

Review

From designer Lewis acid to designer Brønsted acid towards more reactive and selective acid catalysis

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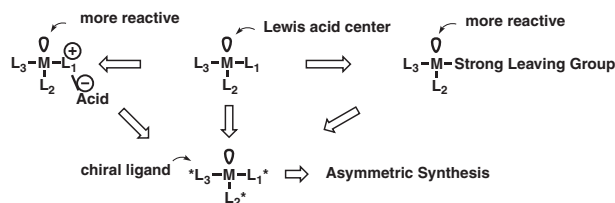
Abstract: This review focuses on the development of acid catalysis for selective organic transformations conducted in our laboratories for the past 30 years. Several important concepts in designing of catalysts are described with some examples. Further, recent developments in super Brønsted acid and their applications in a one-pot procedure to construct complex molecules with high diastereoselectivities are described.

Keywords: Lewis acid-Lewis base cooperative system, bulky aluminum reagent, chiral Lewis acid catalysis, combined acid catalysis, super Brønsted acid

Introduction

Generally, main group organometallic has an empty orbital to accept electrons. This makes the species highly Lewis acidic (Scheme 1). We speculate that this singular feature offers unique opportunities for the creation of numerous new reagents for selective organic synthesis. For example, the reactivity of these molecules depends on the choice of ligand. If the ligand is strongly electron withdrawing, the resulting metal center will significantly increase its acidity. If we are able to attach other metals to the ligands, we also expect to realize highly reactive species whose reaction will be influenced by the stereochemical feature of the attached ligands. Thus, asymmetric synthesis will be possible using such an acidic catalyst if we can use a chiral ligand directly connected to the metal center.

Most of our research has been based on these Lewis acid features of main group molecules, which are summarized in this review article. This, coupled with Professor K. Tamao's research (see accompanying review article), provides a breadth of information on the rich chemistry of main group



Scheme 1.

elements which I am sure has vast potential in future science of chemistry. In other words, our research utilizes the stereochemical features of main group molecules while Professor Tamao focuses on the electronic characters of these molecules by the ligands designed.

A proton is very small but highly reactive, and it is the oldest catalyst for organic synthesis. A large number of basic organic transformations are catalyzed by proton. It is a long-standing dream of synthetic chemists to control the reactivity of proton and to make it a general synthetic tool of selective organic synthesis. Described herein is over 30 years of our research in this field.

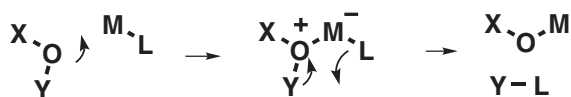
Aluminum amide: Lewis acid-Lewis base cooperative system

The Lewis acid-Lewis base cooperative system (Scheme 2) plays an important role in organic synthesis. For example, rearrangement from epoxides to allylic alcohols is known to proceed with strong base reagents; this is a typical example of

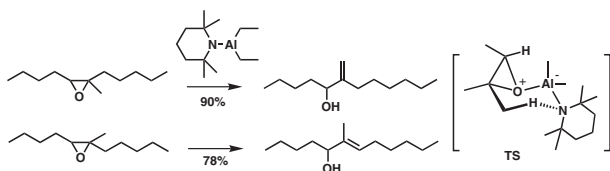
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Scheme 2.



Scheme 3.

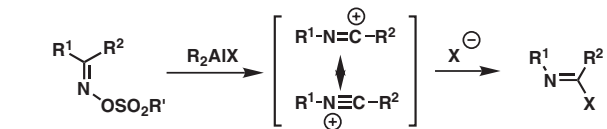
an acid-base cooperative system. However, in some cases, the efficiency of the rearrangement is not adequately efficient. Rather the rearrangement was found to proceed smoothly and rapidly using more oxyphilic aluminum amides.

Diethylaluminum 2,2,6,6-tetramethylpiperide reacted with the epoxide rapidly and gave the allylic alcohols highly efficient (Scheme 3).¹⁾ The observed strict regioselectivity originated from the stereoselective coordination of a sterically less hindered epoxide lone pair with the nitrogen of aluminum amide. Thus, the Lewis basicity of nitrogen was increased significantly by coordination of epoxide to aluminum. This is a nice example of an oxyphilic Lewis acid-Lewis base cooperative reaction system.

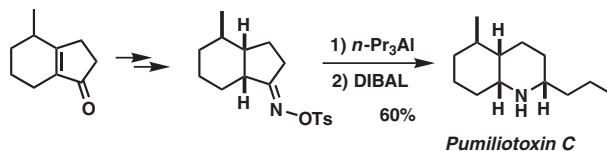
These Lewis acid-Lewis base cooperating systems are not only effective as an intramolecular system. An intermolecular version of the process was developed as follows. Reexamination of Beckmann rearrangement using organoaluminum reagents under aprotic conditions led to the abstraction of the sulfonyl group, followed by capture of the intermediary iminocarbocation or alkylidyne-ammonium ion with the nucleophilic group (X; R_2AlX (X = H, R, SR' , SeR')) on the aluminum (Scheme 4). Thus, aluminum reagents act not only as a Lewis acid but also as a nucleophile.²⁾ This method opens a new synthetic entry to a variety of alkaloids such as Pumiliotoxin C.³⁾

Chiral acetal and its application in organic synthesis

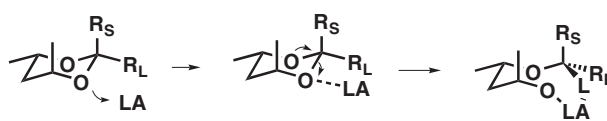
Chiral acetals derived from aldehydes and (2R,4R)-2,4-pentanediol are cleaved selectively by organoaluminum reagents (Scheme 5).⁴⁾⁻⁸⁾



Scheme 4.



