

Bifunctional Molecular Catalysts with Cooperating Amine/Amido Ligands

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1. Introduction

The chemistry of transition metal-based molecular catalysts has progressed with discoveries of novel catalytic transformations as well as understanding the reaction mechanisms. Particularly, significant efforts have been continuously paid to develop bifunctional molecular catalysts having the combination of two or more active sites working in concert, to attain highly efficient molecular transformation for organic synthesis. We have recently developed metal–ligand cooperating bifunctional catalysts (*concerto catalysts*), in which the non-innocent ligands directly participate in the substrate activation and the bond formation. The concept of bifunctional molecular catalysis is now an attractive and general strategy to realize effective molecular transformation.¹

In 1995, Noyori and co-workers reported an unprecedented effect of diamine ligands on the enantioselective hydrogenation of simple aromatic ketones with BINAP-Ru(II) system [BINAP = 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl].² A combination of RuCl₂[(*S*)-binap](dmf)_n, chiral 1,2-diamine, and KOH showed an extremely high activity toward ketone hydrogenation than the classical BINAP–Ru catalyst. Subsequently, a prototype of a conceptually new phosphine-free Ru catalyst bearing *N*-sulfonylated 1,2-diamines as chiral ligands was developed for highly efficient asymmetric transfer hydrogenation of ketones.³ Detailed experimental and theoretical analyses of the real catalysts revealed that both an amidoruthenium complex having a square-planar geometry

and a coordinatively saturated hydrido(amine)ruthenium complex are involved in the catalytic cycle as depicted in Figure 1. The amido complex has sufficient Brønsted basicity to dehydrogenate readily secondary alcohols including 2-propanol to produce the hydrido(amine) complex. The NH unit bound to the metal center in the amine complex exhibits a sufficiently acidic character to activate ketonic substrates. During the interconversion between the amido and the amine complexes, the metal/NH moiety cooperatively assists the hydrogen delivery via a cyclic transition state where H⁻ and H⁺ equivalents are transferred in a concerted manner from the hydrido(amine) complex to the C=O linkage or from 2-propanol to the amido complex without direct coordination to the metal center (outer-sphere mechanism). This unique concept of the bifunctional transition metal based-molecular catalysts leads to reactions with high rates and excellent stereoselectivities because the reactions proceed through a tight-fitting assembly of the reactants and chiral catalysts.

Figure 2 lists some representative examples of well-defined bifunctional molecular catalysts recently developed in our group. The concept of the chiral bifunctional η⁶-arene–Ru complexes, RuH(Tsdpen)(η⁶-arene), [Tsdpen = *N*-(*p*-toluenesulfonyl)-1,2-diphenylethylenediamine] has been successfully extended to analogous Cp*Rh and Ir complexes, Cp*MH(Tsdpen) [Cp* = η⁵-C(CH₃)₅, M = Rh, Ir].⁴ In addition to the *N*-sulfonylated diamine complexes, group 8 and 9 metal complexes with diamines (N–N),⁵ aminophosphines (P–N),⁶ aminoethanethiols (S–N),⁷ and *o*-aminomethylphenyl (C–N)⁸ ligands have been

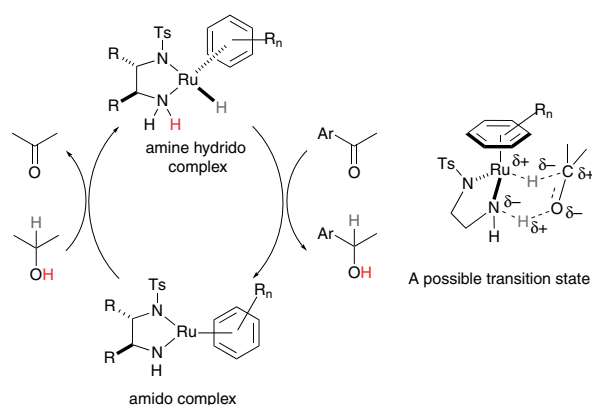


Figure 1. Concept of *Concerto* molecular catalysis: Interconversion of the amido and the amine hydrido Ru complex via a possible six-membered transition state.

extensively developed as the bifunctional molecular catalyst bearing the metal/NH effect.

