

**Development of Innovative Molecular Transformations via Cationic Rhodacycles as Active Species**

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**【Outline of survey】**

It is well known that metallacycles are efficient intermediates of cycloadditions for the synthesis of various cyclic compounds. Recently, we first discovered that cationic rhodium(I) complexes bearing BINAP-type bisphosphine ligands are highly effective catalysts for [2 + 2 + 2] cycloadditions via metallacycles. In this research, we investigate a variety of methods for the generation of highly reactive cationic rhodacycles and their reactivity toward novel catalytic molecular transformations. We also examine the mechanism of these catalyses and develop asymmetric variants of these catalyses. Finally, we apply these catalyses to the synthesis of novel chiral ligands, extended  $\pi$ -conjugated compounds, functional polymers, and biologically active compounds.

**【Expected results】**

The catalyses developed by this research enable the catalytic asymmetric synthesis of chiral functionalized aromatic compounds with ease. The present catalyses serve as a powerful tool for the synthesis of novel chiral ligands and extended  $\pi$ -conjugated compounds, which may contribute to the growth of the Japanese chemical industry. Furthermore, elucidation of the reaction mechanism provides a new principle for the catalyst design.

**【References by the principal investigator】**

- Asymmetric Assembly of Aromatic Rings To Produce Tetra-*Ortho*-Substituted Axially Chiral Biaryl Phosphorus Compounds. Nishida, G.; Noguchi, K.; Hirano, M.; Tanaka, K.\* *Angew. Chem. Int. Ed.* **2007**, *46*, 3951–3954.
- Rh-Catalyzed Synthesis of Helically Chiral and Ladder-Type Molecules via [2 + 2 + 2] and Formal [2 + 1 + 2 + 1] Cycloadditions Involving C–C Triple Bond Cleavage. Tanaka, K.\*; Kamisawa, A.; Suda, T.; Noguchi, K.; Hirano, M. *J. Am. Chem. Soc.* **2007**, *129*, 12078–12079.

**【Term of project】** FY2008– 2012

**【Budget allocation】**

**65,400,000 yen** (direct cost)

**【Homepage address】**

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