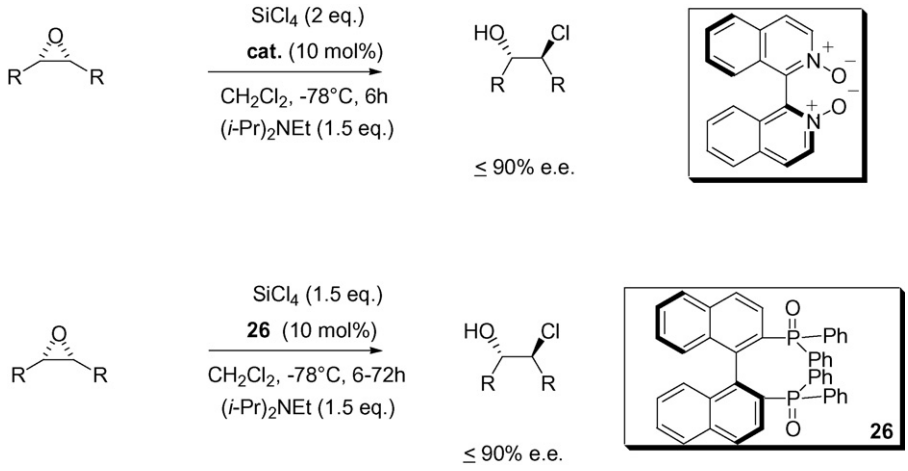
Scheme 22.



Scheme 23.



Scheme 24.



Scheme 25.

the oxygen atom of the substrate activating it towards nucleophilic substitution. The attack of the chloride ion proceeds in an S_N2 fashion. The enantioselectivity depends on the substrate's structure. A higher level of enantiomeric excess was obtained for acyclic substrates, whereas for cyclic substrates it also depends on ring size.

Recently, Denmark et al. investigated different aspects of the reaction [75] as the use of different chlorosilane sources and stoichiometry, catalyst loading, internal quench and kinetic and non-linear effect. This survey highlights that only silicon tetrachloride affords the product with high level of stereocontrol: only one chlorine is released and in the course of the reaction the nature of silicon reagent does not change; the selectivity does not change with catalyst loadings ranging from 100 to 4 mol%, but it decreases with a 2 mol% loading. This behavior suggests that a single pathway mechanism is active in the 100–4 mol% range. The authors conclude that probably more than one molecule of catalyst is involved in the stereochemistry determining step.

Fu and co-workers [76] reported a new family of chiral catalysts capable of promoting the opening of *meso*-epoxides with high enantioselectivity (up to 98% e.e.) in the presence of tetrachlorosilane via a hexacoordinate silicate (Scheme 24).

The choice of catalyst **43** is the result of the screening of a series of enantiopure pyridine *N*-oxides where the authors show that increased steric hindrance increases the level of stereocontrol. An electron-poor aromatic group of the substrate leads to the chlorohydrin with the highest selectivity: the enantiomeric excess depends on electronic effects. A positive non-linear correlation between the enantiomeric excess of the catalyst and the enantiomeric excess of the product was also observed.

Nakajima et al. [77] showed that chiral bipyridine *N*,*N*′-dioxides catalyzed both the enantioselective allylation and enantioselective ring opening of *meso*-epoxides with trichlorosilyl derivatives (Scheme 25). The catalyst acts as a bidentate ligand forming a hexacoordinate silicate. When the reaction was carried out in dichloromethane the best stereoselectivity was obtained. The role of Hunig's base is probably that of scavenging the hydrogen chloride which otherwise would reduce the selectivity of the process.

More recently, Nakajima's group showed [78] that also the chiral phosphine oxide (*S*)-BINAPO provided the product of ring opening of *meso*-epoxides with high enantioselectivity (up to 90% e.e.) in the presence of tetrachlorosilane and diisopropylethylamine, whose presence seems to be necessary in order to obtain a good level of stereocontrol (Scheme 25).

5. Outlook and perspectives

In the present review the most relevant results in the field of stereoselective reactions catalyzed by hypervalent silicate compounds have been reported and briefly discussed, with a special attention to the most recent contributions to the area. It was the

aim of this work to show how hypervalent silicates represent a powerful tool for a modern synthetic chemist.

Since hypervalent silicon species may work through different activation mechanisms, they have recently attracted much attention for their versatility and for the possibility to develop several, catalytic processes. In this context the use of substoichiometric amounts of an organic compound of relatively low molecular weight and simple structure capable to promote reactions in the absence of costly and possibly toxic transition metals-based catalyst is very attractive. Indeed tuning the chemistry of penta and/or hexavalent silicon compounds by the design and the synthesis of chiral organocatalytic species is not only feasible, but highly desirable, with the goal to develop always new enantioselective reactions in the presence of cheap, low toxic and environmental friendly species such as silicon-based reagents.

On the basis of these considerations it is easy to predict that we will see a continously increasing interest in the field of stereoselective reactions promoted by chiral Lewis bases [79]; hopefully, this review will stimulate further research in a very exciting area, where hypervalent silicate species [80] will play a decisive role in inventing and developing new, highly chemical and stereochemical efficient catalytic systems of low environmental impact.

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