As related bifunctional catalysts studied by other research groups, Figure 3 represents several group 8 and 9 metal complexes in which protic functional groups on the ancillary ligands works cooperatively with the metal center to catalyze hydrogenation, transfer hydrogenation, and so on. The Zhang's (A)⁹ and Grützmacher's catalysts (B)¹⁰ having tridentate protic amine ligands can help the H⁺/H⁻ transfer in a similar manner to our bifunctional catalysts. The Shvo's catalyst (C)¹¹ can release the catalytically active species, cyclopentadienyl and cyclopentadienone complexes, and the OH group plays a vital role as a proton mediator to promote hydrogen transfer processes. Recently, Milstein developed new PNN pincer complexes (D)¹² as highly active redox catalysts and found

their unique hydrogenation/dehydrogenation mechanism via dearomatization. Fujita and Yamaguchi have designed Cp*Ir complexes (E)¹³ having 2-hydroxypyridine and pyridonate ligands which efficiently promote dehydrogenation of secondary alcohols by the aid of the acidic OH function. Kitamura and Tanaka demonstrated that the acidic nature of 2-quinoline carboxylic acid on a CpRu fragment (F) effects a C–O bond activation of allyl alcohols to afford allyl ethers.¹⁴

This article focuses on the outline of our recent progress in the bifunctional molecular catalysts based on the metal/NH synergy, and their utilization to asymmetric redox transformations and related enantioselective C–C and C–N bond formation reactions.

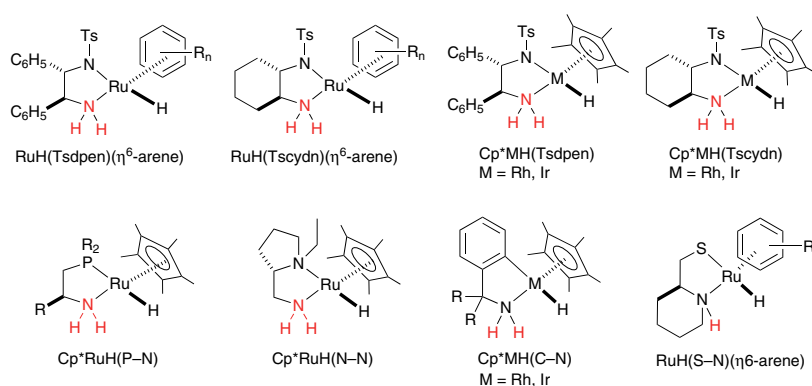


Figure 2. Bifunctional catalysts bearing protic chelate amine ligands.

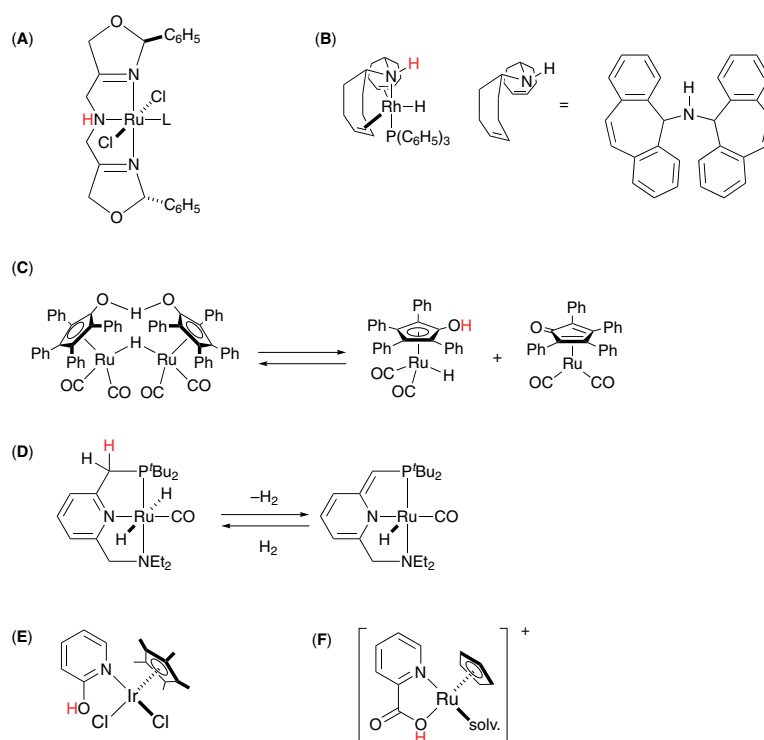


Figure 3. Related examples of metal-ligand cooperating catalysts having protic functional moiety.

2. Asymmetric Transfer Hydrogenation Using Bifunctional Catalysts^{1c}

In general, 2-propanol can be used as a safe, nontoxic, environmentally friendly hydrogen source. Although the asymmetric reduction in 2-propanol gives satisfactory results, an inherent drawback of the hydrogen transfer reaction is its reversibility, leading to limited conversion determined by thermodynamic factors of the system and the deterioration of enantiomeric purity of the products upon a long exposure of the reaction mixture to the catalyst. On the other hand, formic acid is amenable to the asymmetric reduction in an irreversible fashion leading to 100% conversion.¹⁵

