Homogeneous Catalysis Research

R. Morris Bullock

James Franz	-	Free Radical Reactions; Bond Strengths
Daniel DuBois	-	Organometallic Synthesis, Electrochemistry, Thermodynamics
Morris Bullock	-	Metal Hydride Reactivity; Catalytic Hydrogenations
John Linehan	-	High Pressure Studies, *Operando* Catalysis
Wendy Shaw	-	Solid State NMR, Stimulus-Responsive Catalysts
Thomas Autrey	-	Hydrogen Storage in Amine-Borane Complexes

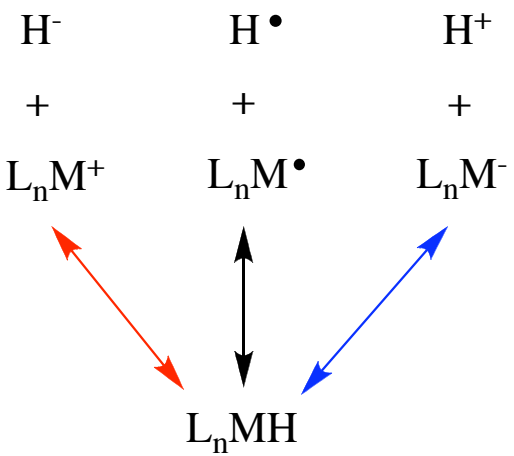
Capabilities – Homogeneous Catalysis and Organometallic Chemistry at PNNL

- Synthesis and Characterization of Organometallic and Organic Molecules
- Design and Synthesis of Ligands (*e.g.*, Specialized Phosphines)
- Evaluation of Fundamental Thermodynamic Properties

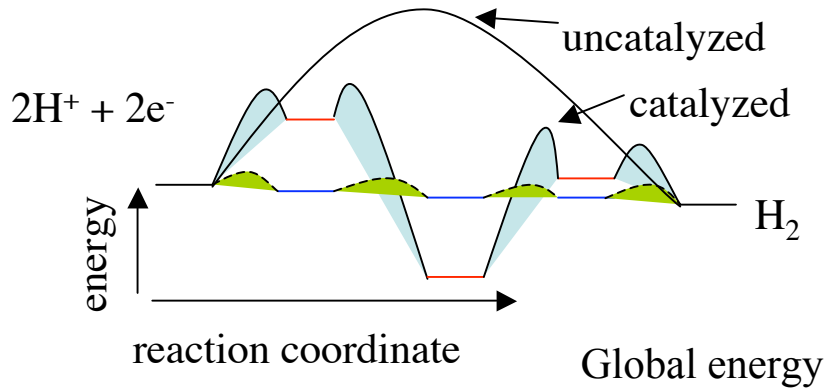
  (Bond Dissociation Energies, pK_a, etc.)
- High Pressure NMR, IR and XAFS spectroscopy
- Multinuclear Solid State NMR (^{1}H, ^{11}B, ^{13}C, + many others)
- Triple Resonance Solution NMR
- Laser Flash Photolysis and Kinetics; Mechanistic Studies
- Laser Photoacoustic Experiments (Calorimetry)

