

Research Highlights

Asymmetric catalysis

- New protocols for hydrovinylation (>95% yields, ~100% branched-selectivity in additions of ethylene) of vinylarenes and strained olefins that are amenable to asymmetric catalysis (publications 36, 39, 41, 46, 60, 61, 70, 72) and for a related intramolecular cyclization of α,ω -dienes (publication 37, reviews 7, 19).
- Asymmetric hydrovinylation of vinylarenes. Achieved high enantioselectivity (~ >95% yield, ~ >9% ee, S/C up to 1200) for a variety of substrates useful for the synthesis of widely used 2-arylpropionic acids (publication numbers 36, 54, 61, 62, 65). First use of 'hemilabile ligand' concept in asymmetric catalysis (publication 41, 62).
- Asymmetric hydrovinylation of 1,3-dienes yields, ee's >95% (publication 69)
- Generation of all-carbon quaternary centers using asymmetric hydrovinylation in ee's up to 99% (publication # 70)
- Asymmetric hydrocyanation. Using electronic effect as a key control element, highest reported enantioselectivity (up to 95% ee) for the Ni-catalyzed asymmetric hydrocyanation was achieved (publications 26, 31, 33, reviews 3, 4, 8).
- First practical asymmetric hydrocyanation of 1,3-dienes (publication 71)
- Rh(I)-catalyzed asymmetric hydrogenation. Electronic and Steric Effects
 - (a) Using electronic effects in *D*-glucose-derived diarylphosphinite ligands, a practical synthesis (ee ~97-99%, S/C 10,000) of *both D and L* amino acids was achieved via Rh(I)-catalyzed hydrogenation (publications 29, 35, 38).
 - (b) Recognition of the quasi-enantiomeric relationship between the 2,3- and 3,4-positions of pyranoside-based ligands (publications 29, 35).
 - (c) A highly selective (ee >97%) hydrogenation route to functionalized tetrahydroquinolines (publication 51)
 - (d) Electronic and steric tuning of a DIOP-like ligand matched the best ee's (99%) reported for simple enamide reductions (publication 48).
- Electronic effects of ligands alone causes reversal of enantioselectivity in Pd(0)-catalyzed allylation reactions of malonate salts (publications 32, 40)
- Electron-deficient phosphinites enhances the enantioselectivity in Rh(I)-catalyzed asymmetric hydroformylation of vinyl arenes (publication 30)
- Kinetic resolution of secondary alcohols. A new Y-catalyzed acyl transfer reaction (publication 44) and a conceptually new metal-catalyzed kinetic resolution of secondary alcohols using chiral Y-complexes (publication 55)
- Design and synthesis of new ligands and complexes for asymmetric catalysis
 - (a) Highly functionalized phospholanes from *D*-mannitol (publication 45)
 - (b) Use of phospholanes for asymmetric Pd-catalyzed allylation (publication 47)
 - (c) Water-soluble Rh-phosphinite complexes for aqueous-phase hydrogenation (publications 42, 50)
 - (d) Rh-hydroxyphospholane complex catalysts that can be recycled multiple times in aqueous hydrogenation reactions (publication 53)
 - (e) Air- and water-stable *bis*-carbene complexes of Pd, Ni and Rh from binaphthol (publication 43)

Free radical chemistry

- Discovered two novel control elements in the well-known hex-5-enyl radical cyclization
 - (a) C₄-allylic oxygen effect to produce the uncommon 1,5-*trans* substitution in cyclopentane formation ([publications 16, 17, 22, 25, review 13](#)).
 - (b) Axial vs equatorial 2-but-3-enyl tether give opposite annulation stereoselectivity in the formation of a bicyclo[4.3.0]system ([publications 21, 25](#)).
 - (c) Applications of (a) for the synthesis of prostaglandin-like molecules (e. g., Corey lactone) from 3-deoxy glucose ([publication 17](#)).
 - (d) These studies also provided a number of new protocols for carbohydrate-to-carbocyclic conversions ([review 5](#)).
- Utility of a paramagnetic reagent, Cp₂Ti-Cl, for the generation of organic radicals from epoxides for the following reactions: hex-5-enyl radical cyclization [*with W. A. Nugent*], inter molecular C-C bond formations, H-atom reduction, deoxygenation, and addition-elimination reactions of vinylstannanes ([publications 20, 23, 24, 28, 67](#))
- A new chemistry of Barton intermediates for the synthesis of *N*-glycosides via C₁-C₂ bond-formation ([publications 56, 58](#))

Chemistry of low-valent Zr and Ti

- Use of low-valent Ti and Zr reagents (Cp₂M) for enyne cyclization ([publication 19](#)) [*With W. A. Nugent*] Control of exo-cyclic olefin stereochemistry and synthesis of invictolide Highly functionalized cyclopentanes from carbohydrate enynes ([review 5](#))
- Use of Tebbe reagent for C-glycoside synthesis via 1-methylenesugars ([publication 15](#))

Organosilicon/Organotin Chemistry

- Use of organosilicon reagents for unusual carbon-carbon bond forming reactions
 - (a) Thermal and fluoride-catalyzed Michael reactions of silyl ketene acetals ([publication 9](#))
 - (b) A new nucleophilic aromatic substitution in nitro-compounds ([publications 10, 11](#))
 - (c) A new synthesis of indoles and oxindoles ([publication 14](#))
- Synthesis and use of R₃SiSnR'₃ as bis-functionalization reagents ([publication 13, 67](#))
 - (a) R₃Si-SnR'₃-mediated cyclization of 1,6-diynes and establishment of axial chirality in the products ([publications 49, 59](#)).
 - (b) R₃Si-SnR'₃-mediated cyclization of allenynes: Synthesis of highly functionalized carbocyclic and heterocyclic compounds ([publications 52, 64, 66](#)).
- [*with O. Webster, W. Hertler, W. B. Farnham and D. Sogah*] Group Transfer Polymerization (GTP) of acrylate monomers ([publications 7, 8, 18](#)).
 - (a) Demonstrated the first nucleophilic catalysis (using [Me₂N]₃S⁺ Me₃SiF₂⁻) of GTP while investigating fluoride-catalyzed 1,4-additions of ketene silyl acetals to α,β-unsaturated esters ([publication 9](#)). For history see: *J. Polym. Sci. Part A*, **2000**, 38, 2855.
 - (b) [*with W. B. Farnham*] Provided the first evidence for the associative Si-group transfer mechanism in group transfer polymerization.

Miscellaneous

- Reported the first example of an oxyanion-assisted retro-Diels-Alder reaction ([publication 6](#))

- Demonstrated the use of allylic trifluoroacetates in unreactive substrates for Pd(0)-catalyzed allylation. A new C-glycoside synthesis ([publication 12](#))
- Y-salen complexes open mesoepoxides with TMS-X (substrate /catalyst ratio ~10,000). Kinetic evidence provided for bimetallic activation. ([publication 73](#))