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Ten years of research in Chicago

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1. New design of asymmetric catalysts

Jacobsen's concept of a privileged ligand for asymmetric catalysis is popular in catalytic asymmetric synthesis. Among these privileged ligands, probably the one most frequently used would be the salene ligand. Although this ligand is widely used for numerous organic transformations, we believe its conformational equilibrium among trans, cis-, and cis-forms may create the existence of multiple possible transition states for the reaction, which could cause undesired by-paths of the transformation compared to the single-pathway process. The equilibrium among these three forms is usually very rapid and it has been believed to be rather difficult to freeze only a single conformer to the others.

We believed that if we used the longer chains from 7 to 9 carbon-length to bridge the nitrogen–nitrogen atoms, we would be able to freeze such equilibrium with rigorous steric requirements and thus be able to generate a stable and pure single isomer of cis- or cis-form without any equilibria. Although such a larger ring bridge might decrease the stability of the metal complex significantly, we felt this problem might be avoided if we chose a coordinating functional group, which was exceedingly strong toward metal ions. 8-Hydroxyquinoline was perfect for our purpose because this group is known to be the privileged heterocycle for numerous metal ions and, in fact, over 50 metal ions are known to coordinate to this ligand forming stable complexes. When we mixed our new ligand with a variety of metal ions, the metal containing the nine-membered ring was generated quite rapidly and quantitatively. As expected, the X-ray crystallographic analysis showed the resulting relatively rigid metal complex existed with the expected cis- configurations. In fact, the metal center of these complexes is always chiral and in the case of octahedral metal complexes the remaining two coordinating sites are non-equivalent. Such non-equivalent coordinating sites would provide us both sterically very crowded and less crowded sites on the metal ion, and thus offer asymmetric inductions otherwise unattainable. Based on this hypothesis, the following asymmetric reactions have been discovered: asymmetric pinacol coupling, NH reactions, allenylation, propargylation, Michael addition, Pudovik reaction, Strecker reaction, and nitroso-hetero-Diels–Alder reactions. Each reaction reduced the possible transition states and also two possible coordinating sites aligned specifically by electric and steric requirements.^{13,28,33,36,39,46,54,56,57}

(1) Catalytic asymmetric pinacol coupling reaction

(2) Catalytic asymmetric Nozaki–Hiyama allylation reaction

(3) Catalytic asymmetric allenylation reaction

(4) Catalytic asymmetric Mukaiyama–Michael addition reaction

(5) Catalytic asymmetric Pudovik reaction

(6) Asymmetric Strecker synthesis

The original preparation of the 8TBOX (tethered bis(8-quinolinate)) ligand requires relatively lengthy steps, which makes this ligand system rather unpopular despite its broad scopes of reactions. Fortunately, we have recently succeeded in simplifying the synthesis significantly starting from readily available chiral binaphthol [unpublished result].

2. Catalytic asymmetric oxidation

The second project was catalytic asymmetric oxidation reactions. We believe asymmetric oxidation reaction is far less developed than asymmetric reduction processes, although the former has certainly matured rapidly over recent decades. Since our collaboration with Professor Barry Sharpless over 40 years ago, I was interested in using the vanadium catalyzed asymmetric epoxidation reaction despite his clear description of ligand deceleration effects. Incidentally, we were also very much interested in the asymmetric epoxidation of homo- and bishomo-allylic alcohols, which, I believed, would provide a nice logical approach for the asymmetric synthesis of polyether natural products and other polyhydroxy compounds.

Our tested strategy was very simple: arranging two hydroxamic acids in a single chiral molecule as the ligand. This strategy indeed worked very well for asymmetric epoxidation without any ligand deceleration phenomena. Immediately, we tested not only allylic alcohols but also homo- and bishomoallylic alcohols with a few successes.^{8,23,30,31,44}

Although the vanadium system had not given us completely promising results in homo- and bishomoallylic systems, when we turned our attention to switching of the metal center from vanadium to hafnium the results were remarkable. This 'heavy metal effect' is unexpectedly marvelous and even bishomoallylic alcohol asymmetric oxidation proceeds quite efficiently.