- **Analysis and Design of Homogeneous Catalysts**

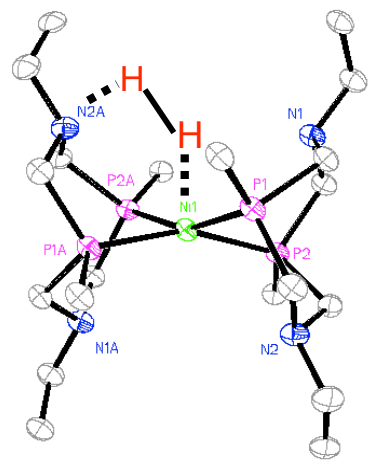
An Energy-Based Approach to Catalysis



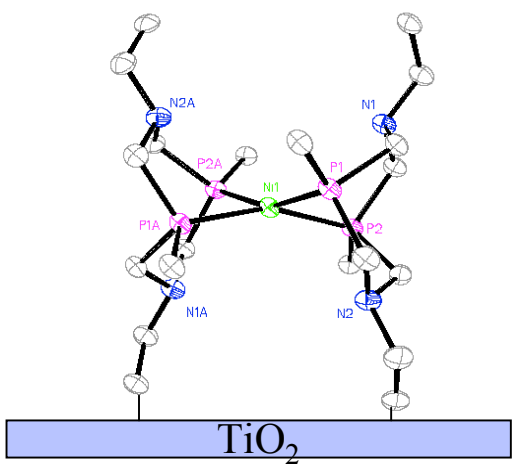
Determination of solution bond dissociation free energies and factors controlling them



Global energy maps

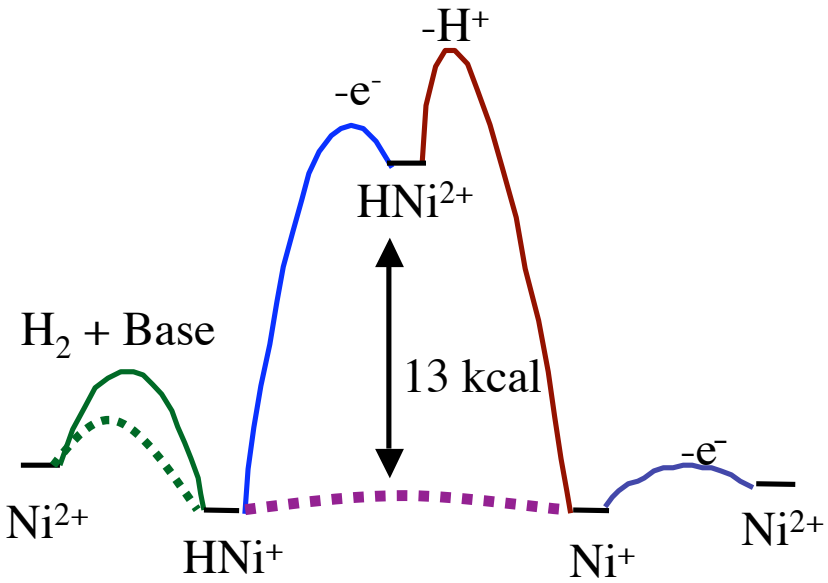


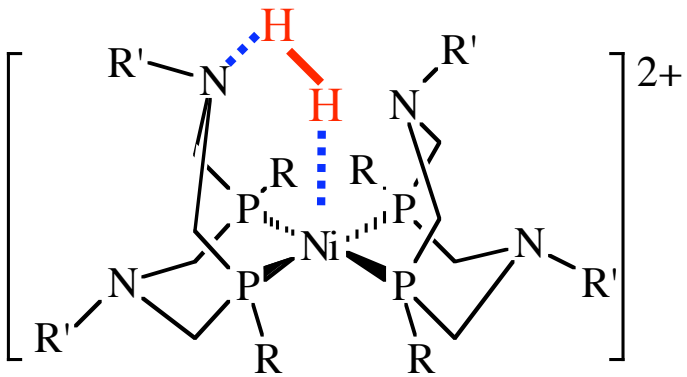
Optimized molecular catalyst



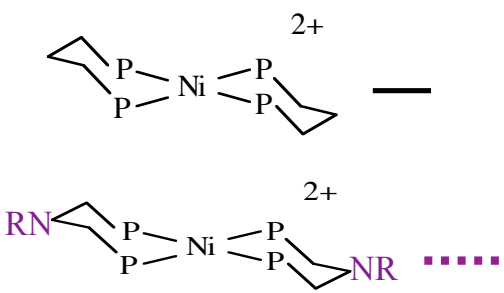
Interfacial catalyst

Use of Energy Maps and Proton Relays to Develop Catalysts for H_2 Production / H_2 Oxidation