Asymmetric reduction of simple aromatic ketones with a mixture of formic acid and triethylamine containing the bifunctional catalyst is characterized by high efficiency in terms of activity, selectivity, wide substrate scope, and practicability. The bifunctional hydrido(amine)-Ru complex is coordinatively saturated, and the catalyst system tolerates amino, ester, cyano,

nitro, azide, and chloro groups as well as heteroaromatic rings and the alkyne linkage,^{1c} as summarized in Figure 4. Carbon–nitrogen double bonds are also reducible with a mixture of formic acid and triethylamine containing chiral Ru or Rh catalysts to the corresponding amines with a high level of enantiomeric excesses.¹⁶

A series of Cp*Ru(P–N) complexes bearing the protic phosphine-amine ligands also serve as highly efficient catalysts for transfer hydrogenation as shown in Figure 5. Based on the reversible hydrogen transfer mechanism via interconversion between both the amido and amine complexes, the redox process can be successfully applied to rapid racemization of chiral alcohols¹⁷ as well as regioselective oxidative transformation of diols to lactones using acetone.¹⁸ A chiral Cp*Ru(P–N) complex accomplishes enantioselective isomerization of allylic alcohols to β -substituted ketones, and the following ring-closing metathesis affords (*R*)-muscone¹⁹ with a moderate ee.

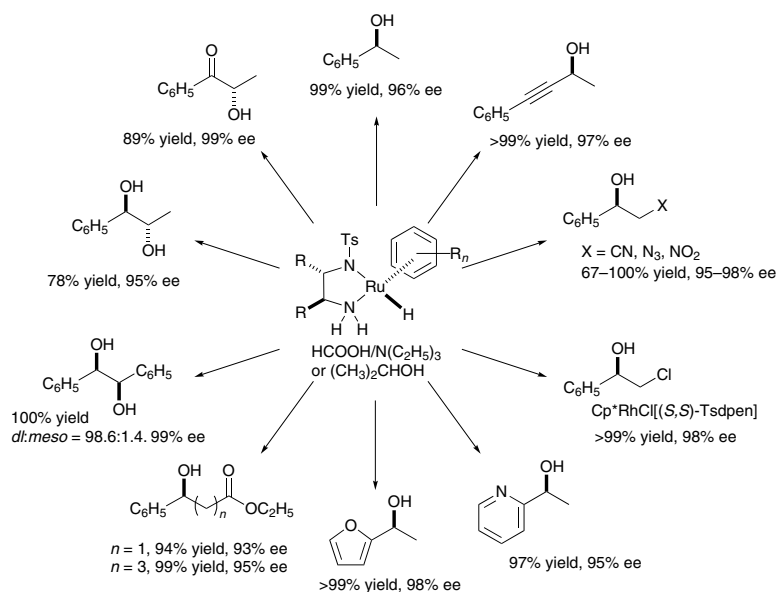


Figure 4. Asymmetric transfer hydrogenation of ketones with chiral Ru and Rh catalysts.

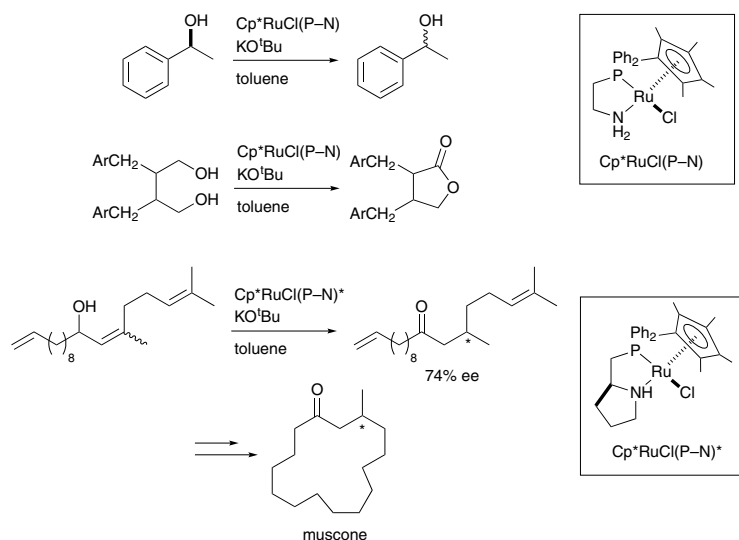


Figure 5. Hydrogen transfer reactions with Cp*Ru(P–N) catalysts.

