

## Efficient Organic Synthesis via Nickellacycle as an Active Key Intermediate

Masanari Kimura

(Graduate School of Science and Technology, Nagasaki University)

The combination of Ni(acac)<sub>2</sub> catalyst and triethylborane promotes homoallylations of aromatic aldehydes and  $\alpha,\beta$ -unsaturated aldehydes with isoprene to form 3-methyl-4-pentenols with excellent 1,3-*anti* stereoselectivity. Sterically congested aliphatic aldehydes and ketones undergo the similar homoallylations with 1,3-dienes by using diethylzinc as a reducing agent. 1,3-Cyclohexadiene is one exception among dienes examined and undergoes allylation instead of homoallylation. Aldimines prepared from aldehydes and primary amines undergo homoallylation with 2-substituted-1,3-dienes in the presence of diethylzinc and Ni catalyst to afford bis-homoallyl amines with excellent 1,3-*syn* stereoselectivity.

When dimethylzinc is employed in place of diethylzinc under similar conditions, dimethylzinc serves as a methylating agent to bring about the three-component coupling reactions. The methyl group of dimethylzinc and an aldehyde add to a conjugated diene in 1,4-fashion and provide a homoallyl alcohol in good yields. In the presence of catalytic amount of Ni(acac)<sub>2</sub>, the four components of dimethylzinc, internal alkynes, 1,3-butadiene, and carbonyls combine in this order in a 1:1:1:1 ratio under ambient temperature to furnish (3*E*,6*Z*)-octadienyl alcohols with excellent regio- and stereoselectivities. These reactions proceed via nickellacycle intermediates which are generated via oxidative cyclization of Ni(0) species with conjugated diene and carbonyl compounds.