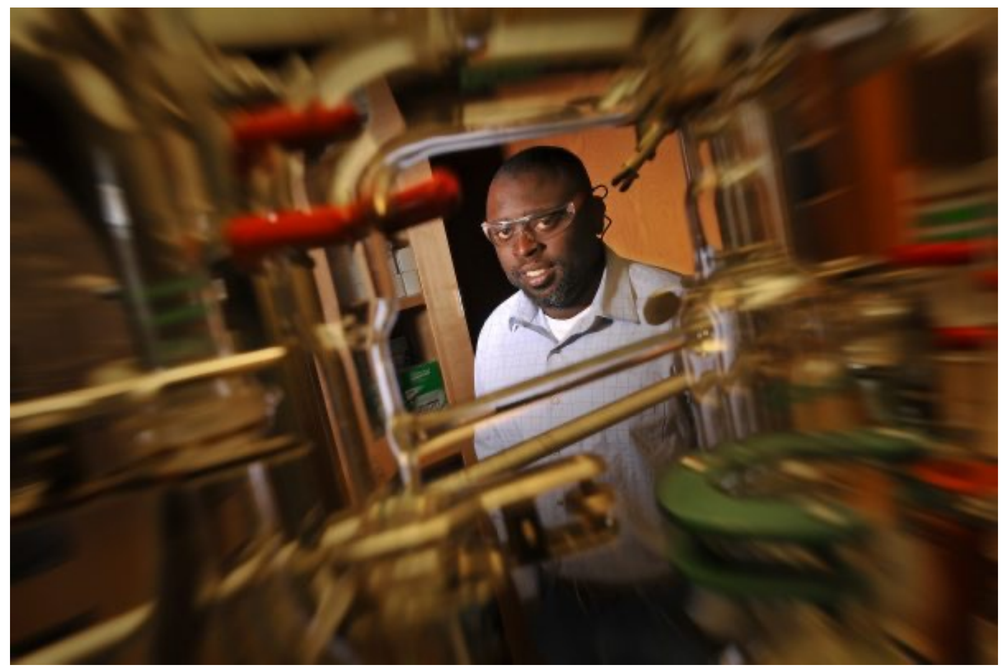
Elon A. Ison



Connor, Akira, Isaac J., John B.,
Shirley, Chris, Jose

Ison Lab Website:
https://isonlab.wordpress.ncsu.edu/

@TNTchemprof

Background and Personal

General

- Citizen of Trinidad and Tobago and the US
- BS *Magna cum Laude* (Chemistry) at Kean University (1999)
- PhD at University of Florida (2004) with James Boncella
    - Dissertation: *Orbital interactions in group 6 imido-diamido complexes*
- Post doc at Purdue with Mahdi Abu-mar
- Currently Associate Professor of Chemistry, North Carolina State University (2006-Present)
- > 85 Publications since 2001, > 1450 Citations since 2007

Recognition

- ORAU Ralph E Powe award 2009
- NSF CAREER award 2010
- Organometallics Fellow 2012
- Center of Enabling New Technologies through Catalysis

Research Interests

- Homogenous catalysis
- Kinetics and mechanisms of inorganic reactions
- Inorganic/organometallic synthesis

Research in the Ison Group

'Our research encompasses many areas, from the development of useful synthetic organic methodologies for organic chemistry to the mechanistic principles that underlie catalytic oxidations.'

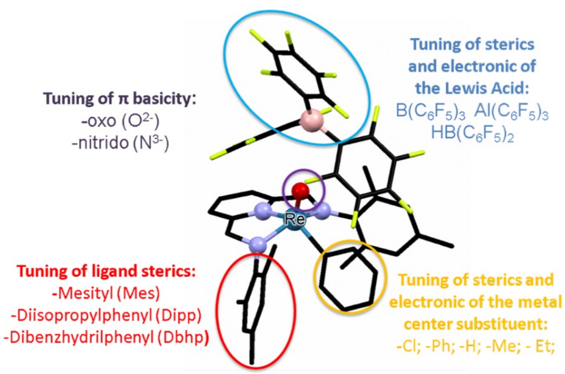
Four main research interest areas:

