

BOSTON UNIVERSITY DEPARTMENT OF CHEMISTRY Colloquium Series



The 2004 Novartis Lecture

Enones as Latent Enolates in Catalysis: Discovery of Catalytic Carbon-Carbon Bond-Forming Hydrogenations



Elemental hydrogen is the cleanest and most cost-effective chemical reductant available to humankind. However, use of hydrogen as a terminal reductant in catalytic reductive carbon-carbon bond formation is presently restricted to processes involving migratory insertion of carbon monoxide,

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e.g., a I kene hydroformylation and related Fischer-Tropsch type reactions. Recently, Professor Krische's laboratory developed the first catalytic system to enable trapping of the organometallic intermediates that appear transiently in the course of catalytic hydrogenation. Through implementation of cationic Rh-based catalyst systems, the hydrogen-mediated reductive coupling of enones, dienes, and diynes to carbonyl partners has been realized. A key mechanistic feature of these transformations relates to the heterolytic activation of elemental hydrogen (H₂ + M-X \rightarrow M-H + HX), which enables mono-hydride based catalytic cycles for which direct alkyl-hydrogen reductive elimination manifolds are disabled. These results support the feasibility of developing a broad new family of catalytic "carbon-carbon bond-forming hydrogenations." In his talk, Professor Krische will describe ongoing studies aimed at extending this fundamentally new pattern of reactivity to the reductive coupling of basic chemical feedstocks.