3. Catalytic Hydrogenation of Polar Substrates with Bifunctional Catalysts⁶

Since we reported an effect of alcoholic solvent facilitating the heterolytic cleavage of H₂ bound to the 16-electron [Cp**Ru*{Me₂N(CH₂)₂NH₂}]⁺ (Cp**Ru*(N–N)) fragment in 2001,²⁰ we have systematically tested catalytic hydrogenation of polar substrates other than ketones, and found that the replacement of the tertiary amino group with a tertiary phosphino group has led to the expansion in the scope of the Ru/NH bifunctionality. For example, Cp**Ru*(P–N) complex, [Cp**Ru*{Ph₂P(CH₂)₂NH₂}]⁺, selectively delivers hydrogen to the non-substituted C–O bond in a variety of terminal epoxides, leading to the formation of the corresponding *sec*-alcohols, while Cp**Ru*(N–N) complexes are totally inactive.²¹

The Cp**Ru*Cl(P–N) catalyst allows the straightforward catalytic hydrogenation of *N*-acylcarbamates and carboximides to afford *N*-protected amines and alcohols selectively.²² Notably, the present hydrogenation is applicable to the reductive transformation. The deprotection of the primary amine from *N*-phthalimides with this bifunctional catalyst can be also applied to Gabriel amino acid synthesis. For instance, the HCl salt of L-Phe methyl ester with no loss of optical purity is obtainable from the hydrogenolysis of *N*-phthaloyl-L-Phe methyl followed by HCl treatment. Hydrogenolysis of chiral *N*-acyloxazolidones, which are useful synthetic intermediates in the asymmetric synthesis developed by Evans gives chiral alcohol and the original chiral auxiliary without any loss in the optical purity as shown in Figure 6.^{23a} The chiral version of the Cp**Ru*(P–N) catalyst bearing the chiral P–N ligand derived from L-proline promotes the enantioselective hydrogenation of prochiral 4-arylglutarimides via desymmetrization to provide the corresponding δ -hydroxyamides with excellent ee values and in high yields. Further synthetic elaboration has furnished chiral piperidinone derivatives, which serve as important synthetic intermediates for a number of physiologically active chiral compounds including the antidepressant paroxetine.

The Cp**Ru*(P–N) catalysts also promote the hydrogenation of esters and carboxamides to give alcohols or amines under more forcing conditions.^{23b} This hydrogenation procedure will provide a powerful alternative method for classical reduction using stoichiometric amounts of metal hydride reagents.

4. Aerobic Oxidation with Bifunctional Catalysts²⁴

When molecular oxygen can be used as a hydrogen acceptor for the dehydrogenative oxidation of alcohols with the bifunctional catalyst, aerobic oxidation becomes a simple and minimal organic waste process. Fortunately, we found a new family of isolable bifunctional amido-Ir complexes bearing a C–N chelating amine ligands, Cp**Ir*[$\kappa^2(N,C)$ -(NHCR₂-2-C₆H₄)] (R = C₆H₅ and CH₃), and the corresponding hydrido(amine) complexes, Cp**Ir*H[$\kappa^2(N,C)$ -(NH₂CR₂-2-C₆H₄)], which serve as efficient catalysts for transfer hydrogenation of ketones, promote catalytic aerobic oxidation of alcohols.^{8a}

The catalytic reaction of 1-phenylethanol proceeds smoothly under atmospheric pressure of air containing amido-Ir complex, Cp**Ir*[$\kappa^2(N,C)$ -(NHC(C₆H₅)₂-2-C₆H₄)] (Figure 7).²⁵ The hydrido(amine)-Ir complex, Cp**Ir*H[$\kappa^2(N,C)$ -(NH₂C(C₆H₅)₂-2-C₆H₄)], and binary catalyst systems, including the chloro(amine)-Rh and -Ru complexes and KOC(CH₃)₃, also provide the oxidation product acetophenone. The reaction of primary alcohols under identical conditions affords the oxidative dimerization product, esters. When a mixture of benzyl alcohols containing combined catalyst of the chloro complex, Cp**Ir*Cl[$\kappa^2(N,C)$ -(NH₂C(C₆H₅)₂-2-C₆H₄)], with an equimolar amount of KOC(CH₃)₃ in THF is stirred under air at 30 °C, the corresponding benzyl benzoate derivatives are obtained.

This aerobic oxidation of alcohols is more appealing when applied to the kinetic resolution of racemic secondary alcohols with chiral amido catalysts (Figure 7). A racemic 1-phenylethanol is efficiently resolved by the chiral Ir complex, Cp**Ir*[(*S,S*)-Msdpen] (Ms = methanesulfonyl), under the aerobic