(I) Frustrated Lewis Pairs

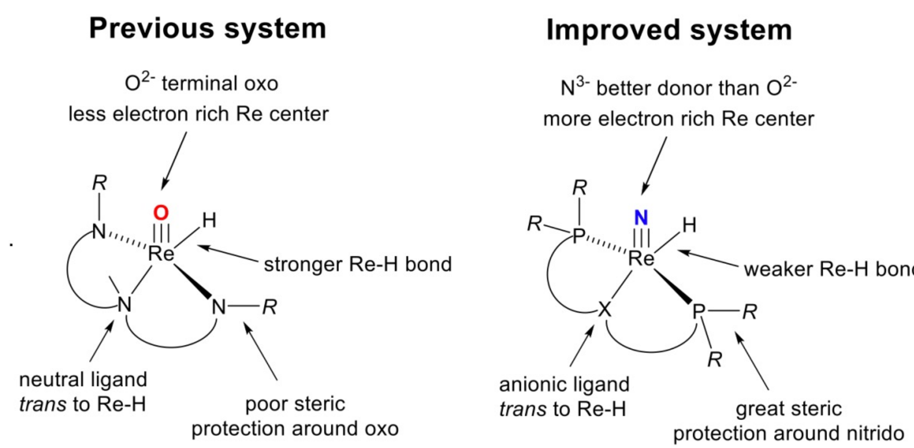
(II) C–H Bond Activation and Functionalization

(III) Carbonylation Chemisty

(IV) Catalysis and Green Chemistry

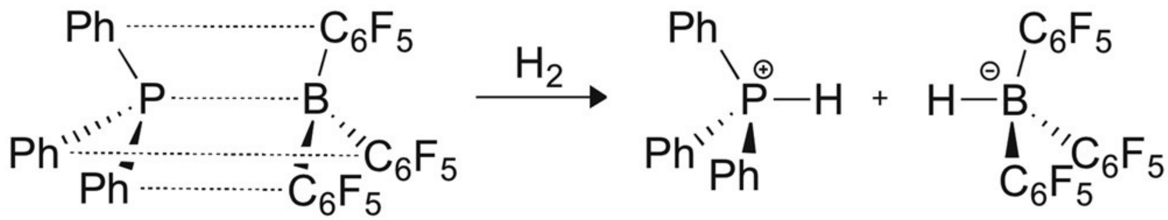


> 40 possible combinations of various steric and electronic demands on the system

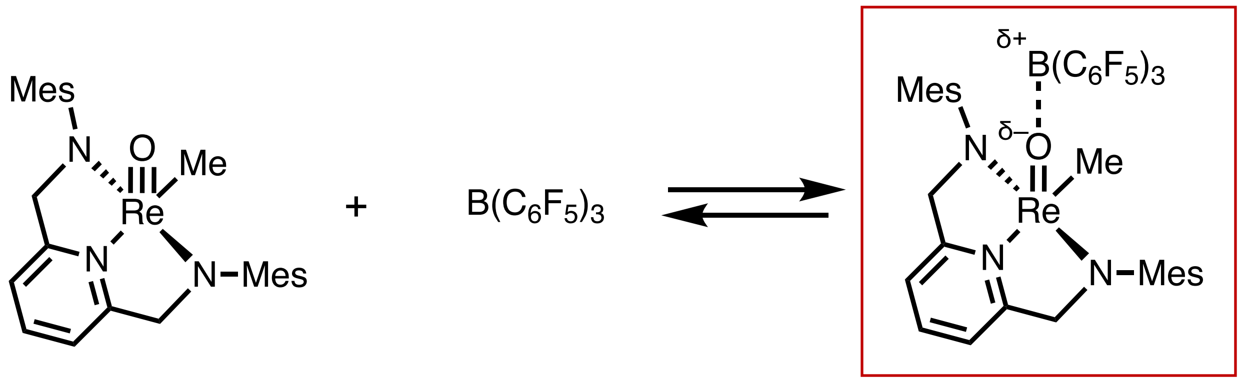


Oxorhenium complex as Lewis base in FLP

Frustrated **L**ewis **P**air (FLP)



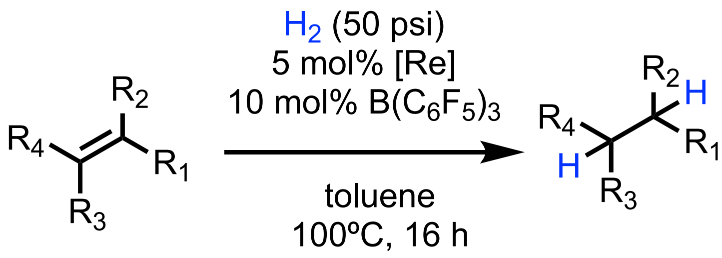
$Ph_3P\bullet B(C_6F_5)_3$ $[Ph_3PH]^+$ $[HB(C_6F_5)_3]^-$



