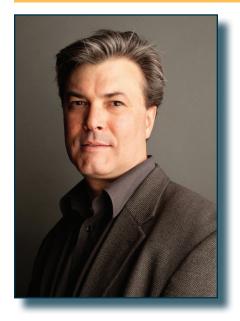


Department of Chemistry



9:45 a.m. Thursday, March 13, 2014 · 331 Smith Hall



Abstract

We are engaged in the first systematic efforts to develop "C-C bond forming hydrogenations" beyond hydroformylation - processes in which two or more reactants are hydrogenated to form a single, more complex product. Using cationic rhodium and iridium catalysts, diverse π-unsaturated reactants reductively couple to carbonyl compounds and imines under hydrogenation conditions, offering a byproduct-free alternative to stoichiometric organometallics in a range of classical C=X (X = O, NR) addition processes. This concept is extended further via "C-C bond forming transfer hydrogenation." In such processes, the exchange of hydrogen between alcohols and π -unsaturated reactants triggers the generation of aldehyde-organometal pairs that combine to give products of carbonyl addition. Direct alcohol CH-functionalization in this manner is bypasses discrete alcohol-to-aldehyde redox manipulations and is byproductfree. This new pattern of reactivity enables direct C-C coupling of methanol and other renewable alcohols (ethanol and glycerol) to abundant π -unsaturated reactants (α-olefins, styrene, butadiene and isoprene) to furnish higher alcohols, and has been used to construct diverse polyketide natural products (bryostatin, roxaticin, 6-deoxy erythronolide).

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Professor Michael Krische

Department of Chemistry University of Texas at Austin

Formation of C-C Bonds via Catalytic Hydrogenation and Transfer Hydrogenation

Research interests: first systematic efforts to develop C-C bond forming hydrogenations beyond hydroformylation processes wherein two or more reactants are hydrogenated to form a single, more complex product.

Me Me Ru₃(CO)₁₂ (2 mol%) ŌН ŌН BIPHEP (6 mol%) 80% Yield 93% Yield OH OH PhMe (2 M), 130 °C Me **REDOX-Independent** Me Me Hydroxycarbonyls and ŌН ŌН **Diones also Participate** 90% Yield 70% Yield (S)- or (R)-Ir-SEGPHOS Me Me Me Me Me Me (5 mol%) ОН OН OН ArCO₂H (10 mol %) ŌН ŌН ÓН C Allyl Acetate (200 mol%) Cs₂CO₃ (100 mol %) Me Me Me THF-H₂O, 100 °C ŌΗ ŌΗ ŌН 24 h 70% yield, ≥ 20:1 dr 74% yield, ≥ 20:1 dr From (S)-Ir-Catalyst From (R)-Ir-Catalyst Dehydrogenation No Protecting Groups, No Discrete Alcohol Oxidation, Not Observed No Premetalated Reagents, No Chiral Auxiliaries

Website: http://www.cm.utexas.edu/michael_krische REVIEWS: (a) Bower, J. F.; Krische, M. J. Top. Organomet. Chem. 2011, 43, 107. (b) Hassan, A.; Krische, M. J. Org. Proc. Res. Devel. 2011, 15, 1236. (c) Moran, J.; Krische, M. J. Pure Appl. Chem. 2012, 84, 1729.
Geary, L. M.; Glasspoole, B. W.; Kim, M. M. Krische, M. J. J. Am. Chem. Soc. 2013, 134, 3796.
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Host: Professor Andrew Harned Refreshments will be served prior to the seminar.