R = R' = Ph



Overpot. > 0.7 V
Turnover freq. < 0.5 s^{-1}

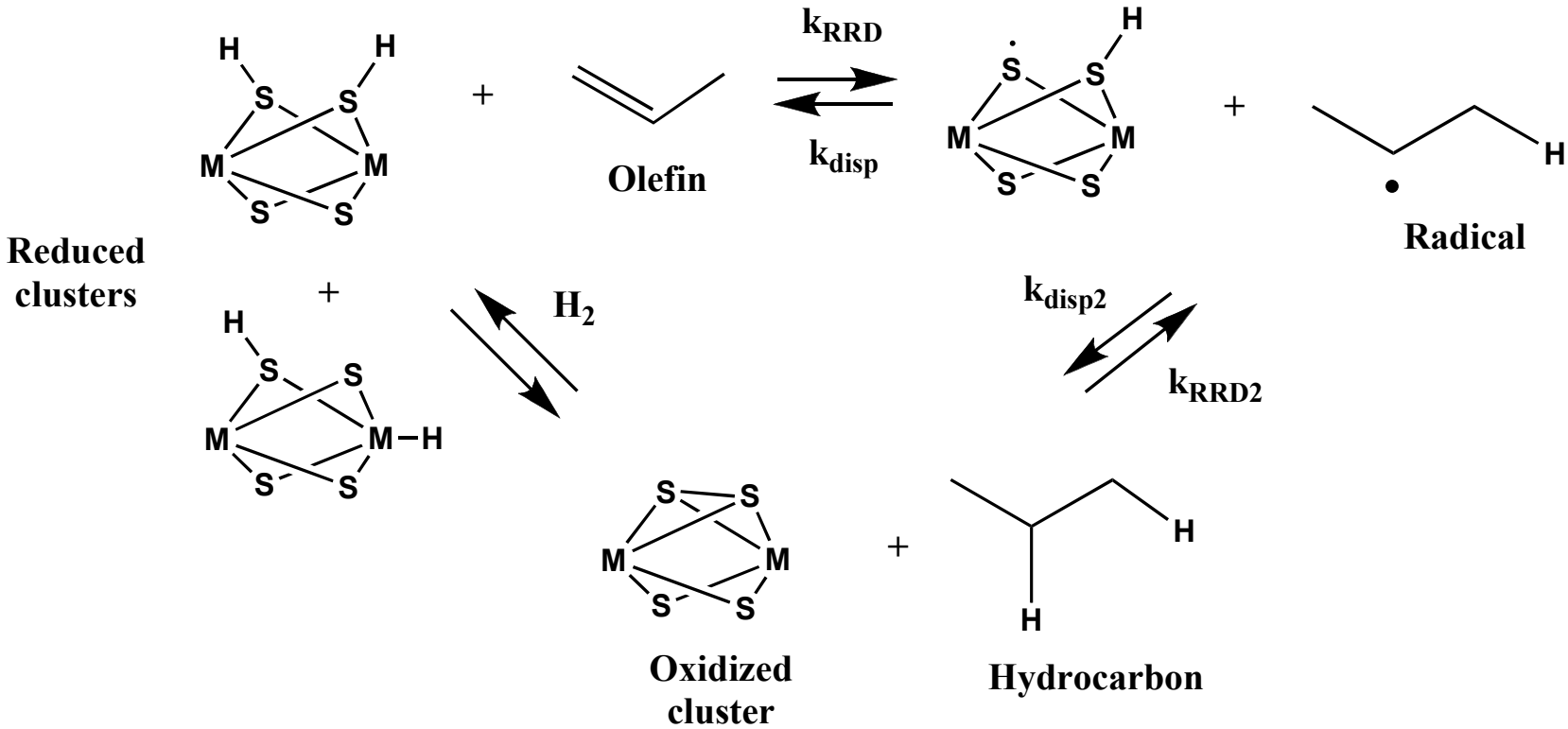
Overpot. < 0.1 V
Turnover freq. < 0.5 s^{-1}

