Toward Industrial Applications of Homogeneous Catalysts

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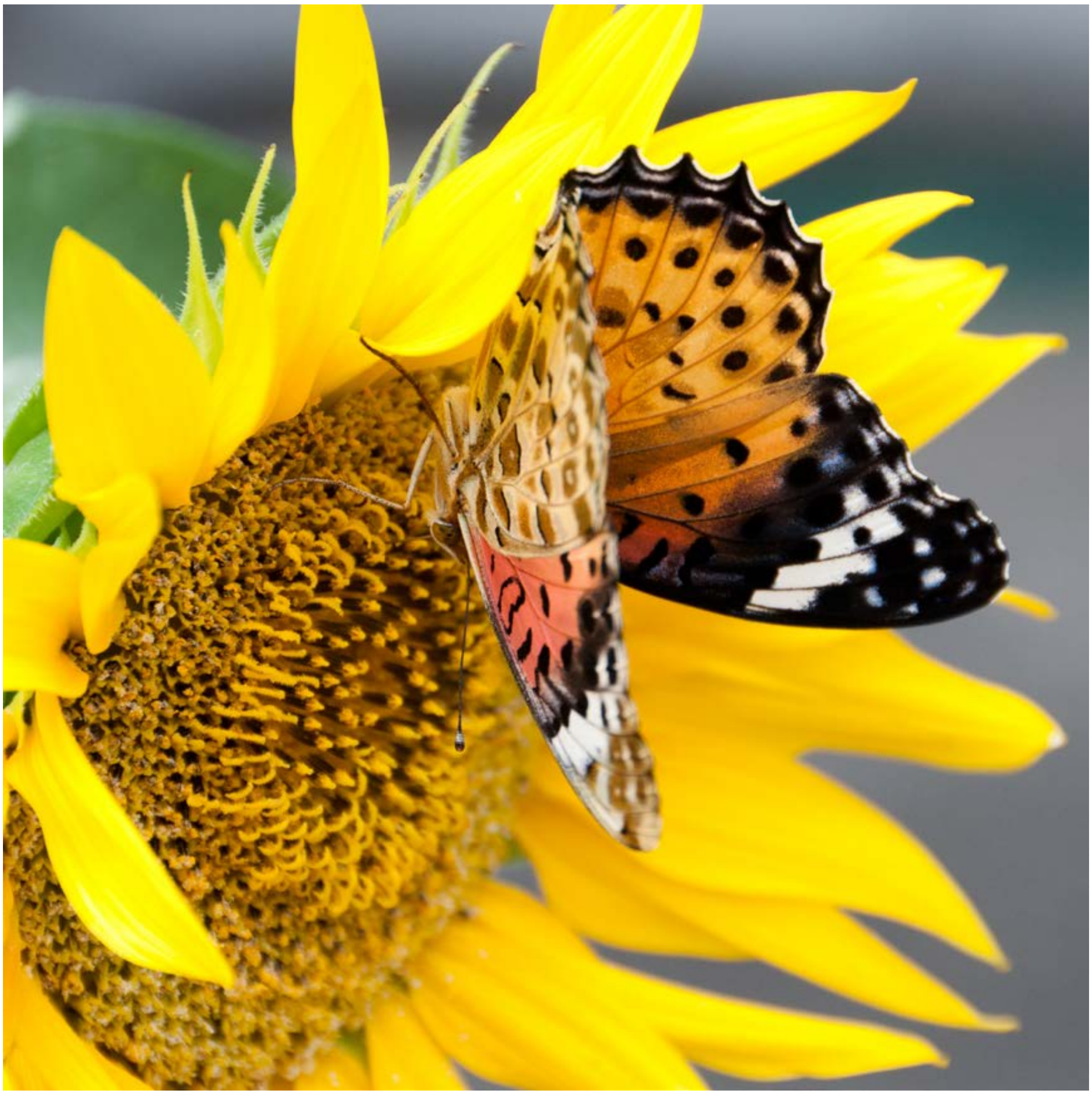

