This laboratory aims at establishment of new synthetic methodologies and new functional materials by designing well-defined catalysts based on transition metal chemistry. New concepts and ideas of molecular-based catalysts are accumulated by mechanistic investigations using kinetic techniques on the reaction intermediates and elementary processes. The research subjects include: (1) development of novel ligand systems for catalysis, (2) functionalization of organic substrates on transition-metal clusters, and (3) development of highly efficient ways of constructing functional organic molecules.
**Stereocontrolled Synthesis and Optical Properties of All-cis Poly(phenylene vinylenes) (PPVs): A Method for Direct Patterning of PPVs**

Poly(phenylene vinylenes) (PPVs) belong to the group of π-conjugated polymers that have applications in light-emitting diodes (LEDs), lasers, and solar cells. Although stereoregularity of vinylene linkages in the polymer backbone is also known to profoundly affect the optical properties of PPVs, efficient ways of regulating the geometries of vinylene linkages have remained almost unexplored. Geometrically pure, all-cis poly(phenylene vinylenes) (PPVs) are synthesized by Suzuki-Miyaura-type polycondensation of 2,5-dioctyloxy-1,4-benzenediboronic acid with (Z,Z)-bis(2-bromoethenyl)benzenes, which are prepared by ruthenium-catalyzed (Z)-selective double hydrosilylation of diethynylbenzenes, followed by bromodesilylation of the resulting (Z,Z)-bis(2-silylethenyl)benzenes with N-bromosuccinimide. The all-cis PPVs thus obtained undergo one-way photoisomerization to the corresponding trans-PPVs both in solution and in the solid. This phenomenon is applied to direct microscale patterning of PPVs onto a quartz substrate.

**C-Si Reductive Elimination from cis-Vinyl(silyl)platinum(II) Complexes**

While the transition-metal-catalyzed silylation reactions of unsaturated hydrocarbons such as hydrosilylation, bis-silylation, and borylsilylation are generally assumed to involve C-Si reductive elimination as the product-forming step, detailed information on this elementary process has been limited. The complexes cis-Pt(\(\text{CH} = \text{CH}_2\))(SiR_3)(PMe_2Ph)_2 (R_3=Ph_3, (C_6H_4Me-p)_3, (C_6H_4OMe-p)_3, MePh_2, FPh_2) have been prepared by the reactions of trans-PtCl(SiR_3)(PMe_2Ph)_2 with Mg(CH=CH_2) in THF, followed by trans-cis isomerization of the resulting trans-alkenyl(silyl) complexes in solution promoted by CO. The Complexes undergo C-Si reductive elimination in toluene-\(d_8\) to give platinum(0) complexes coordinated with vinylsilanes. Kinetic data have suggested a direct reaction path without dissociation of the phosphine ligand.

**Synthesis and Property of BrCCH- and BrCCBr-Coordinated Tetrairon Clusters**

Haloalkynes have been recognized as useful C_2 synthetic intermediates in organic chemistry. However, the coordination chemistry of haloalkynes has yet to be explored in detail. We succeeded in the stepwise bromination of two acetylene ligands in \(\eta^5\)-C_5H_4MeFe(\(\eta^1\)HCCH)_2] using N-bromosuccinimide (NBS). The bromoacetylene part displays high reactivities toward a variety of nucleophiles such as water, ZnR_2 (R=Me, Et), HC≡CMgBr, LiS\(_2\)Tol, pyridine, and 4,4'-bipyridyl.

**Grants**