Overpot. ≅ 0.35 V
Turnover frequency = 350 s^{-1}

Turnover frequency for Ni-Fe hydrogenase is 700 s^{-1}

Air stable
No CO inhibition

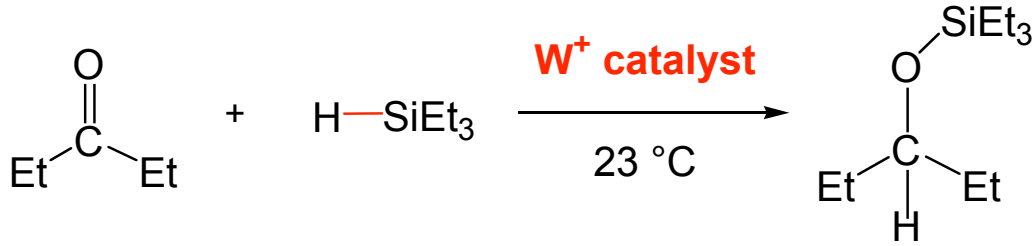
Understanding the Role of μ-SH Bonds in Hydrogenation and S-H Bond Cleavage at the Molecular Level



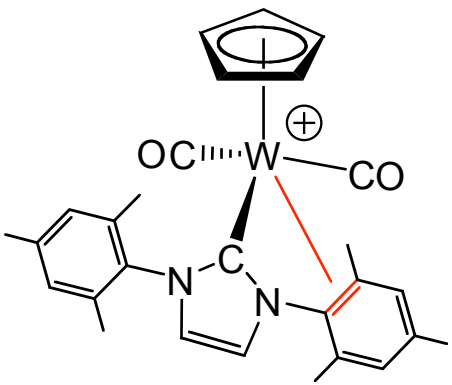
Kinetic, thermochemical and computational studies of S-H bonds

- Transfer hydrogenation pathways at sulfide sites
- *Sulfur-based* reactivity mediated by the metal

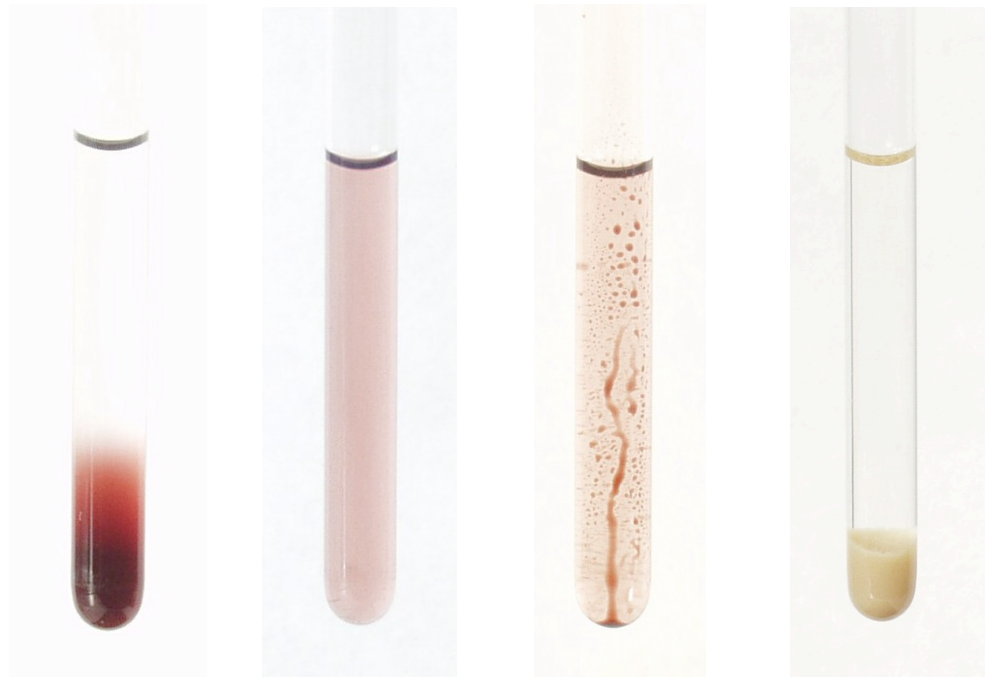
Catalytic Hydrosilylation of a Ketone
A Self-Separating Recyclable Catalyst in a Solvent-Free Reaction