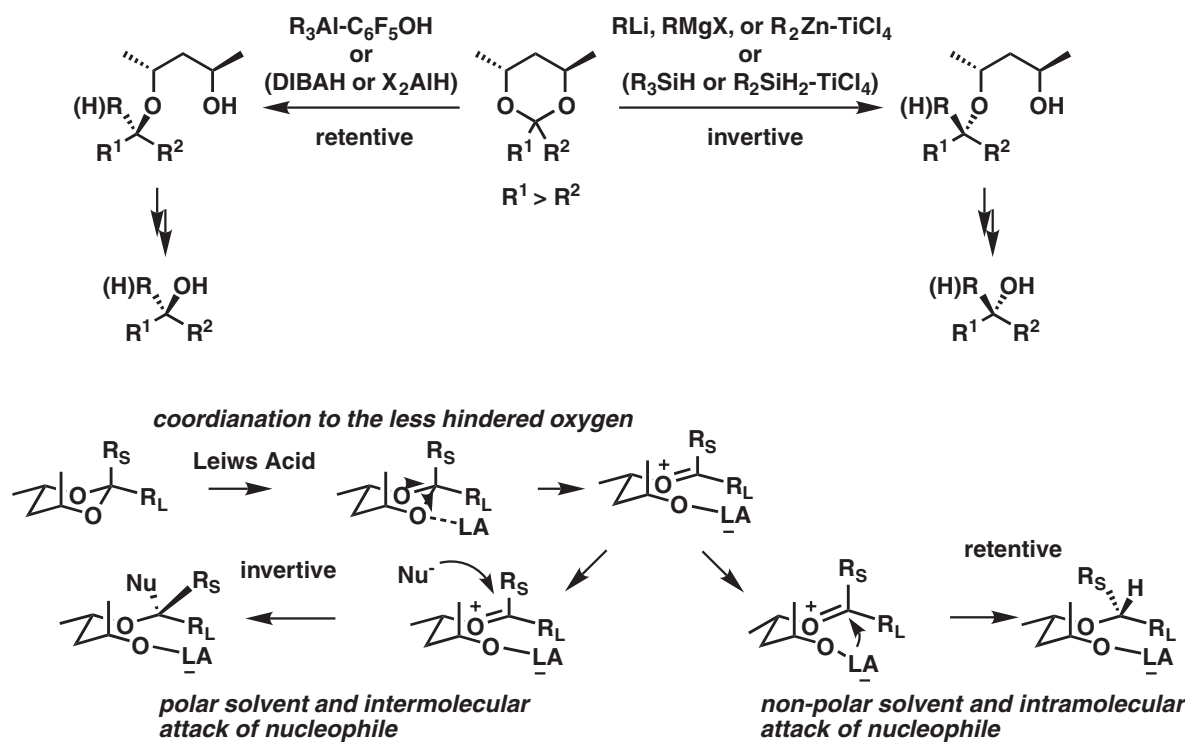
Scheme 5.



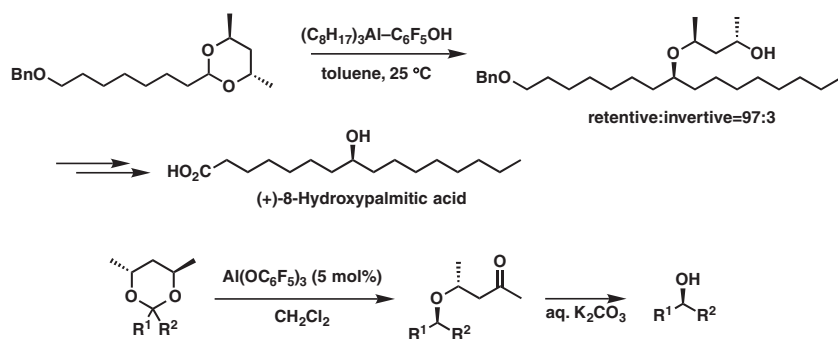
The reaction proceeds *via* the retentive-alkylation process with >95% selectivity in most cases. The reaction of acetals derived from (2R,4R)-2,4-pentanediol and ketones in the presence of a catalytic amount of aluminum pentafluorophenoxide produces reductively cleaved products with high diastereoselectivity. These reactions (Scheme 6) are useful means of diastereoselective cleavage of acetals: an intramolecular Meerwein-Ponndorf-Varley reductive and Oppenauer oxidative reaction on an acetal template.⁹⁾

In sharp contrast, alkylative cleavage of the same chiral acetals using Lewis acid-alkylmetal systems and reductive cleavage of the same acetals using Lewis acid-trialkylsilane or dialkylsilane systems occur inversely.¹⁰⁾⁻¹⁴⁾ Examples of this concept in synthesis are shown in Scheme 7. Methods are heavily dependent on the selective formation of the intermediary ion pair of Lewis acid (aluminum) and Lewis base (acetal oxygen).

