

VII-I Precise Synthesis of Functional Macromolecules Using Organometallic Complexes

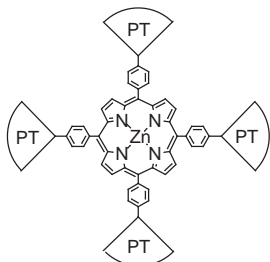
Macromolecules, in which not only molecular weight and chemical sequence but also secondary structures are well controlled, attract much attention due to their novel properties and functionalities. Precise synthesis of such macromolecules is one of the goals for the development of new functional materials. This project focuses on precise synthesis of helical or dendritic macromolecules using organometallic complexes, which act as living polymerization catalysts or building blocks. We also examined the physical and chemical properties of the resulting polymers.

VII-I-1 Platinum-Acetylide Dendrimers Possessing a Porphyrin Core

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[Chem. Commun. 2576 (2002)]

Intramolecular energy transfer from platinum-acetylide moieties to the porphyrin core was observed in novel organometallic dendrimers that were prepared from a tetra(4-ethynylphenyl)porphyrin-bridged tetranuclear platinum-acetylide core and platinum-acetylide dendrons by a convergent method.

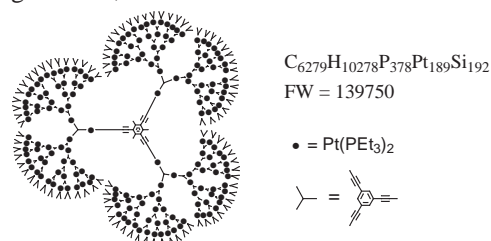


VII-I-2 A Divergent Approach to the Precise Synthesis of Giant Organometallic Dendrimers Using Platinum-Acetylides as Building Blocks

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[Chem. Commun. 280 (2003)]

Giant platinum-acetylides dendrimers were precisely synthesized by a divergent method; the sixth generation dendrimer, the diameter of which is larger than 10 nm, has 189 Pt atoms per molecule, and its molecular weight is as high as 139,750.



VII-I-3 Preparation and Photochemical Properties of Polyisocyanides with Regularly Arranged Porphyrin Pendants

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[Chem. Lett. 506 (2003)]

A novel triblock polyisocyanide having free-base- and zincporphyrins as pendants was prepared by living polymerization with a Pt-Pd μ -ethynediyl complex as an initiator, and irradiated at 420 or 556 nm in a THF solution to cause intramolecular energy transfer from the zinc-porphyrin to the free-base-porphyrin.

VII-J Development of New Catalytic Reactions for Synthesis of N-Heterocyclic Compounds

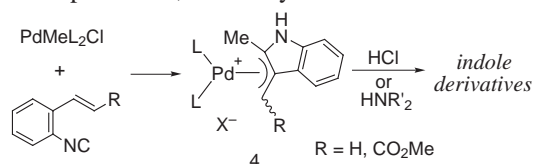
Heterocyclic compounds are found in a wide variety of biologically active natural products, and considerable attention has been directed toward the development of new synthetic methods for useful heterocycles. Our research effort has been directed toward the discovery of new catalytic reactions for the synthesis of N-heterocyclic frameworks using *ortho*-functionalized aryl isocyanides.

VII-J-1 Structure and Reactivity of (η^3 -Indolylmethyl)palladium Complexes Generated by the Reaction of Organopalladium Complexes with *o*-Alkenylphenyl Isocyanide

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[*Organometallics* **21**, 581 (2002)]

The reaction of methylpalladium complexes with *o*-alkenylphenyl isocyanides results in the successive intramolecular insertion of the alkenyl and isocyano groups followed by the 1,3-migration of hydrogen to give (η^3 -indolylmethyl)palladium complexes (**4**) in good yields. Treatment of **4** with diethylamine causes nucleophilic attack at the exo methylene carbon to give 2-methyl-3-aminomethylindole, whereas the reactions with HCl produce 2,3-dimethylindole derivatives.



VII-J-2 A Novel Route to 2,3-Disubstituted Indoles via Palladium-Catalyzed Three-Component Coupling of Aryl Iodide, *o*-Alkenylphenyl Isocyanide and Amine

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[*Tetrahedron Lett.* **43**, 6197 (2002)]

Three-component coupling reactions of aryl iodide, *o*-alkenylphenyl isocyanide and amine in the presence of palladium catalysts produced 2,3-substituted indoles in moderate yields.