- Solvent-free
- Self-separating catalyst
- "¢*heap Metal*$ *for NobleTasks*"



Structure of the tungsten catalyst



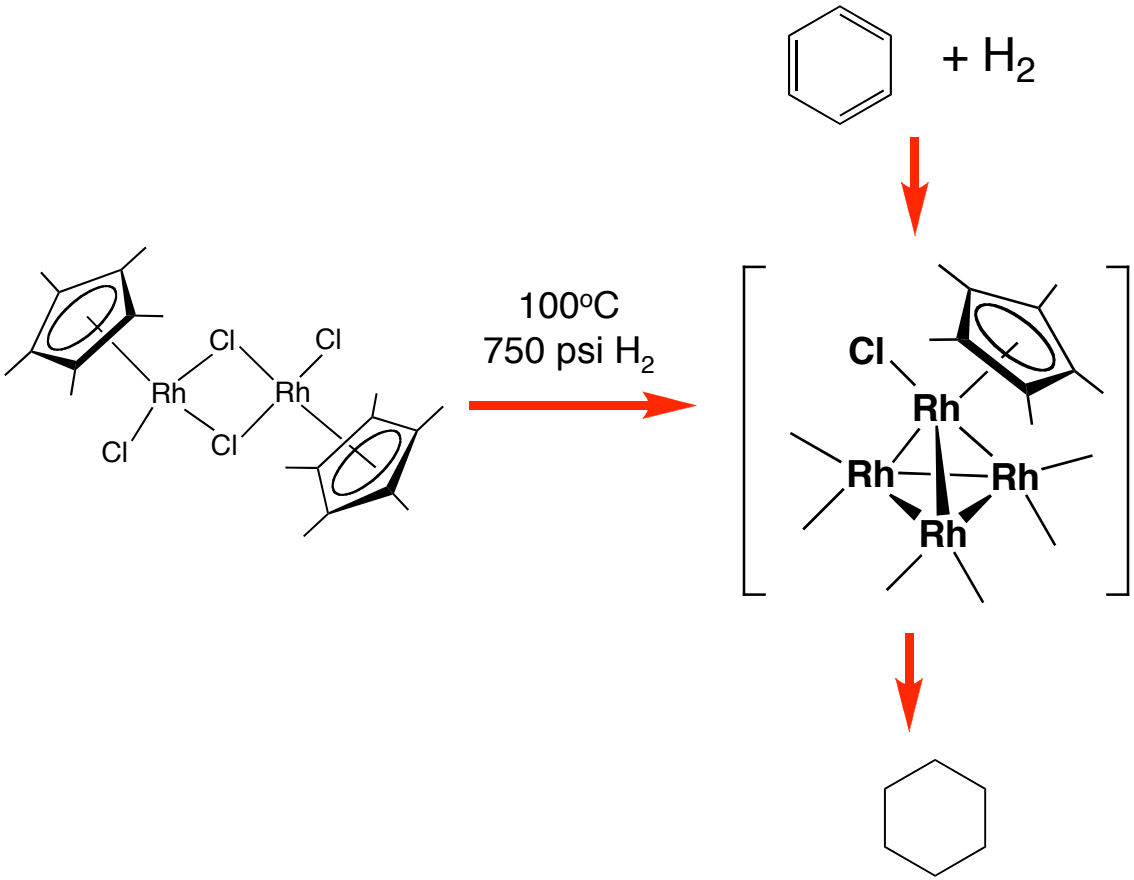
$HSiEt_3$ added to W catalyst. | **Homogeneous catalysis in process.** | **Reaction nearing completion.** | **Self-separating at completion of reaction.**