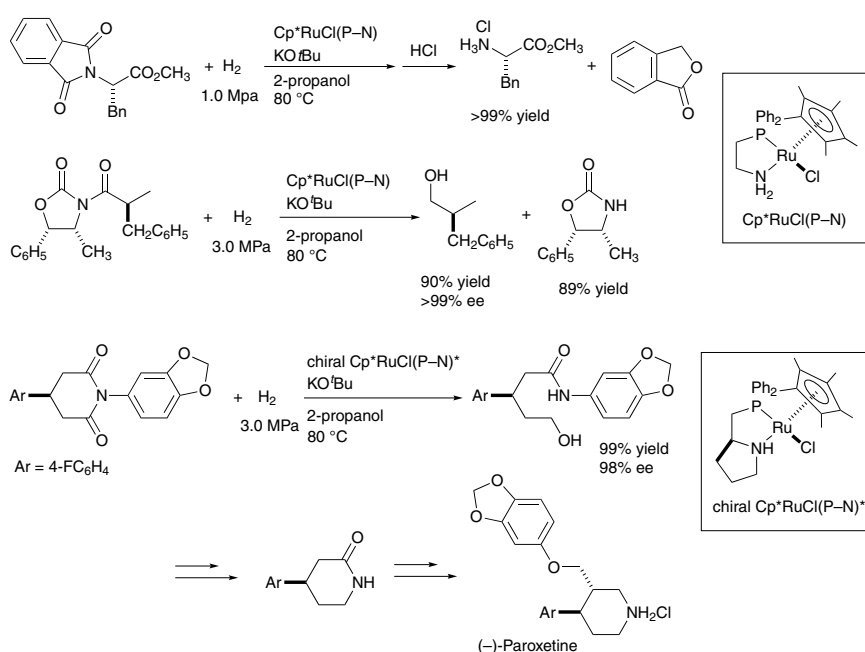


Figure 6. Hydrogenation of *N*-acylcarbamates and carboximides with Cp**Ru*(P–N) catalysts.

condition to give (*R*)-1-phenylethanol with a 48% yield and 98% ee; the k_f/k_s ratio being up to 100.²⁶ Similarly, the reactions of 1-indanol and 1-tetralol at ambient temperature provide the *R*-enantiomers with >99% ee and with 46–50%.

5. Extension to Dinuclear Bifunctional Catalysts Bearing Metal–Nitrogen Bond²⁷

The metal–ligand bifunctional effect realized for the mononuclear half-sandwich amido complex is expected to be operative in imido-bridged dinuclear complexes with M–N bonds. Careful structural analysis and NMR studies revealed that the electron-withdrawing sulfonyl group stabilizes the imido-bridged dinuclear complexes,²⁸ also has an acid/base bifunctional property originated from the M–N bond nature.

A coordinatively unsaturated bis(imido)-bridged dirhodium(III) complex, $[(Cp^*Rh)_2(\mu-N Ts)_2]$ ($Ts = SO_2C_6H_4CH_3-p$) reacts smoothly with H_2 (1 atm) in CH_2Cl_2 for 24 h at room temperature to afford the bis(amido)-bridged

dirhodium(II) complex, $[(Cp^*Rh)_2(\mu-NHTs)_2]$, in 82% yield as shown in Figure 8. It should be noted that in this reaction, H_2 is formally converted into two amido protons and two electrons for the reduction of the dirhodium(III) core in $[(Cp^*Rh)_2(\mu-N Ts)_2]$. The bis(amido) complex was also obtained upon treatment of the bis(imido) complex with an excess of 2-propanol. The generation of two NH protons associated with two-electron reduction of the metal center is in sharp contrast with the dehydrogenation of primary and secondary alcohols, which leads to the formation of hydrido–amine complexes without formal reduction of the metal, as described above.

The bis(amido)-bridged dirhodium(II) complex rapidly reacted with O_2 to form the bis(imido)-bridged dirhodium(III) complex and water.²⁹ Furthermore, the facile redox interconversion between the dinuclear imido and amido complexes can be applied to catalytic aerobic oxidation of H_2 and alcohols.

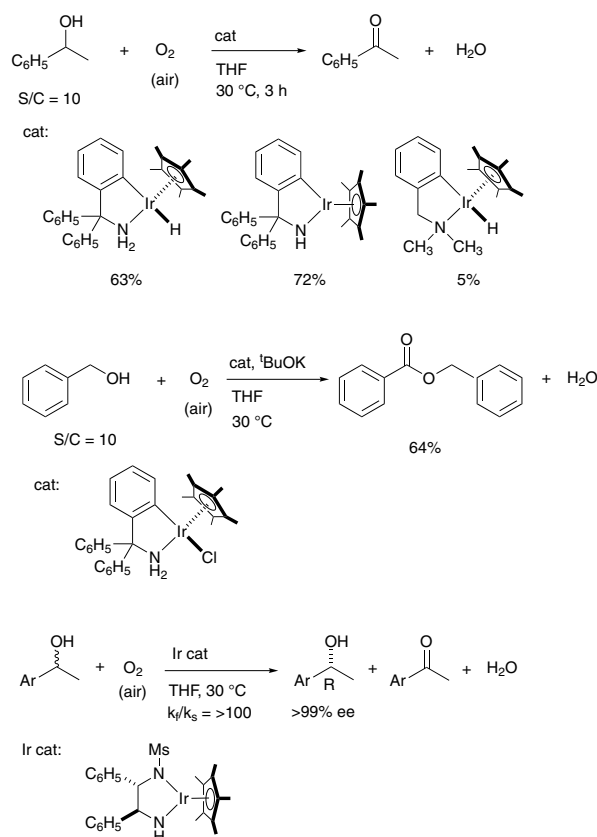


Figure 7. Aerobic oxidation of alcohols with bifunctional Ir catalysts.