These results occurred through simple serendipity but a larger size atom of hafnium metal seemed to have a more suitable space for the anchor functional group than vanadium or titanium ions, which thus allowed larger transition states for bishomo and homoallylic alcohols syntheses.

The heavy metal effect is not only useful for asymmetric epoxidation of bishomoallylic alcohols but also for sulfone amides of imidoes and allylic and homoallylic amides. Furthermore, even simple unsaturated sulfones can be used for asymmetric oxidations. Thus, the sulfone of sulfone amide easily coordinates with a hafnium metal and provides a functional group of future asymmetric oxidations. It was our additional surprise to recognize the outstanding enantioselectivities of *tert*-allylic and homoallylic alcohols, which had never been observed for titanium or vanadium metal catalyst.^{51,61}

The preparation of enantiopure tertiary 2,3-epoxy alcohols is still a long-standing problem for asymmetric oxidation in spite of their highly versatile building blocks, which contain quaternary stereogenic centers. Sharpless' asymmetric epoxidation could not provide an efficient protocol for this issue. The major problems with the method are low reactivity and selectivity due to the steric hindrances. Fortunately, the hafnium catalyst is free of such limitations and thus gave us excellent results as shown below.⁶⁴

In addition to epoxidation processes, we also introduced the nitroso reactions for catalytic asymmetric oxidation. A little over 10 years ago, we discovered the *O*-nitroso-aldol (O-NA) reaction, in which an acid catalyst activates the nitrogen atom rather than oxygen and thus the nucleophile approaches the oxygen atom site of nitroso moiety. The nitroso-aldol reaction was developed very rapidly and both N-NA and O-NA reactions were developed nicely using metal and non-metal catalysts. NA reaction turned out to be a new tool in organic synthesis as a very unique and useful oxidation for introduction of either or both nitrogen and oxygen atoms into the molecule.

The electron densities of nitrogen and oxygen in the nitroso group are competitive and just a slight difference of acidity of catalyst was able to change the activating sites of nitrosobenzene. We believe this could be due to the slight change of acidity on the *ortho* proton of nitrosobenzene. If the acid catalyst has the Lewis base center near the Lewis acid of proton or metal ion of catalyst and could form a relatively stable Lewis acid/Lewis base complex of 6–8-membered ring, then we would expect the O-NA reaction, otherwise the classical N-NA reaction proceeds through a larger ring transition state.

This consideration is not only applicable to acetic acid and nitrosobenzene complex (for O-NA) but also for the silver catalyzed re-action where the oxygen atom attached to phosphorus behaves as the Lewis base. N-NA reaction, on the other hand, takes place in methanol or in the presence of 1:1 BINAP/Ag catalyst.^{3,6,10,12,15,19,24,27,37,41,42,48,55}

Since the pioneering work by Kirby in 1973, nitrosocarbonyl compounds have occupied a prominent position in organic chemistry. Yet these species are very unstable and highly reactive, posing a significant challenge to the synthetic chemist. Traditionally, they are generated in situ as a transient intermediate via oxidation of hydroxamic acid derivatives. During the past few years, aerobic oxidizing processes have emerged, allowing convenient use of these intermediates for organic synthesis. However, despite their high synthetic potential, the success of nitrosocarbonyl compounds is still immature and limited to hetero Diels–Alder and ene reactions. Heretofore, no exciting nitrosocarbonyl aldol reaction has been known and no catalytic enantioselective reactions utilizing nitrosocarbonyl compounds have been reported. Most importantly, the key to the success of this issue is the identification of active MnO_2 as an oxidizing re-agent compatible with the catalytic cycle. This extremely mild oxidant efficiently generates nitrosocarbonyl compounds in situ through the oxidation of hydroxamic acid derivatives and also strictly avoids over-oxidation of the products. Further, the active MnO_2 was found not to significantly inhibit the necessary reactivity of chiral Lewis acids or other metal catalysts. Thus, we have now accomplished a following nitroso-aldol reaction and nitroso-hetero-Diels–Alder reaction, which proceeds smoothly in the presence of chiral catalysts [Refs. 55 and 63 and unpublished results].