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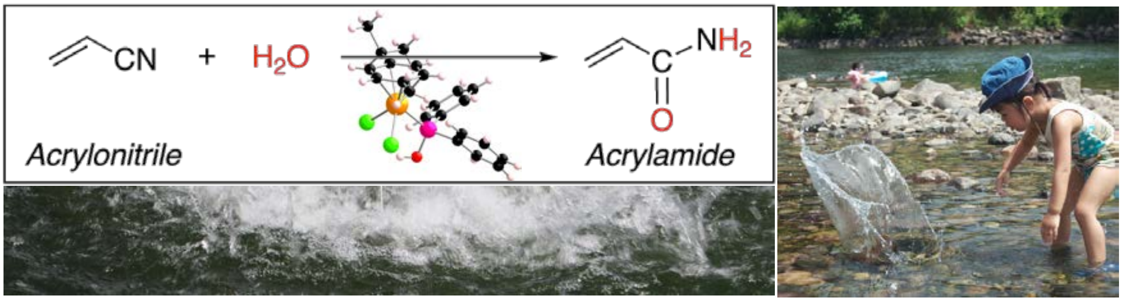
New Homogeneous Catalysts for Production of Acrylamide

TOWARD INDUSTRIAL APPLICATIONS OF HOMOGENEOUS CATALYSTS



Production of acrylamide for the sake of water environment keeping and purification

What is acrylamide ?

- Acrylamide is one of the most important commodity chemicals and most important amides.
- Acrylamide is commercially produced by catalytic hydration of acrylonitrile annually more than 500,000 tons.
- Acryamide (polyacrylamide) is used in coagulators for waste water, additives for paper treatment, and enhanced oil recovery (EOR) agents.

Why do we develop new homogeneous catalysis for acrylamide ?

	Biocatalysis	Chemocatalysis (New Homogeneous Catalysis)
Concentration of Acrylamide	△ very low to 50 %	◎ up to 100 %
Productivity per Time	× unable to heat	◎ able to heat
Waste Water	× necessary to keep activity of biocatalyst	◎ minimum amount of water
Availability of Catalyst	△ cultured in pure water	◎ onsite production

- Homogeneous catalysis has some advantages than biocatalysis in principle. Especially, “zero waste water” is characteristic feature of homogeneous catalysis.

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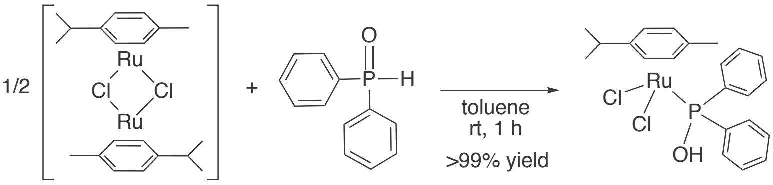
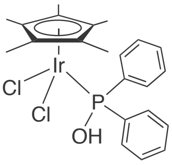
- So many homogeneous catalysts have been developed to date. Except for Parkins' platinum catalyst, activity of these catalysts for production of acrylamide is quite low. (ref. Ghaffar, T.; Parkins, A. W. *Tetrahedron Lett*. **1995**, *36*, 8657.)

New homogeneous catalysts for acrylamide !

- New ruthenium complexes act as a catalyst for hydration of acrylonitrile under neutral conditions.
- The complexes can be prepared easily. For example,



- The reaction proceeds minimun amount of water. The molar ratio of acrylonitrile to water is 1:1.
- The catalytic activity of these catalysts are comparable that reported by Parkins.
- Acrylamide obtained is >99% purity.
- The reaction proceeds at room temperature to 150 °C. The catalysts are thermally stable.
- The catalysts also effective for hydration of aliphatic nitriles, aromatic nitriles , and hetero-aromatic nitriles.
- Catalytic hydration of polyacrylonitrile proceed.
- Other phosphorus compounds have been found as a effective ligand.
- New iridium complexes have been found. For example,



Patent

- Title: Metal complex compound and amide production method that utilizes said metal complex compound
- Patent No.: WO 2012/017966 A1 (PCT/JP2011/067531)
- Applicant: Okayama University
- Inventors: Toshiyuki Oshiki and Makoto Muranaka