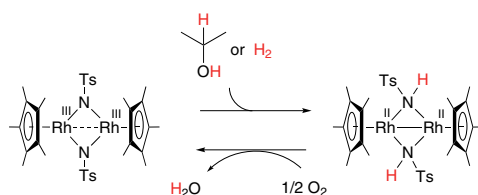


Figure 8. Interconversion between imido-bridged dirhodium(III) and amido-bridged dirhodium(II) complexes.

6. Asymmetric Conjugate Addition with Bifunctional Catalysts³⁰

The basic amido complexes can react with certain acidic organic compounds, leading to an amine complex bearing a metal bonded carbon nucleophile. For example, we have found that the purple-colored amido Ru complex, Ru[(*R,R*)-Tsdpen](η^6 -mesitylene), smoothly reacts with dimethyl malonate in toluene below $-30\text{ }^\circ\text{C}$ to give a yellow crystalline complex, Ru[CH(CO₂CH₃)₂][(R,R)-Tsdpen](η^6 -mesitylene).³¹ If the amine complexes bearing a metal-bonded nucleophile generated from an amido metal complex with certain acidic compounds can attack to electron-deficient acceptors, the catalytic C–C bond formation could be achieved. In fact, a chiral Ru catalyst, Ru[(*S,S*)-Tsdpen](η^6 -arene) efficiently promotes enantioselective Michael addition of dimethyl malonate to cyclic enones or nitro olefins to give the corresponding adducts with excellent ee's (Figure 9). NMR and DFT analyses of the Michael addition reaction of 1,3-dicarbonyl compounds to cyclic enones catalyzed by bifunctional Ru catalysts revealed that the enantioselective C–C bond formation proceeds through intermediate formation of chelating ion pairs that coordinate a molecule of enone via the Ru metal center producing a highly organized environment for the C–C bond formation, yielding selectively only one enantiomer of the product.^{31b}

The scope of the enantioselective conjugate addition with chiral amido catalysts is extensible to the Ir-catalyzed reaction of α -cyanoacetates with dialkyl azodicarboxylates that affords the direct amination products, the hydrazine adducts.³² When the acetylenic esters are used as electrophiles, enantioselective

and *Z* selective conjugate addition of α -cyanoacetate with bifunctional chiral catalysts proceeds smoothly to yield chiral adducts having a quaternary carbon center with an excellent ee.³³

7. Summary

This article focuses on recent advances in chemistry of conceptually new *the Concerto Catalysis* with bifunctional transition metal-based molecular catalysts including the stereo-, regio- and chemoselective reductive or oxidative transformation as well as enantioselective C–C and C–N bond formations via Michael-type conjugate additions. The rational design of the cooperating amine ligand that adjust the balance of the electronic factors on the M/NH units in the bifunctional catalysts is crucial to exploit characteristic catalyst performance with a wide scope and high practicability. We believe the present bifunctional molecular catalysts offer a great opportunity to open up new fundamentals for selective molecular transformation including asymmetric synthesis.

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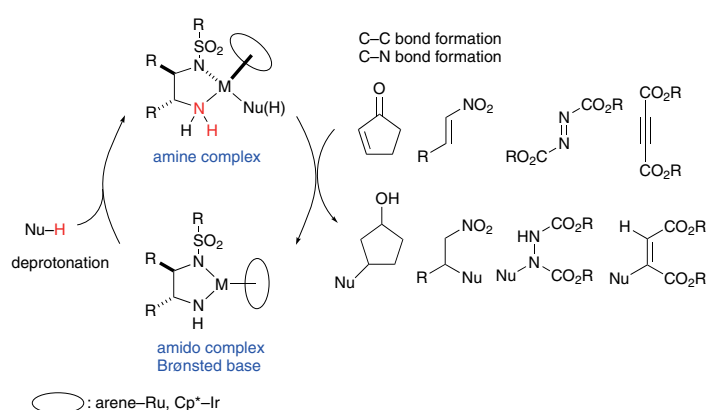


Figure 9. Asymmetric 1,4-addition to enones and nitroalkenes with chiral bifunctional Ru or Ir catalysts.