3. Combined acid catalyst for construction of complex structures

Our research on chiral Lewis acid catalysis dates back to the early 1980s when we used our CAB and amino acid derived catalyst for asymmetric aldol as well as Diels–Alder reactions. Since then, amino acid and tartaric acid derived catalyst have developed very rapidly and the importance of these ligands for designing asymmetric catalyst is now broadly recognized. We proposed a combined acid catalyst between Lewis acid/Lewis acid, Lewis acid/Brønsted acid, Brønsted acid/Lewis acid, and Brønsted acid/Brønsted acid catalysis both intermolecularly and intramolecularly, which is now the general concept for designing asymmetric acid catalyst.

For example, Brønsted acid activated Lewis acid and Lewis acid activated Lewis acid catalyst, BLA and LBA, respectively, have been used for the generation of quaternary stereogenic centers by Diels–Alder reaction. Specifically, these catalysts have been proven to be highly effective for the asymmetric construction of a quaternary stereogenic center.

LA (Brønsted acid activated Lewis acid)

Scheme exemplifies boron based BLA, which achieved high selectivity through the double effect of intramolecular hydrogen bonding interaction and attractive – donor–acceptor interaction in the transition state.

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 homo-dimeric associative interaction. However, full recognition of this interaction as a synthetically powerful tool does not yet appear to be widespread. It may be further extended to include an asymmetric catalysis design. Shown below is an example of LLA of chiral boron reagent activated by various achiral Lewis acids including SnCl_4 , AlCl_3 , FeCl_3 , and others. Various other LLA systems have since been reported and molecular calculations provided that verify the Lewis acid activated Lewis acid transition state.

The general classifications of combined acid catalysis.

Type of combined acid catalysis	General Structure	Examples
Brønsted acid assisted Lewis acid catalyst (BLA) Enhancement of Lewis acidity by the combination with Brønsted acid		
Lewis acid assisted Lewis acid catalyst (LLA) Enhancement of Lewis acidity by the combination with Lewis acid		
Lewis acid assisted Brønsted acid catalyst (LBA) Enhancement of Brønsted acidity by the combination with Lewis acid		
Brønsted acid assisted Brønsted acid catalyst (BBA) Enhancement of Brønsted acidity by the combination with Brønsted acid		

BLA for Diels-Alder Reaction

LBA

Combining Lewis acids and Brønsted acids to give Lewis acid-assisted Brønsted acid (LBA) catalysts provided an opportunity to design a unique chiral proton. Namely, the coordination of a Lewis acid to the hetero atom of the Brønsted acid significantly increased its original acidity. Very recent publication of a beautiful demonstration by Corey's group showed that this LBA system is very effective for the synthesis of a number of natural products.

BBA

Hydrogen bonding can frequently be observed inside enzymes, and such a weak interaction has 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. Shown below are examples of such BBA for our nitroso-aldol reaction.^{3,6,10,12,15,19,24,27,37,41,42,47–50,55}

4. From Lewis acid to Brønsted acid catalysis

Our research on acid catalyst originated from our long-standing interest in designing an artificial proton catalyst. To search for more selective and reactive acidic catalysts, we gradually returned to highly acidic Brønsted acid, ‘super Brønsted acid catalyst’, which is known to be more acidic than sulfuric acid. Acids such as trifluoromethane sulfonic acid, bistrifuryl imide, and tristrifluorsulfonyl-methane are typical super Brønsted acids, and these environmentally acceptable metal free acids will be very useful in future organic synthesis.

These Brønsted acids can react with silyl enol ether to generate more reactive silicon Lewis acid and, importantly, can be regenerated to original Brønsted acids by various Lewis bases. Thus, when we used bis-trifluoroamide for silicon derived organic transformations including Mukaiyama aldol and Sakurai allylation reactions, the required acid catalyst went down as low as 0.01 mol %.