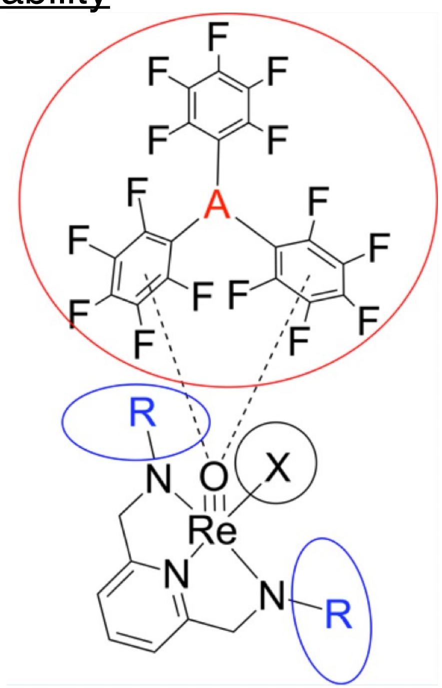
Lewis base Lewis acid FLP

N. S. Lambic, R. D. Sommer, E. A. Ison *J. Am. Chem. Soc.* **2016,** *138,* 4832-4842

Olefin hydrogenation catalyzed by Re=O/LA FLP

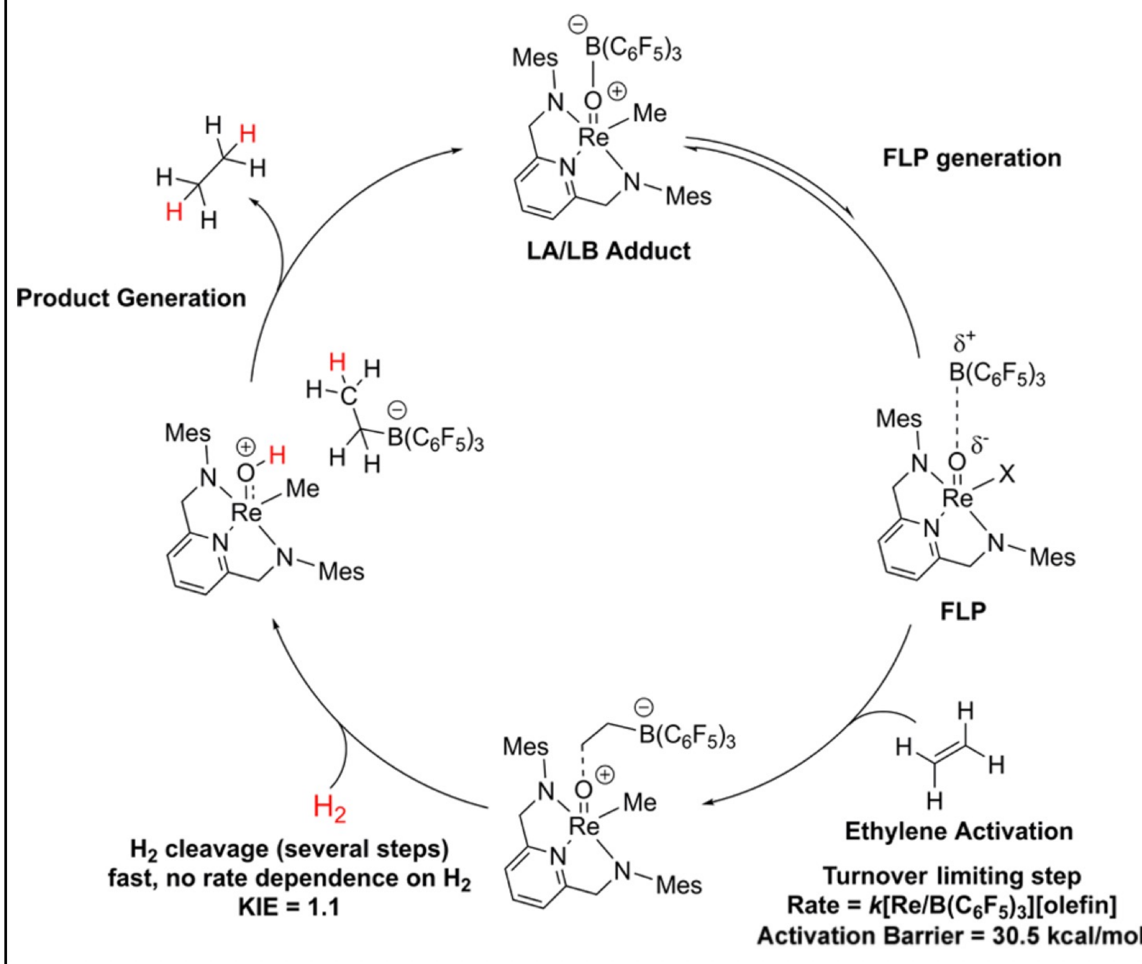


Tunability



Steric/electronic effects easily altered

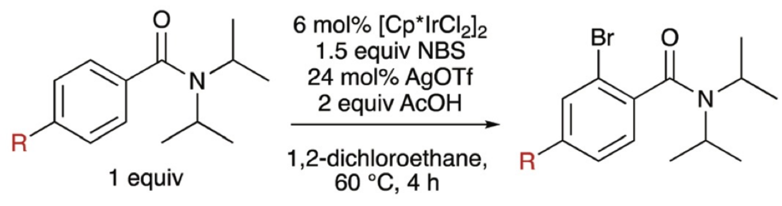
Mechanism



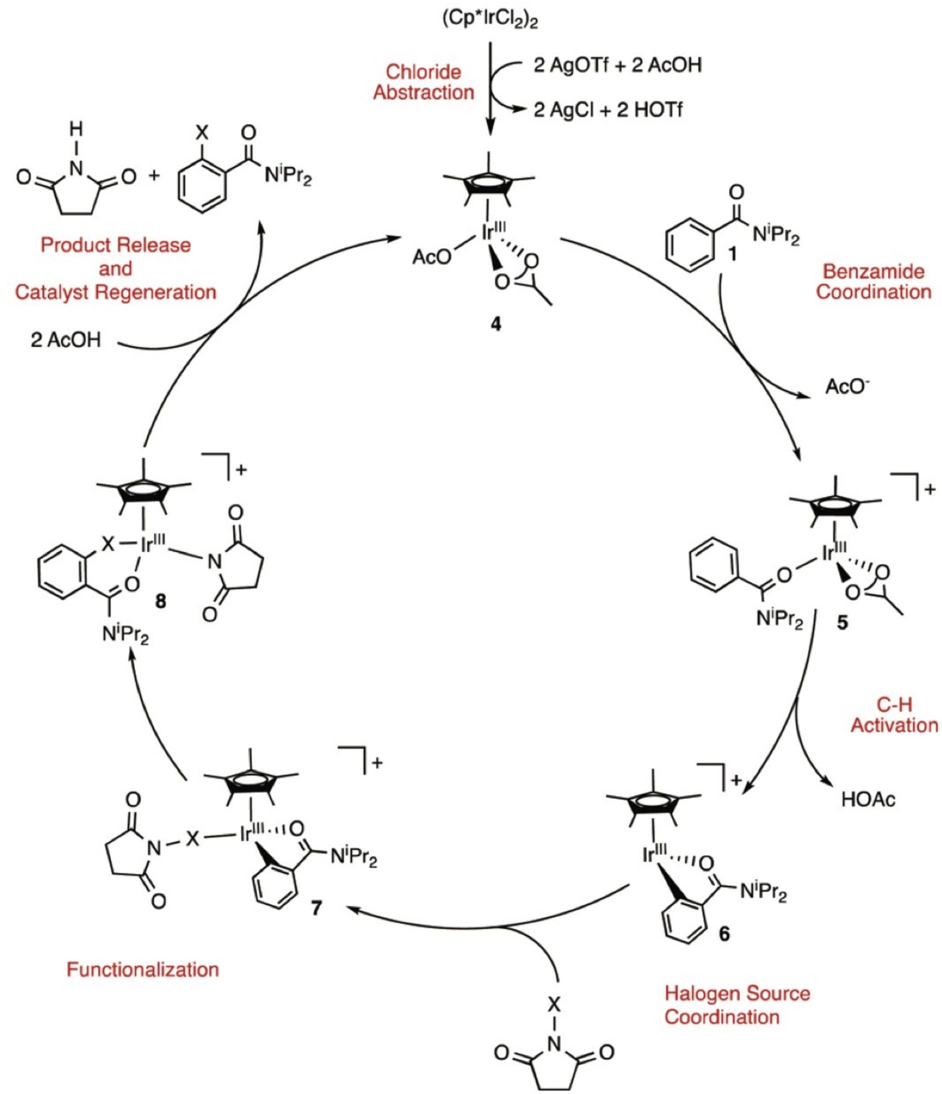
Proposed mechanism with FLP formation

N. S. Lambic, R. D. Sommer, E. A. Ison *ACS Catalysis.* **2017,** *7,* 1170-1180