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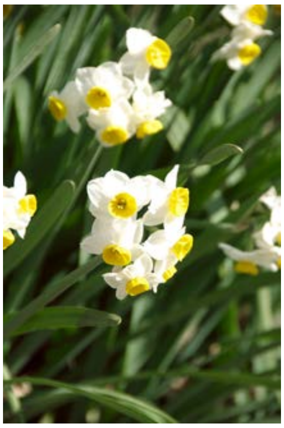
This work was supported by the JSTproject to develop "innovative seeds" and an Industrial Technology Research Grant Program in 2006 from NEDO of Japan.



Hydrogen Generation from Concentrated Formic Acid

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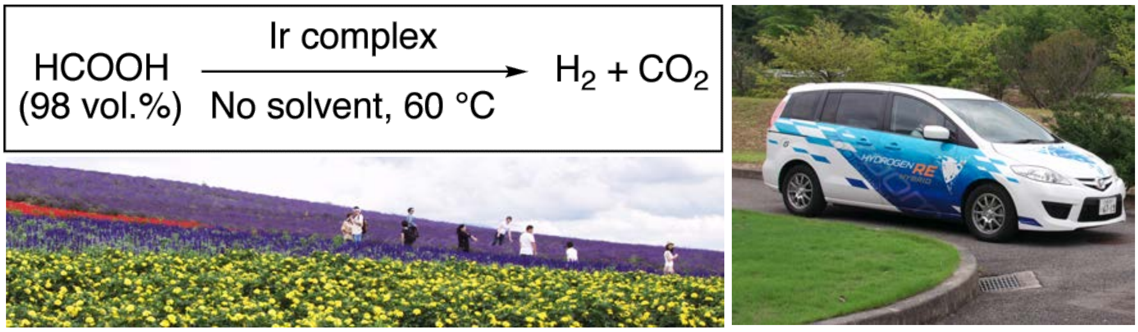


$$\underset{\text{(98 vol.\%)}}{HCOOH} \xrightarrow[\text{No solvent, 60 °C}]{\text{Ir complex}} H_2 + CO_2$$

Catalytic decomposition of formic acid without formation of carbon monoxide

Catalytic decomposition of formic acid

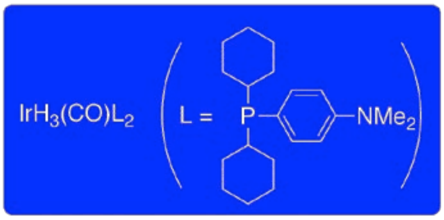
- Formic acid is one of the most important commodity chemicals.
- Formic acid is commercially produced annually more than 720,000 tons. For example, hydrolysis of methyl formate derived from methanol and carbon monoxide.
- Thermal decomposition of formic acid gives water and carbon monoxide. In contrast, catalytic decomposition of that gives hydrogen and carbon dioxide.
- Hydrogen has been attracted attention as a new clean energy. Hydrogen fuel cell is one of the most attractive R&D area.

Why do we develop new homogeneous catalysis for hydrogen production ?

- Many homogeneous catalysts have been developed to date. Most of the reported examples the catalyst decomposes *dilute* formic acid. Moreover, an additive, such as and organic amine and sodium formate, is necessary component in many cases. (ref. Czaun, M.; Goeppert, A.; May, R.; Haiges, R.; Prakash, G. K. S.; Olah, G. A. *ChemSusChem* **2011**, *4*, 1241–1248.)
- It is challenging target that catalytic decomposition of *concentrated formic acid under mild temperature conditions (below 100 °C) without any additives*.

New homogeneous catalysts for hydrogen production !

- New iridium complexes act as a catalyst for generation of hydrogen from concentrated formic acid below 100 °C without any additives. For example,



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- The turnover frequency (h^{-1}) is up to 5000 at 60 °C.
- The reaction proceed without formation of carbon monoxide.
- The catalysts can be reused up to 10 times without loss of those activities.