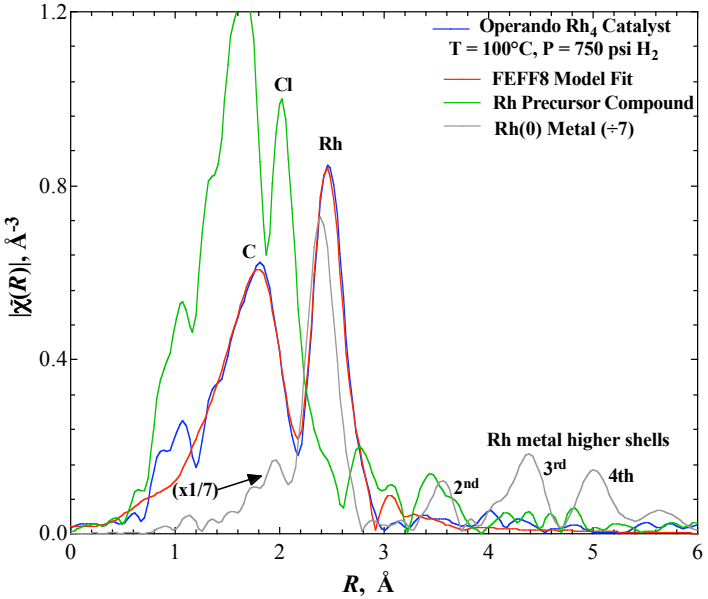
Nature **2003**, 424, 530

Catalytic Hydrogenation of Benzene: Homogeneous or Heterogeneous? . . . A 20+ Year-Old Controversy

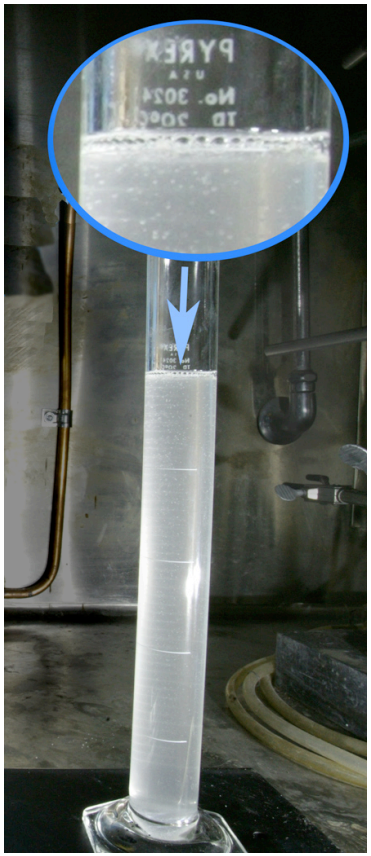
Finke's results (*J. Am.Chem. Soc.* 2005, *127*, 4423) were interpreted as heterogeneous Rh(0) metal (nano-particles) as the catalytic species.

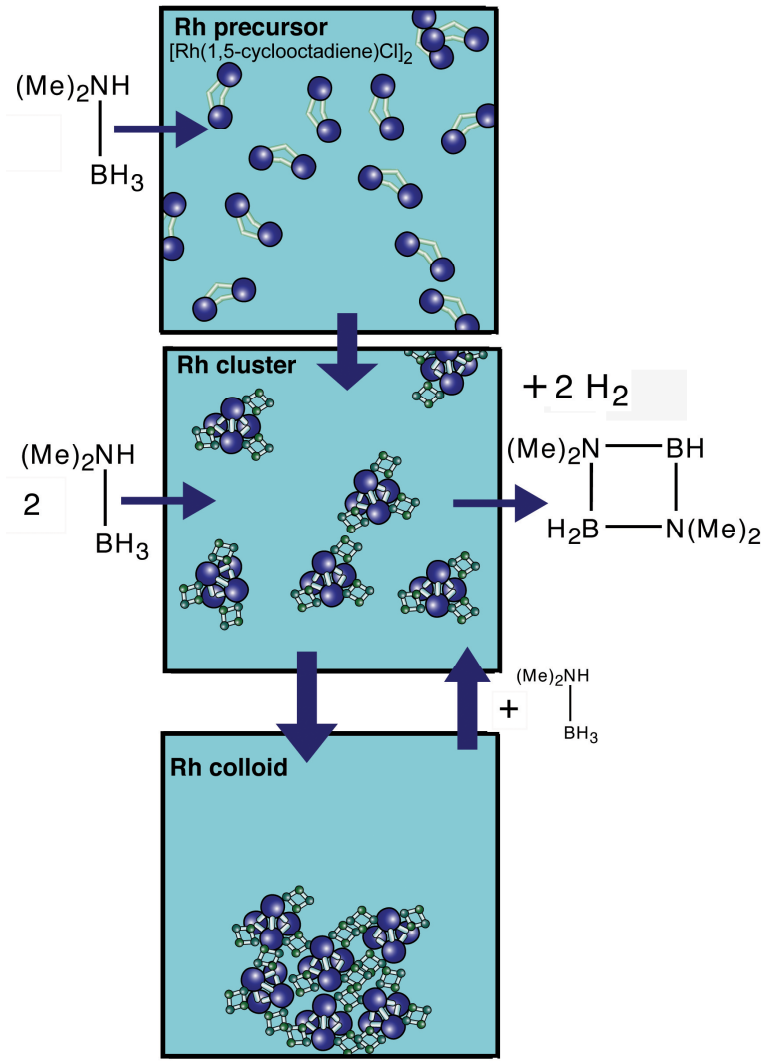
Operando **(100°C, 750 psi H_2) XAFS shows a** ***homogeneous*** **Rh_4 cluster as the predominant (>98%) species during the reaction.**