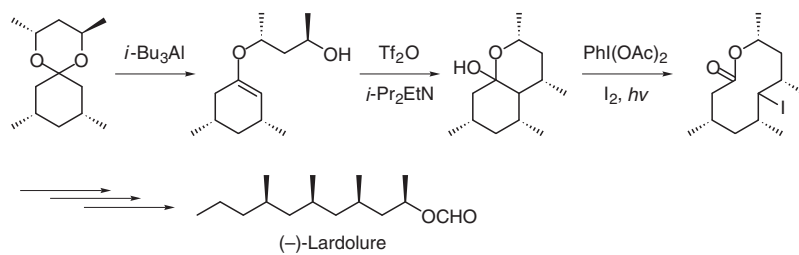
(-)-Lardolure has been synthesized based on this discovery (Scheme 8).¹⁵⁾ The compound was prepared straightforwardly by intramolecular cyclization of vinyl ether alcohol derived from spiro-acetal *via* triisobutylaluminum and further ring enlargement of the afforded bicyclic hemiacetals. In this simple total synthesis, the entire chirality of the product was transferred exclusively from the chirality of optically active 2,4-pentanediol.



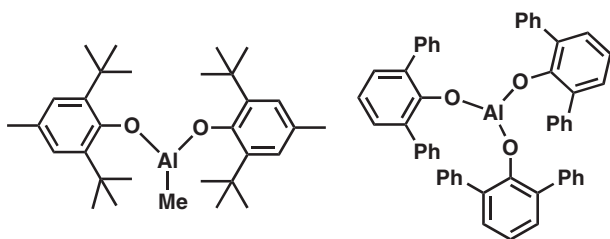
Scheme 6.



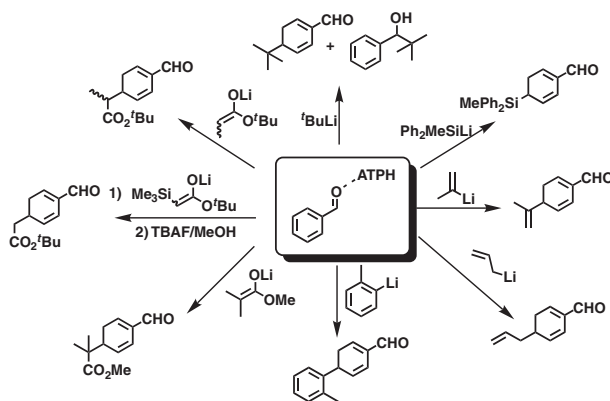
Scheme 7.



Scheme 8.



Scheme 9.



Scheme 10.

Bulky aluminum reagents

Most aluminum compounds in solution exist as dimeric, trimeric, or higher oligomeric structures. In contrast, methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenoxide) (MAD) and aluminum tris(2,6-diphenylphenoxide) (ATPH) (Scheme 9) are monomeric in organic solvent because of the large frontal steric effects of bulky ligands. Lewis-acidity of these reagents decreases with the coordination of more electron-donating aryloxides, but this can be compensated for by loosening of the aggregation. Compared with classical Lewis acids, the significant steric effect of our aluminum reagents plays an important role in numerous selective organic syntheses.^{16)–18)}

Examples: Selective 1,6-addition of alkylolithiums to aromatic carbonyl substrates such as benzaldehyde or acetophenone was achieved with ATPH to give functionalized cyclohexadienyl compounds (Scheme 10).¹⁹⁾ Based on the molecular structure of the benzaldehyde-ATPH complex, it is obvious that the para-position of benzaldehyde is deshielded by the three arene rings, which effectively block the ortho-position as well as the carbonyl carbon from nucleophilic attack. Although conjugate addition to the ATPH-PhCHO complex

did not proceed effectively with smaller nucleophiles, we were able to illustrate that ATPH-ArCOCl is superior to ATPH-PhCHO for the nucleophilic dearomatic functionalization. Several analytical and spectral data showed that the ATPH-PhCOCl complex was more reactive than ATPH-PhCHO (Scheme 11).²⁰⁾

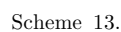
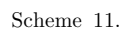
Chiral Lewis acid catalysis

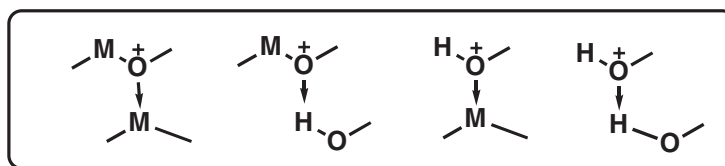
In 1988 an ASI workshop on “Selectivities in Lewis acid promoted reactions” was held in Greece, during which I proposed the mechanism of our asymmetric propargylation reaction using chiral allenyl boronic ester.²¹⁾ In an enantioface differentiating process, the chiral nucleophile was added to the carbonyl group of aldehydes, thus allowing the preparation of the chiral propargylic alcohols.²²⁾ Based on the *anti*-coplanar complex structure of carbonyl-boron-allene moieties, we postulated the clockwise rotation of the O-C bond prior to C-C bond formation (Scheme 12).