References

- 1) a) T. Ikariya, K. Murata, R. Noyori, *Org. Biomol. Chem.* **2006**, *4*, 393. b) K. Muñiz, *Angew. Chem. Int. Ed.* **2005**, *44*, 6622. c) T. Ikariya, A. J. Blacker, *Acc. Chem. Res.* **2007**, *40*, 1300. d) T. Ikariya, *Bull. Chem. Soc. Jpn.* **2011**, *84*, 1.
- 2) a) T. Ohkuma, H. Ooka, S. Hashiguchi, T. Ikariya, R. Noyori, *J. Am. Chem. Soc.* **1995**, *117*, 2675. b) T. Ohkuma, H. Ooka, S. Hashiguchi, T. Ikariya, R. Noyori, *J. Am. Chem. Soc.* **1995**, *117*, 10417.
- 3) a) S. Hashiguchi, A. Fujii, J. Takehara, T. Ikariya, R. Noyori, *J. Am. Chem. Soc.* **1995**, *117*, 7562. b) K.-J. Haack, S. Hashiguchi, A. Fujii, T. Ikariya, R. Noyori, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 285.
- 4) a) K. Murata, T. Ikariya, R. Noyori, *J. Org. Chem.* **1999**, *64*, 2186. b) K. Mashima, T. Abe, K. Tani, *Chem. Lett.* **1998**, 1199. c) K. Mashima, T. Abe, K. Tani, *Chem. Lett.* **1998**, 1201.
- 5) M. Ito, M. Hirakawa, K. Murata, T. Ikariya, *Organometallics* **2001**, *20*, 379.
- 6) a) M. Ito, T. Ikariya, *Chem. Commun.* **2007**, 5134. b) M. Ito, A. Osaku, C. Kobayashi, A. Shiibashi, T. Ikariya, *Organometallics* **2009**, *28*, 390. c) M. Ito, T. Ikariya, *J. Synth. Org. Chem. Jpn.* **2008**, *66*, 1042.
- 7) a) M. Ito, Y. Shibata, A. Watanabe, T. Ikariya, *Synlett* **2009**, 1621. b) M. Ito, A. Watanabe, Y. Shibata, T. Ikariya, *Synlett* **2010**, 29, 4584.
- 8) a) S. Arita, T. Koike, Y. Kayaki, T. Ikariya, *Organometallics* **2008**, *27*, 2795. b) J.-B. Sortais, V. Ritleng, A. Voelklin, A. Holuigue, H. Smail, L. Barloy, C. Sirlin, G. K. M. Verzijl, J. A. F. Boogers, A. H. M. de Vries, J. G. de Vries, M. Pfeffer, *Org. Lett.* **2005**, *7*, 1247.
- 9) Y. Jiang, Q. Jiang, X. Zhang, *J. Am. Chem. Soc.* **1998**, *120*, 3817.
- 10) a) P. Maire, T. Büttner, F. Breher, P. Le Floch, H. Grützmacher, *Angew. Chem. Int. Ed.* **2005**, *44*, 6318. b) T. Zweifel, J.-V. Naubron, T. Büttner, T. Ott, H. Grützmacher, *Angew. Chem. Int. Ed.* **2008**, *47*, 3245. c) T. Zweifel, J.-V. Naubron, H. Grützmacher, *Angew. Chem. Int. Ed.* **2009**, *48*, 559.
- 11) a) Y. Blum, D. Czarkie, Y. Rahamin, T. Shvo, *Organometallics* **1985**, *4*, 1459. b) Y. Shvo, D. Czarkie, Y. Rahamin, D. F. Chodosh, *J. Am. Chem. Soc.* **1986**, *108*, 7400.
- 12) a) J. Zhang, G. Leitus, Y. Ben-David, D. Milstein, *J. Am. Chem. Soc.* **2005**, *127*, 10840. b) C. Gunanathan, Y. Ben-David, D. Milstein, *Science* **2007**, *317*, 790. c) S. W. Kohl, L. Weiner, L. Schwartsburd, L. Konstantinovski, L. J. W. Shimon, Y. Ben-David, M. A. Iron, D. Milstein, *Science* **2009**, *324*, 74.
- 13) a) K. Fujita, N. Tanino, R. Yamaguchi, *Org. Lett.* **2007**, *9*, 109. b) R. Yamaguchi, C. Ikeda, Y. Takahashi, K. Fujita, *J. Am. Chem. Soc.* **2009**, *131*, 8410.
- 14) a) S. Tanaka, H. Saburi, Y. Ishibashi, M. Kitamura, *Org. Lett.* **2004**, *6*, 1873. b) S. Tanaka, H. Saburi, M. Kitamura, *Angew. Chem. Int. Ed.* **2005**, *44*, 1730. c) S. Tanaka, T. Seki, M. Kitamura, *Angew. Chem. Int. Ed.* **2009**, *48*, 8948.
- 15) A. Fujii, S. Hashiguchi, N. Uematsu, T. Ikariya, R. Noyori, *J. Am. Chem. Soc.* **1996**, *118*, 2521.
- 16) a) N. Uematsu, A. Fujii, S. Hashiguchi, T. Ikariya, R. Noyori, *J. Am. Chem. Soc.* **1996**, *118*, 4916. b) J. Mao, D. C. Baker, *Org. Lett.* **1999**, *1*, 841.
- 17) M. Ito, A. Osaku, S. Kitahara, M. Hirakawa, T. Ikariya, *Tetrahedron Lett.* **2003**, *44*, 7521.
- 18) a) M. Ito, A. Osaku, A. Shiibashi, T. Ikariya, *Org. Lett.* **2007**, *9*, 1821. b) M. Ito, A. Shiibashi, T. Ikariya, *Chem. Commun.* **2011**, 2134.
- 19) M. Ito, S. Kitahara, T. Ikariya, *J. Am. Chem. Soc.* **2005**, *127*, 6172.
- 20) M. Ito, M. Hirakawa, K. Murata, T. Ikariya, *Organometallics* **2001**, *20*, 379.
- 21) M. Ito, M. Hirakawa, A. Osaku, T. Ikariya, *Organometallics* **2003**, *22*, 4190.
- 22) a) M. Ito, A. Sakaguchi, C. Kobayashi, T. Ikariya, *J. Am. Chem. Soc.* **2007**, *129*, 290. b) M. Ito, C. Kobayashi, A. Himizu, T. Ikariya, *J. Am. Chem. Soc.* **2010**, *132*, 11414.
- 23) a) M. Ito, L. W. Koo, A. Himizu, C. Kobayashi, A. Sakaguchi, T. Ikariya, *Angew. Chem. Int. Ed.* **2009**, *48*, 1324. b) M. Ito, T. Ootsuka, R. Watari, A. Shiibashi, A. Himizu, T. Ikariya, *J. Am. Chem. Soc.* **2011**, *133*, 4240.
- 24) T. Ikariya, S. Kuwata, Y. Kayaki, *Pure Appl. Chem.* **2010**, *82*, 1471.
- 25) S. Arita, T. Koike, Y. Kayaki, T. Ikariya, *Chem. Asian J.* **2008**, *3*, 1479.
- 26) S. Arita, T. Koike, Y. Kayaki, T. Ikariya, *Angew. Chem. Int. Ed.* **2008**, *47*, 2447.
- 27) S. Kuwata, T. Ikariya, *Dalton Trans.* **2010**, *39*, 2984.
- 28) a) K. Ishiwata, S. Kuwata, T. Ikariya, *Organometallics* **2006**, *25*, 5847. b) H. Arita, K. Ishiwata, S. Kuwata, T. Ikariya, *Organometallics* **2008**, *27*, 493.
- 29) K. Ishiwata, S. Kuwata, T. Ikariya, *J. Am. Chem. Soc.* **2009**, *131*, 5001.
- 30) a) T. Ikariya, I. D. Gridnev, *Chem. Rec.* **2009**, *9*, 106. b) T. Ikariya, I. D. Gridnev, *Top. Catal.* **2010**, *53*, 894.
- 31) a) M. Watanabe, K. Murata, T. Ikariya, *J. Am. Chem. Soc.* **2003**, *125*, 7508. b) I. D. Gridnev, M. Watanabe, H. Wang, T. Ikariya, *J. Am. Chem. Soc.* **2010**, *132*, 16637.
- 32) Y. Hasegawa, M. Watanabe, I. D. Gridnev, T. Ikariya, *J. Am. Chem. Soc.* **2008**, *130*, 2158.
- 33) Y. Hasegawa, I. D. Gridnev, T. Ikariya, *Angew. Chem. Int. Ed.* **2010**, *49*, 8157.