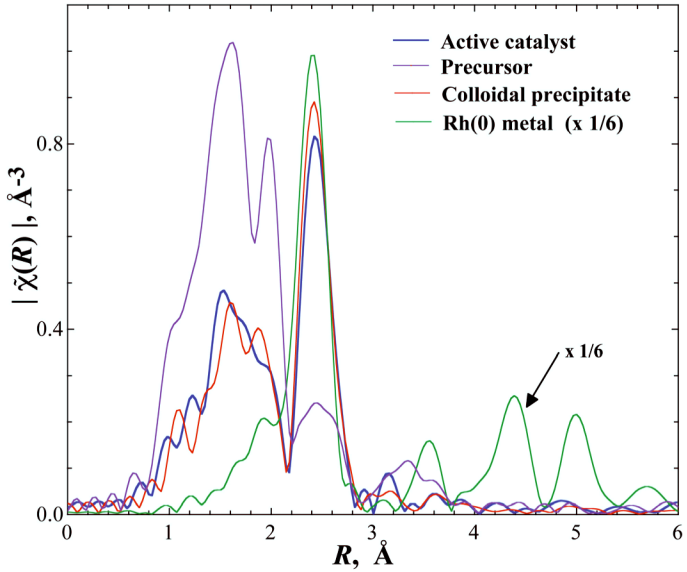


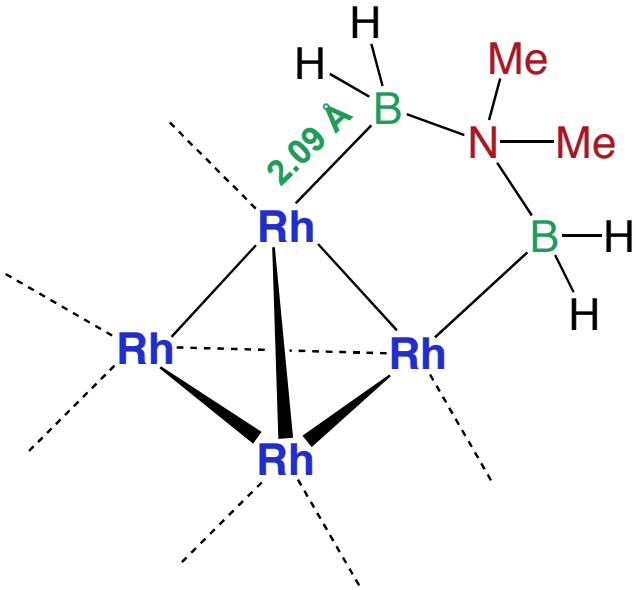


Hydrogen Storage: *Operando* Methods in Catalysis









J. Am. Chem. Soc., **2005**, 127, 3254