The reaction scheme shown above demonstrates that the symmetry element coordinated on the metal center does have a significant effect on the direction of the C-O rotation and thus on the asymmetric induction of the reaction. We therefore initiated new projects to develop a chiral Lewis acid catalyst which had C-*n* symmetry elements.

On this basis chiral Lewis acid catalyst which has the C-2 symmetry element was designed and tested for various asymmetric syntheses, and in 1985 we reported a zinc reagent and in 1988 a bulky aluminum reagent (Scheme 13).^{23),24)} The zinc reagent was used for asymmetric cyclization of unsaturated aldehyde and the aluminum reagent for asymmetric hetero-Diels-Alder reaction with Danishefsky diene. Both reagents effectively discriminate the enantioface of aldehydes.

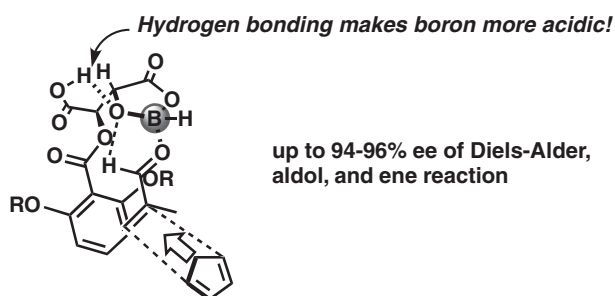
This work was the forerunner of a vast amount of present-day research on the binaphthol based chiral Lewis acid catalyst. Furthermore, we and other groups have reported various kinds of chiral Lewis acid catalysts which have C-2 symmetry elements and all of them have proven quite effective for asymmetric carbon-carbon bond forming processes.^{25),26)} Not only main group metal catalysts but also transition metal catalysts having the C-2 symmetric structure can be used for asymmetric synthesis *via* selective activation of carbonyls.²⁷⁾





Combined acid catalysis

In 1988 we reported a chiral Lewis acid catalyst of an acyloxyboron with a tartaric acid ligand.²⁸⁾ This was the first chiral Lewis acid catalyst for aldol, ene, and Diels-Alder reactions. The high reactivity of the tartaric acid derived catalyst may originate from intramolecular hydrogen bonding of

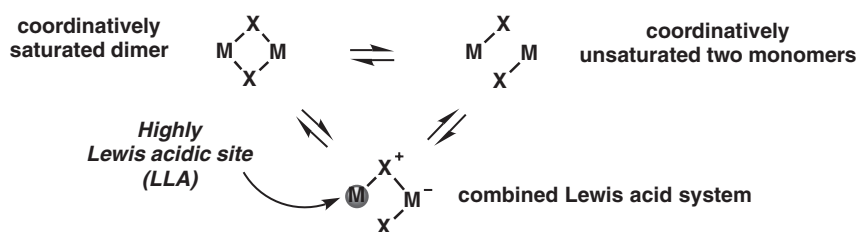


Scheme 14.

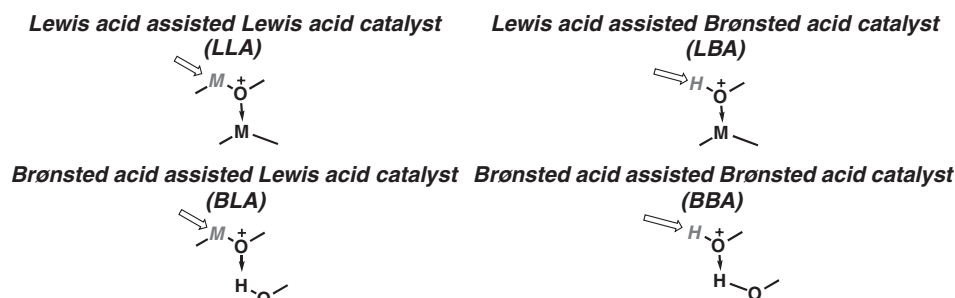
the terminal carboxylic acid to the alkoxy oxygen (Scheme 14). The same catalyst provided the first asymmetric catalyst of allylation of carbonyl compounds using allyltrimethylsilane.

This was the first example of the “combined acids system for asymmetric synthesis” (Scheme 15).²⁹⁾ It is known that coordinatively unsaturated monomers are far more Lewis acidic than doubly bridged coordinatively saturated dimers.³⁰⁾ A mono-coordinated complex, however, can generate and is even more Lewis acidic than the monomer through the formation of a singly bridged dimer. This species is the combined acid catalyst.

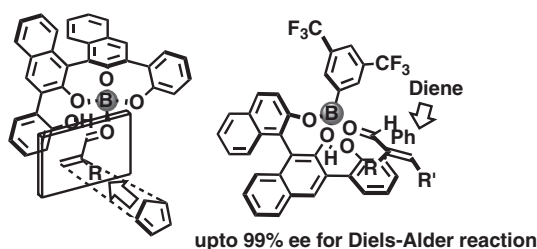
It should be emphasized that we anticipated a more or less intramolecular assembly of such combined systems rather than intermolecular arrangements. Thus, proper design of the catalyst structure is essential for success. The concept of combined acids (Scheme 16), which can be classified into Brønsted acid assisted Lewis acid (BLA),



Scheme 15.