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Yoshihito Kayaki was born in Tokyo, Japan, in 1969. He received his Ph.D. from Waseda University in 1997 under the supervision of Prof. A. Yamamoto. While at Waseda, he was appointed to a research fellowship of the Japan Society for the Promotion of Science. He joined the research group of Prof. T. Ikariya in 1998 and served as the group leader of the PRESTO project of JST from 2001 to 2005. He is currently an assistant professor at Tokyo Institute of Technology. His research interests lie in the area of synthetic and mechanistic studies of organometallic compounds as well as reaction chemistry relevant to CO₂ utilization.

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Takao Ikariya completed his Ph.D. degree supervised by Prof. A. Yamamoto in 1976 at Tokyo Institute of Technology and then he was appointed as an assistant professor in the Department of Synthetic Chemistry at the University of Tokyo. He discovered a prototype of chiral Ru-BINAP complex and successfully developed asymmetric hydrogenation with the Ru-BINAP complexes. He spent Prof. R. H. Grubbs' group at Caltech for one and a half years in 1979-1981 as a postdoctoral fellow. In 1985, he moved to the central research center of NKK Co. In 1991, he joined in the ERATO Molecular Catalysis Project of JST, which was directed by Prof. R. Noyori. Then Ikariya was promoted to professor at Tokyo Institute of Technology in 1997. He received the Chemical Society of Japan Award in 2009 and the Humboldt Research Award in 2011. His current research interests include powerful and practical molecular catalysis in both liquid solvents and supercritical fluids.