The observed low catalyst loading is explained by the unique reactivity of super Brønsted acid catalyst and super silyl catalyst, which are inextricably linked together through the quick generation of silyl Lewis acid from super Brønsted acid and silyl enol ether (or allylsilane). Since Me₃SiNTf₂ is a moisture sensitive reagent, a small amount of water in the reaction mixture decomposes it to give Me₃SiOH and HNTf₂. Me₃SiOH will react with Me₃SiNTf₂, and provide inert Me₃SiOSiMe₃ and HNTf₂. The regenerated HNTf₂ will readily react with allyltrimethylsilane or silyl enol ether, and provide a catalyst of Me₃SiNTf₂. Repetition of this cycle produces strictly anhydrous conditions; thus this catalytic cycle constitutes a self-repair system for Lewis acid catalysis. The same catalytic repair system is also effective with silyl enol ether. This observation came from the general future of super Brønsted acid because of the regeneration of the same Lewis acid catalyst even after it had deteriorated.^{9,40}

Encouraged by these observations, we next turned our attention to exploring successive Mukaimaya aldol synthesis. The tris(trialkylsilyl) silyl (super silyl) group is known as a popular reagent for radical chemistry, however, it is relatively unexplored for cationic organic synthesis. We discovered that these silyl groups are very unique and, despite the structurally giant moiety, the reactivity of silyl enol ether was comparable to or even higher than the smaller silicon derivatives. Furthermore, because of its size, we were able to stop the reaction after the mono-aldol stage. If we needed to proceed to the dialdol stage, we could do this by the use of excess silyl enol ether at slightly higher temperature. Furthermore, in the presence of the activating additive of silyl cation, we found the trialdol product was obtainable. We believe this is the first general aldol synthesis of hydroxy aldehyde. Fortunately, diastereoselectivity was excellent in every case and we could prepare stereochemically almost pure aldehydes after the reaction. With these results in hand, we were able to build up poly-ketide structures by successive addition of silyl enol ethers in one pot, which had been sort of a dream synthesis since the discovery of aldol reaction...and now this simple dream has come true.^{26,34,38}

The exceptional diastereoselectivity, 'control' and reactivity of the TTMSS group can be attributed to the two classic arguments of sterics and electronics. The TTMSS group is extraordinarily bulky, and has been said 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 double aldol products with high diastereoselectivity. The reason for the *syn* selectivity is shown in Fig. 1 where the conformation is not subjected to the unfavorable steric interaction between the Lewis acid coordinated oxygen and the R group that is present in another conformation, which will generate the *anti* product. After this second addition occurs, the aldehyde has - and - TTMSSoxy groups and if catalyst coordination occurs, the complex is likely too bulky for further additions. It should be noted that the 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 -bond, which are able to hyper-conjugate to orbital of the enolate or silyl cation, respectively.²⁶

As described above, the triple aldol reaction did not proceed under normal reaction conditions. However, when we added 10 mol % of iodobenzene, the reaction proceeded smoothly to generate the desired triple aldol product almost exclusively. Later, we found that iodo acetylene works even more effectively and the equivalent of iodo acetylene added to Brønsted acid catalyst gave us the triple aldol product efficiently. We believe the true catalyst for this reaction is silylenium cation stabilized by iodo acetylene, which is believed to be more reactive and structurally less demanding.

The use of the TTMSS group, also referred to as the super silyl group, is one of the keys for this reaction and its unique reactivity caused us to consider it as ‘the second generation of Mukaiyama aldol reaction’.

After these discoveries, we carefully examined diastereoselectivities inherent in the various aldol reactions including 1,2-Felkin, 1,3 and 1,5-selectivities associated with super silyl governed reactions, and found that excellent stereochemical control using the super silyl directing group does provide desired *syn* or *anti* aldol adducts with selectivity and specificity, which are otherwise unattainable. Observed excellent stereochemical control for 1,2-, 1,3-, and 1,5- asymmetric inductions demonstrated its vast potential for the straightforward synthesis of complex molecules. Virtually almost all of the stereochemical requirements of the synthesis of poly-ketides, for example, are able to be accomplished by switching the *E* or *Z* silyl enol ether of propionaldehyde and the choice of proper reagents. It is noteworthy that these syntheses proceed in a single pot with successive addition of the appropriate silyl enol ether.^{52,58–60}