Scheme 16.



Scheme 17.

Lewis acid assisted Lewis acid (LLA), Lewis acid assisted Brønsted acid (LBA), and Brønsted acid assisted Brønsted acid (BBA), can be a useful tool for designing asymmetric catalysis, because combining such can bring out their inherent reactivity by associative interaction, and also provide a more organized structure, both of which allow the securing of an effective asymmetric environment.

BLA: Scheme 17 exemplifies another boron based BLA which achieves high selectivity through the double effect of intramolecular hydrogen bonding interaction and attractive π - π donor-acceptor interaction in the transition-state.³¹⁾

LLA: Reactive Lewis acid-assisted Lewis acid (LLA) catalysts are relatively well known. Electron-deficient metal compounds can be further activated as electrophiles through hetero- and homodimeric associative interaction. However, full recognition of this synthetically powerful tool does not yet appear to be widespread. It may be further

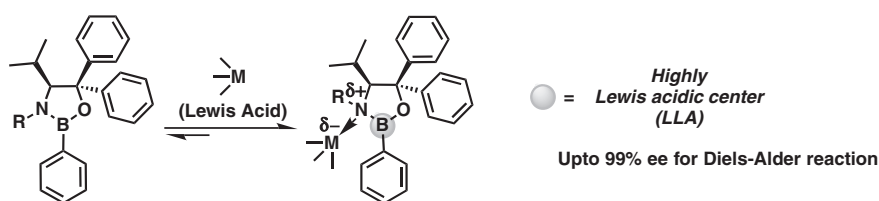
extended to include an asymmetric catalysis design. Scheme 18 is an example of LLA of chiral boron reagent activated by various achiral Lewis acids including SnCl_4 , AlCl_3 , FeCl_3 , and others.³²⁾

LBA: Combining Lewis acids and Brønsted acids to give Lewis acid-assisted Brønsted acid (LBA) catalysts can provide an opportunity to design a unique chiral proton⁶⁰. Namely, the coordination of a Lewis acid to the hetero atom of the Brønsted acid could significantly increase its original acidity. An example is shown in Scheme 19.³³⁾

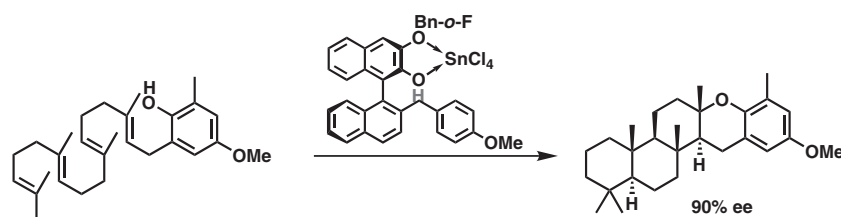
BBA: Hydrogen bonding can frequently be observed inside enzymes, and such a weak interaction has/plays a crucial role in organizing their three dimensional structure. Additionally, the hydrogen bonding is often involved in the reaction inside the active site of an enzyme. Such an elegant device could be applicable to asymmetric catalysis. Especially for Brønsted acid catalysis, the design of these catalysts would result not only in formation of a highly organized chiral cavity but also in an increase in the Brønsted acidity of the terminal proton in a much milder way than that of the LBA system (Scheme 20).³⁴⁾

Brønsted acid as a new tool for asymmetric synthesis

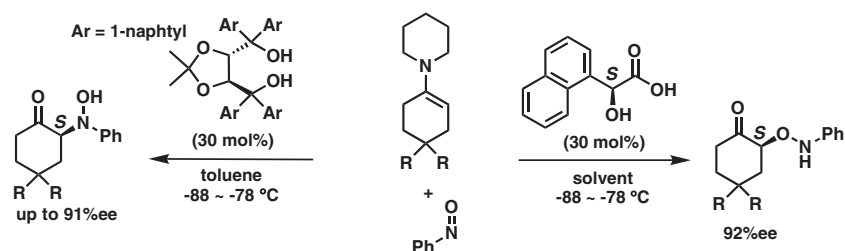
Brønsted acid will be an even more important catalyst in future because it is environmentally benign. Generally, Brønsted acid which is stronger



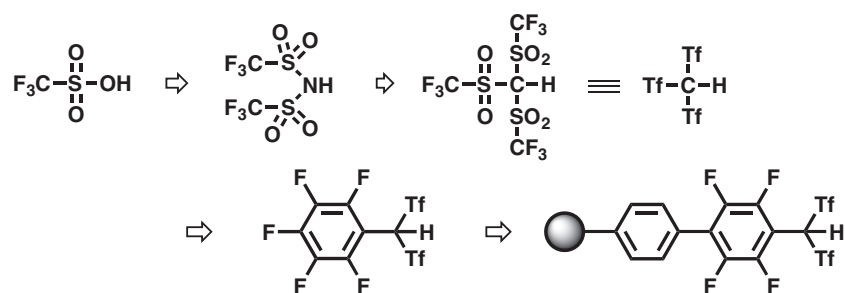
Scheme 18.



