

The 7th Green and Sustainable Chemistry Award

Professor Teruyuki Kondo
Graduate School of Engineering, Kyoto University

Development of Advanced Molecular Transformation of Alkenes by Low-valent Ruthenium Catalysts

Alkenes are key materials in the petrochemical industry, and they are easily available, cheap, reactive, and readily converted into a range of valuable chemicals. Catalytic dimerization, codimerization, and cooligomerization of alkenes are one of the most important methodologies in organic synthesis directed toward green and sustainable chemistry, since in these reactions all the atoms of the starting materials are incorporated into the products without formation of wastes (100% atom-economy).

A prize winner has first succeeded in the synthesis of novel low-valent ruthenium complexes from his original complex, $\text{Ru}(\eta^6\text{-cot})(\eta^2\text{-dmfm})_2$ [cot = 1,3,5-cyclooctatriene, dmfm = dimethyl fumarate], all of which are expected as highly efficient catalysts for alkene oligomerization. Then, he focused his efforts on developing ruthenium-catalyzed highly regio- and stereoselective cooligomerization of *different alkenes*: 1) Ruthenium-catalyzed regio- and stereoselective codimerization of 2-norbornenes with acrylic compounds, 2) Novel synthesis of enamides by ruthenium-catalyzed codimerization and/or cotrimerization of *N*-vinylamides with alkenes, and 3) Unusual *head-to-head* dimerization of styrenes and linear codimerization of styrenes with ethylene catalyzed by ruthenium in the presence of primary alcohols.

[1] Ruthenium-catalyzed Regio- and Stereoselective Codimerization of 2-Norbornenes with Acrylic Compounds

Novel catalyst systems of $\text{RuCl}_3(\text{tpy})/\text{Zn}$ [tpy = 2,2':6',2''-terpyridine] or $[\text{RuCl}_2(\eta^6\text{-C}_6\text{H}_6)]_2/\text{Zn}$ in alcohols were revealed to efficiently catalyze the linear codimerization of 2-norbornenes with acrylic compounds, while the codimerization of 2,5-norbornadiene with acrylic compounds required the addition of triarylphosphines to the catalyst system of $\text{RuCl}_3(\text{tpy})/\text{Zn}$. This reaction provides a straightforward method for introducing norbornyl and norbornenyl substituents on the β -carbon of acrylic compounds with high regio- and stereoselectivity.

[2] Novel Synthesis of Enamides by Ruthenium-catalyzed Codimerization and/or Cotrimerization of *N*-Vinylamides with Alkenes

Regio- and stereoselective synthesis of enamides by $\text{Ru}(\eta^6\text{-cot})(\eta^2\text{-dmfm})_2$ -catalyzed codimerization of *N*-vinylamides with alkenes has been developed. The reaction could be extended to chemo- and regioselective cotrimerization of three different alkenes, such as *N*-vinylacetamide, ethyl acrylate, and ethylene. A mechanism that involves an active (hydrido)ruthenium species rather than a ruthenacyclic intermediate is proposed.

[3] Unusual *head-to-head* Dimerization of Styrenes and Linear Codimerization of Styrenes with Ethylene Catalyzed by Ruthenium

Many transition metal complexes have been reported to effectively catalyze the dimerization of styrenes, which generally gives a head-to-tail dimer, (*E*)-1,3-diaryl-1-butenes. He has found unusual *head-to-head* dimerization of styrenes catalyzed by ruthenium to give (*E*)-1,4-diaryl-1-butene. Addition of primary alcohols is essential for success of the present reaction, and the present catalyst system could be applied to more important and difficult linear codimerization of styrenes with ethylene to give (*E*)-1-aryl-1-butenes in good yields with high selectivity.

The reactions disclosed here are all atom-economical and environmentally benign processes. These findings will offer new methods for the synthesis of novel functional monomers from versatile and inexpensive starting materials.