Metal free chiral Brønsted acid catalysis has recently emerged as a new class of asymmetric organic catalysis. Several chiral Brønsted acids such as urea/thiourea, alcohol, and phosphoric acid have already been reported as chiral electron acceptors of carbonyl and imine compounds. However, compared with chiral metal Lewis acid catalysts, the utility of chiral Brønsted acid catalysts is still limited to the reactive substrates. This drawback can be overcome by designing a chiral Brønsted acid catalyst with higher acidity, which, in turn, will be the most important challenge for Brønsted acid chemistry. Needless to say, in order to increase the acidity of Brønsted acids, we believe it is necessary to increase the stability of the counter anion. For example, a strong chiral Brønsted acid would be achieved by

introduction of the 'NTf' group into the phosphoric acid. We were successful in preparing this super chiral Brønsted acid catalyst, which is able to advance the asymmetric Diels–Alder reaction of unsaturated ketones.²⁹

In 2010, we reported the first 'Brønsted acid catalyzed' Mukaiyama aldol reaction of aldehydes. Mechanistic details revealed that the actual catalyst could be changed from the Brønsted acid to the silylated Brønsted acid (Lewis acid) depending on the reaction temperature. It was amazing to find that Brønsted acid catalysis is more reactive and selective than the corresponding Lewis acid catalyst. I believe a truly reactive but stereochemically shielded Brønsted acid catalyst will be designed in future for the reaction of aldol, ene, and allylation processes.⁴⁵ Although this perspectives describes the most of my contributions during our research in Chicago, there are still several additional topics for further study in future.^{1,2,4,5,7,11,14,16–18,20–22,25,32,35,43,53,62}

5. Conclusions

Basically, chemistry cannot be viewed as conclusive at any level and she will continue to 'grow up' indefinitely. Thus, my dream is that all of these projects will continue to target perfection instead of being allowed to fade out. We wish to continue to contribute some of those projects at Nagoya.

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I would like to acknowledge the many outstanding contributors in my research laboratory in Chicago. If some of the chemistry mentioned in this review is significant, the honor is attributable to these individuals.

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Biography

Hisashi Yamamoto was born in Kobe, Japan in 1943. He received his Bachelor from Kyoto University under the supervision of Professors H. Nozaki and R. Noyori and Ph.D. from Harvard University under the mentorship of Professor E.J. Corey. 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 Arthur Holly Compton Distinguished Service Professor at the University of Chicago. In 2012, he moved back to Japan as director of Molecular Catalyst Research Center at Chubu University. During his research career over three decades, the research group of Yamamoto has developed a wide range of new reagents and reactions. In particular, his research laid the foundation for modern designer Lewis and Brønsted acid chemistry. His group has invented many methods for carbon–carbon bond formation, for constructing various ring system, for interconversion of functional groups, for controlling relative and absolute stereochemistry, and for efficient synthesis of natural and unnatural products. His current interests are mainly development of new synthetic reactions in the field of acid catalysis including designer Lewis and Brønsted acids, and combination of these two acid systems targeting more versatile, more selective, and more reactive catalysts, aiming at environmentally benign systems. He has been honored to receive the Chemical Society of Japan Award for Young Chemist in 1977, IBM Science Award in 1988, Houkou

Award in 1991, Chunichi Press Award, 1992, Prelog Medal in 1993, the Chemical Society of Japan Award in 1995, Toray Science and Technology Award in 1997, the Max-Tishler Prize in 1998, Tetrahedron Chair, in 2002, Le Grand Prix de la Fondation Maison de la Chimie in 2002, National Prize of Purple Medal (Japan) in 2002, Molecular Chirality Award in 2003, Yamada Prize in 2004, and Tetrahedron Prize in 2006, The Karl-Ziegler Professorship Award in 2006, The Japan Academy Prize in 2007, Honorary Member of the Chemical Society of Japan in 2008, ACS Award for Creative Work in Synthetic Organic Chemistry in 2009, and Grand Prize of Synthetic Organic Chemistry in 2009, fellow of American Academy of Arts and Sciences in 2011, Noyori Prize in 2011, and Fujiwara Prize in 2012.