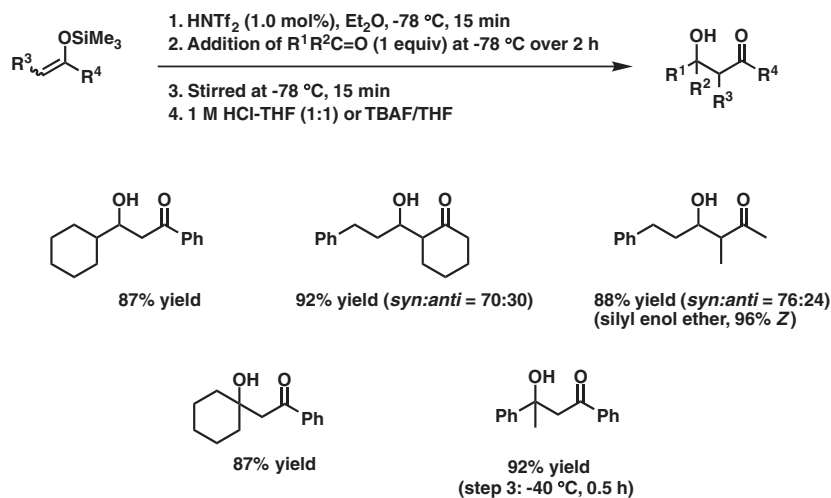
Scheme 19.



Scheme 20.



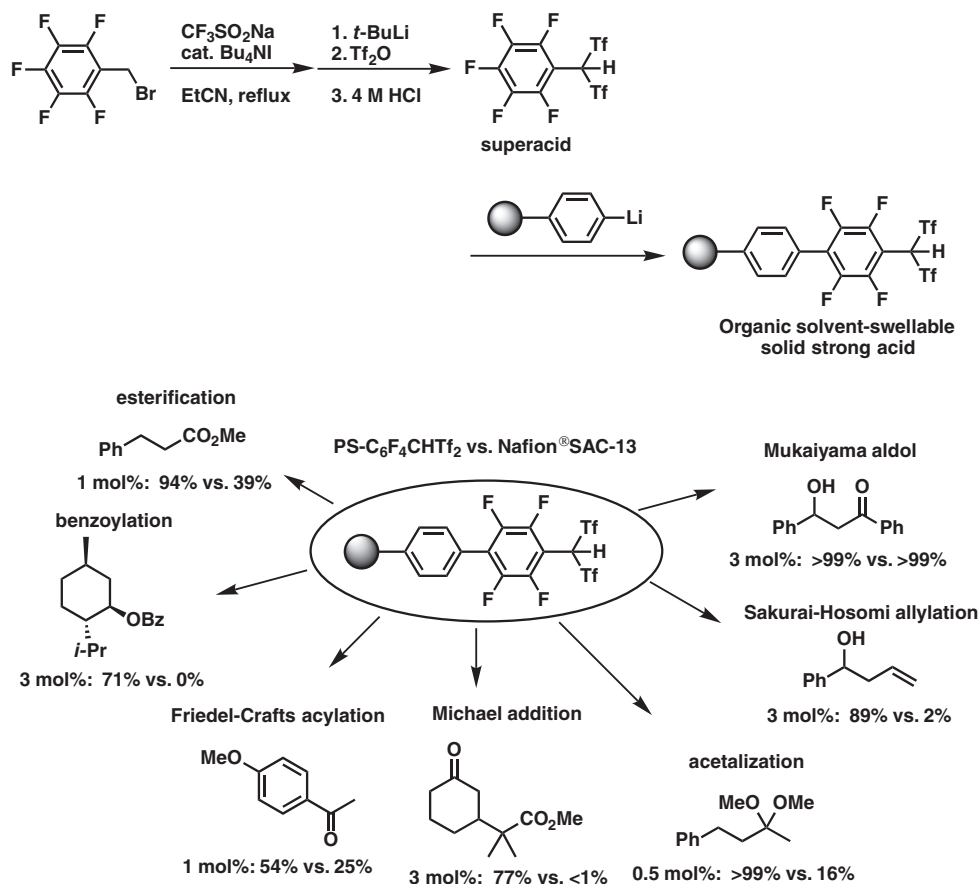
Scheme 21.



Scheme 22.

than 100% sulfuric acid is called super Brønsted acid by Gillespie.³⁵⁾ The vast potential of these reagents in the application to lithium batteries and fuel cells is well recognized. Scheme 21 shows a developing trend towards even more environmentally friendly but highly acidic reagents. Furthermore, the sterically larger conjugate base of such a super acid system creates a soft reagent, an important feature for organic reactions.

Once highly acidic Brønsted acids are in hand, we can also use it as an effective Lewis acid catalyst for various organic transformations. This is simply because the metal attached to such a super conjugate base makes the metal site very reactive. The broad utility of these reagents has been demonstrated by simple Mukaiyama aldol reaction as shown in Scheme 22 in which only 1 mol% of catalyst is necessary for the reaction.³⁶⁾

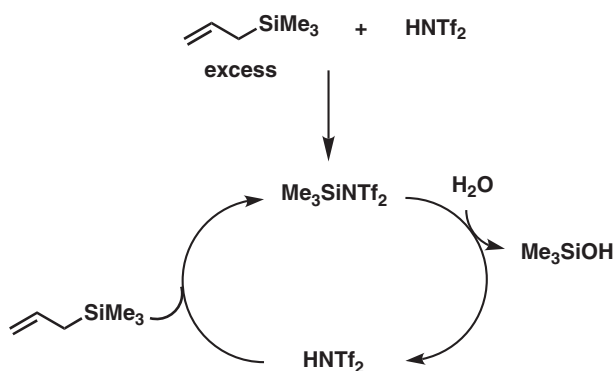


Scheme 23.