Patent

- Title: Metal complex compound and hydrogen production method and hydrogenation method that utilizes said metal complex compound
- Patent No.: PCT/JP2011/077061
- Applicant: Okayama University
- Inventors: Makoto Muranaka and Toshiyuki Oshiki

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RESEARCH INTERESTS

1) Development of new homogeneous catalysts for production of industrially important chemicals.
    - Metathesis catalysts for production of polydicylopentadiene. (Joint Project with RIMTEC Corporation)
    - Highly active hydration catalysts for production of acrylamide
    - Hydrogen generation from concentrated formic acid
2) Design and synthesis of transition-metal complexes.
3) Synthesis of new organic luminescent materials.

POSITIONS

Dec. 2008 - present
Associate Professor, Research Center at Okayama Research Park , Okayama University

Jul. 2002 - present
Associate Professor, Graduate School of Natural Science Technology, Okayama University

Nov. 1998 - Jun. 2002
Assistant Professor, Graduate School of Natural Science Technology, Okayama University

Apr. 1996 - Oct. 1998
Research Fellow, Japan Society for the Promotion Science, Osaka University and Chiba University

Apr. 1991 - Mar. 1995
Researcher, Catalysis Research Center, MItsubishi Chemical Co., Ltd.

EDUCATION

Apr. 1998 - Oct. 1998
Post-Doctoral Fellow, Department of Chemistry, Chiba University, Advisor: Prof. Tsuneo Imamoto

Apr. 1995 - Mar. 1998
Ph.D. in Inrganic Chemistry, Department of Chemistry, Osaka University, Advisor: Prof. Kazushi Mashima

Apr. 1988 - Mar. 1991
M.Sc. in Organic Chemistry, Department of Chemistry, Chiba University, Advisor: Prof. Tsuneo Imamoto

Apr. 1985 - Mar. 1988
B.Sc. in Organic Chemistry, Department of Chemistry, Chiba University, Advisor: Prof. Tsuneo Imamoto

AWARD

The Chemical Society of Japan Award for Young Chemists in Technical Development (2006)

Development of New Ruthenium Catalysts for Production of γ-butyrolactone from Dehydrogenation of 1,4-butanediol

SELECTED PAPERS

Catalytic Hydration of Nitriles

(1) 2-Diphenylphosphanyl-4-pyridyl(dimethyl) amine as an effective ligand for the ruthenium(II) complex catalyzed homogeneous hydration of nitriles under neutral conditions, *Catal. Today* **2011**, *164*, 552-555.

(2) The Hydration of Nitriles Catalyzed by the Combination of Palladium Nanoparticles and Copper Compounds, *Chem. Lett.* **2009**, *38*, 360-361.

(3) Dramatic rate acceleration by a diphenyl-2-pyridylphosphine ligand in the hydration of nitriles catalyzed by Ru(acac)$_2$ complexes, *Organometallics* **2005**, *24*, 6287-6290.

Early Transition-Metal Complexes

1. Alkyne exchange reactions of silylalkyne complexes of tantalum: Mechanistic investigation and its application in the preparation of new tantalum complexes having functional alkynes (PhCCR (R = COOMe, CONMe$_2$)), *Organometallics* **2007**, *26*, 173-182.
2. Dialkylchromium complexes bearing a hydrotris(3,5-dimethylpyrazolyl)borate ligand: synthesis and crystal structures of Tp*CrMe$_2$(DMAP) and Tp*Cr(CH$_2$Ph)$_2$(DMAP) (DMAP = 4-dimethylaminopyridine), *J. Organomet. Chem.* **1998,** *569(1-2)*, 15-19.
3. Tp*Sn(Cl)Bu$_2$ as a convenient reagent for the preparation of hydrotris(3,5-dimethylpyrazolyl)borate complexes of niobium, tantalum, and zirconium, *Organometallics* **1997**, *16*, 2760-2762.

Organophosphorus Compounds

1. Unpresedented Srtereochemisty of the Electrophilic Arylation at Chiral Phosphorus, *J. Am. Chem. Soc.* **1992**, *114*, 3371-3374.
2. Synthesis and Reactions of Phosphine-Boranes - Synthesis of New Bidentate Ligands with Homochiral Phosphine Centers via Optically Pure Phosphine-Boranes, *J. Am. Chem. Soc.* **1990**, *112*, 5244-5252.