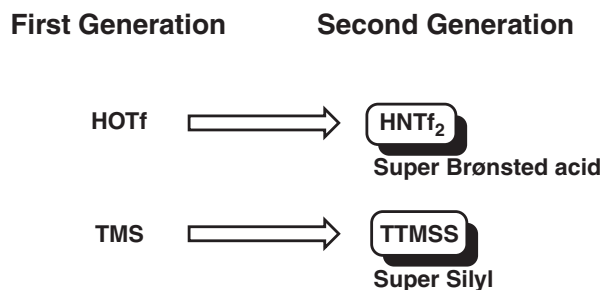
Although the real catalyst in this scheme is not Brønsted acid but $\text{Me}_3\text{SiNTf}_2$, the high reactivity of this acid catalyst came from the high reactivity of Tf_2NH .³⁷⁾ The trifluoromethanesulfonyl (triflyl, Tf) group is one of the strongest neutral electron-withdrawing groups. In particular, it greatly increases the acidity of hydrogen atoms at α -positions. The steric and electronic factors of the aromatic ring on arylbis(triflyl)methanes are expected to greatly influence their Brønsted acidity and their catalytic activity and selectivity for organic reactions. We have developed strong carbon Brønsted acids, pentafluorophenylbis(triflyl)methane and polystyrene-bound tetrafluorophenylbis(triflyl)methane based on this concept (Scheme 23).³⁸⁾ The synthesis of the resin-bound Brønsted acid has been accomplished by using the nucleophilic *para*-substitution reaction of lithium pentafluorophenylbis(triflyl)methide with lithiated polystyrenes as a key step. This is the first example

of a highly acidic heterogeneous Brønsted acid catalyst that is effectively swollen by non-polar organic solvents, and, because of its organic solvent swellable feature, its catalytic activities are much superior to those of Nafion[®] SAC-13.³⁹⁾

As described above, super Brønsted acid catalyst and super silyl catalyst are inextricably linked. This comes from the quick generation of silyl Lewis acid from super Brønsted acid and silyl enol ether (or allylsilane). Since $\text{Me}_3\text{SiNTf}_2$ is a moisture sensitive reagent, a small amount of water in the reaction mixture causes its decomposition to give Me_3SiOH and HNTf_2 . Me_3SiOH will react with $\text{Me}_3\text{SiNTf}_2$, and provide inert $\text{Me}_3\text{SiOSiMe}_3$ and HNTf_2 . The regenerated HNTf_2 will readily react with allyltrimethylsilane, and provide $\text{Me}_3\text{SiNTf}_2$ again.³⁹⁾ The repetition of this cycle should produce strictly anhydrous conditions, and thus this catalytic cycle constitutes a self-repair system for Lewis acid catalysis (Scheme 24). The same cata-



Scheme 24.



Scheme 25.

lytic repair system can also be effective with silyl enol ether.

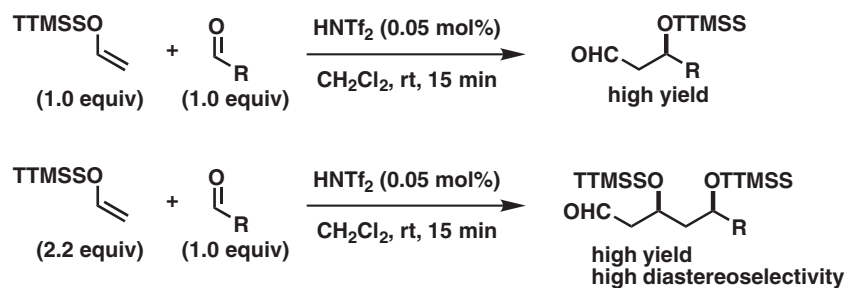
The trimethylsilyl (TMS) group is a widely used protecting group and Lewis acid, as well as an important functional group in certain substrates. For these reasons we deemed the TMS group to be “generation one”. As described earlier (Scheme 22) we have demonstrated that the use of triflimide as a catalyst initiator is very effective for the aldehyde cross-aldol reaction.⁴⁰⁾ The success of this reaction proved to be maximal with the use of triflimide

as the catalyst as well as the use of tris(trimethylsilyl)silyl (TTMSS) enol ethers (Scheme 25).⁴¹⁾ The use of the TTMSS group, also referred to as the super silyl group, is one of the keys to this reaction and its unique reactivity caused us to consider it as a second generation silyl group.

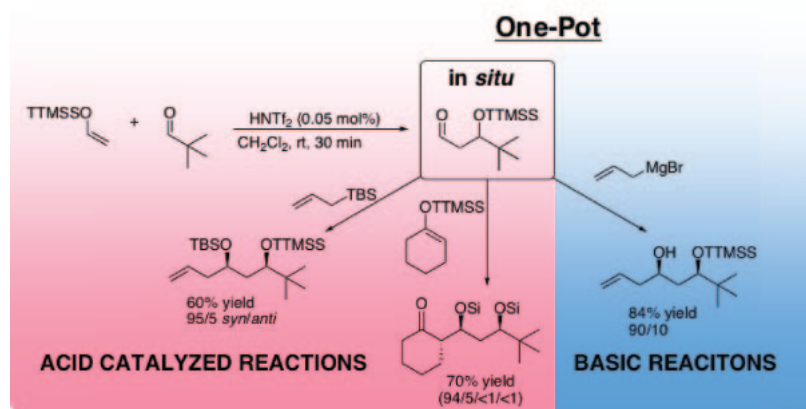
The exceptional diastereoselective “control” and high reactivity of the TTMSS (Super silyl) group can be attributed to the two classic arguments of sterics and electronics. The TTMSS group is extraordinarily bulky, and has been reported to shield molecular skeletons effectively. After the first addition and silyl transfer, the steric encumbrance of this group is likely to kinetically slow down the addition of a second equivalent of nucleophile to a rate that does not compete with the rate of the first addition. When all of the aldehyde starting material has been consumed, a second addition occurs giving the products with high diastereoselectivity. After this second addition occurs, the aldehyde has β - and δ -TTMSSoxy groups and if catalyst coordination occurs, the complex is likely too bulky for further additions (Scheme 26).

Intrigued by TTMSSNTf₂ catalysis, we used ²⁹Si NMR as an indicator of silicon Lewis acidity and found that the central silicon of TTMSSNTf₂ was shifted significantly down-field (>6 ppm) compared to TMS- and TBSNTf₂, and only slightly down-field from pentamethyldisilane-NTf₂ (62.2, 55.9, 55.5, and 60.8 ppm, respectively). This trend shows a considerable difference in the cationic nature of silyl groups with only silicon-carbon bonds versus those with silicon-silicon bonds. This high reactivity of silyl enol ether as well as super silyl cation is probably due to the high homo level of the Si-Si and Si-C sigma bond.

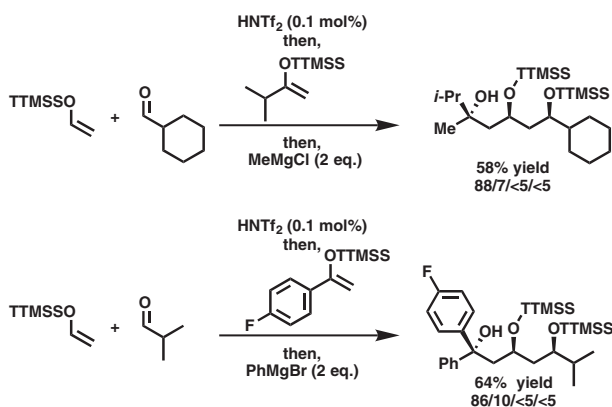
With this outstanding one pot aldol reaction in hand, since the tris(trimethylsilyl)silyl (TTMSS)



Scheme 26.



Scheme 27.



Scheme 28.

silyl enol ether undergoes aldehyde cross-aldol reactions with high selectivity and the extremely low catalyst loading (0.05 mol% of HNTf₂), we can proceed for one-pot sequential reactions where acidic or basic nucleophiles can subsequently be added. Various ketone-derived silyl enol ethers, Grignard reagents, and dienes succeeded successful, generating relatively complex molecular architectures in a single step (Scheme 27). This represents the first case where, in a single pot, highly acidic conditions followed by very basic conditions were tolerated to give products with high diastereoselectivities and good yields.⁴²⁾

Even more recently we have shown that the process can be used for enol ether of ketones which can be generated by carbon centers diastereoselectively in one pot. Scheme 28 shows examples of this reaction as a “four-component one-pot coupling reaction”.⁴³⁾

Acknowledgements

This review is a summary of my scientific achievements in acid catalyzed reactions that were carried out mainly at Nagoya University and subsequently at the University of Chicago. I am grateful to many individuals who collaborated with me on this work.

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Profile

Hisashi Yamamoto received his Bachelor from Kyoto University and Ph. D. from Harvard under the mentorship of Professor H. Nozaki and Professor E. J. Corey, respectively. His first academic position was as Assistant Professor and lecturer at Kyoto University, and in 1977 he was appointed Associate Professor of Chemistry at the University of Hawaii. In 1980 he moved to Nagoya University where he became Professor in 1983. In 2002, he moved to United States as Professor at the University of Chicago. He has been honored to receive the Prelog Medal in 1993, the Chemical Society of Japan Award in 1995, the Max-Tishler Prize in 1998, Le Grand Prix de la Fondation Maison de la Chimie in 2002, National Prize of Purple Medal (Japan) in 2002, Yamada Prize in 2004, Tetrahedron Prize in 2006, and The Karl-Ziegler Professorship in 2006, and The Japan Academy Prize in 2007. His current interests are mainly development of new synthetic reactions in the field of acid catalysis including designer Lewis acid, designer Brønsted acids, and combination of these two acid systems. Recently he is also interested in a new field on asymmetric oxidations and metal catalyst design based on cis-beta configuration.