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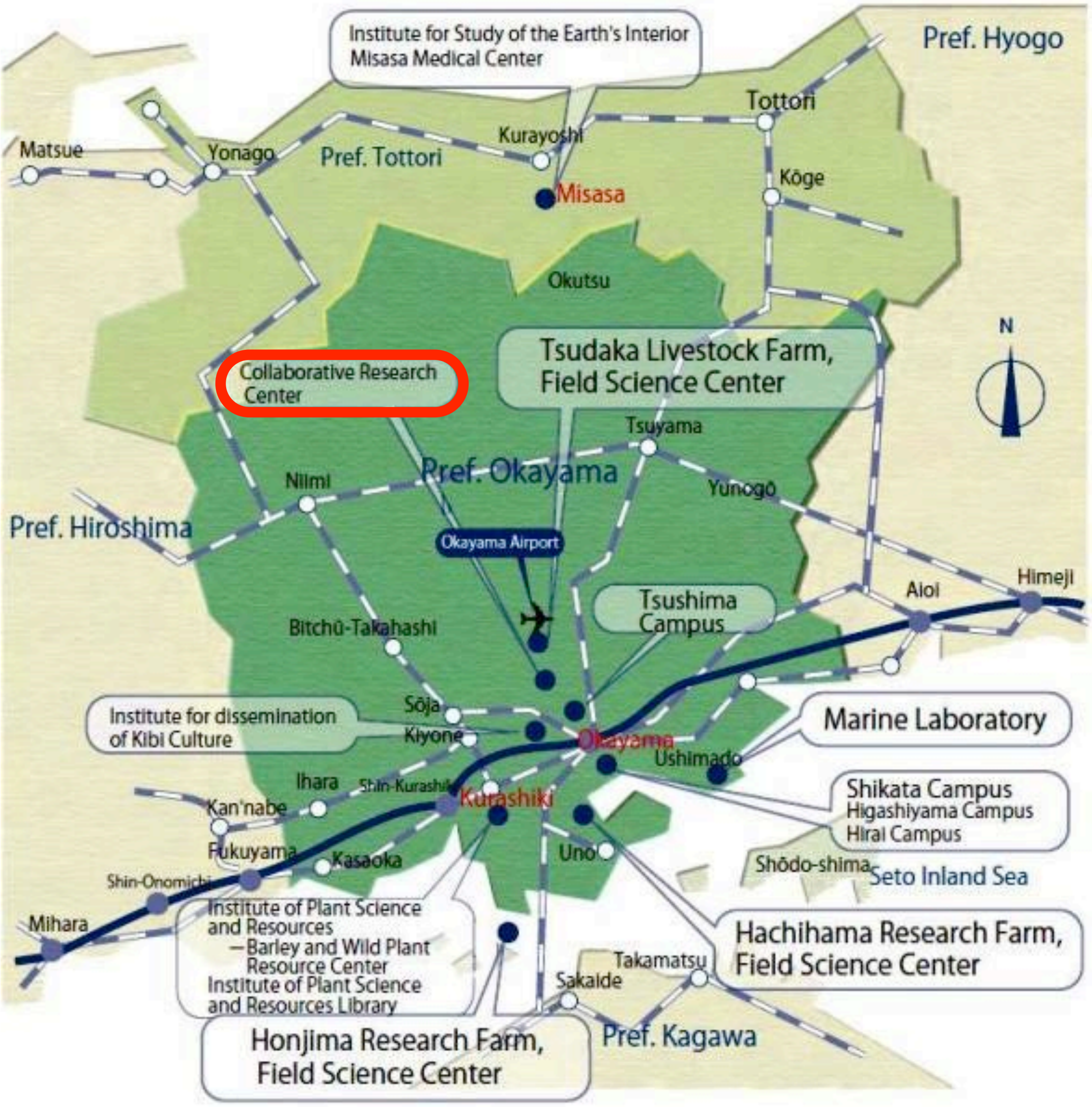

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