Cp*Ir(III)-Catalyzed ortho-Halogenation of Benzamides



R = H, Me, OMe, Cl, F, CF_3, Ph

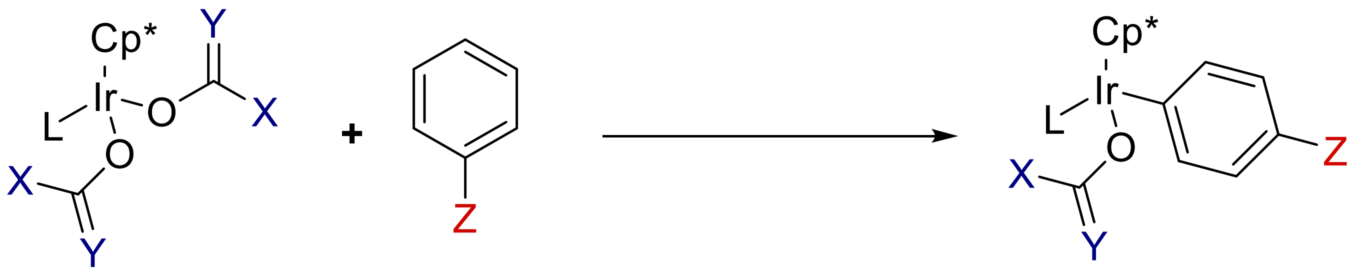


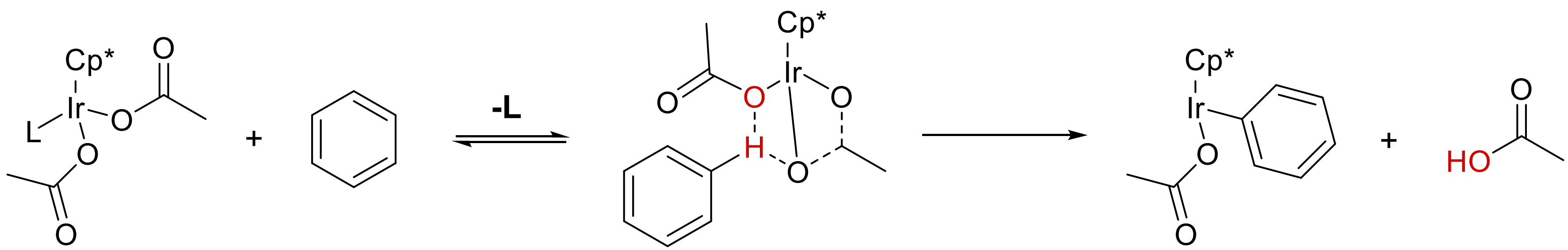
- Ease of halogenation:
  - I > Br >> Cl
- Kinetic orders:
  - [Ir] = 1st
  - Benzamide = (+)
  - NIS = 0
- KIE = 2.5
- Computations: CMD for C—H bond activation
- **6(DMSO)** synthesized:
  - Stoichiometric reaction shows competency in product formation

Dalton Trans. **2020**, *49*, 16166

Mechanistic Studies on the Non-directed C-H Activation of Arenes

L = CO, py, DMSO etc.
X = CH_3, CF_3, t-Bu etc.
Y = O, NH, NMe
Z = EWG, EDG





Proposed Mechanism: Concerted-Metallation-Deprotonation (CMD)

Evidence For CMD Mechanism

- 1st order in [Ir], 1st order in [Ar], Inverse order in [L]
- Hammett plot for EDGs/EWGs shows non-linear behavior ρ = 1.67 (EDG) then ρ = 0 (EWG)
- EDGs in para position have bigger impact on C-H cleavage step (***RDS***), where as EWGs influence the substrate binding step.

Ison, E.A. et al.; *Organometallics,* **2016,** *35,* 2435-2445

Development of Carbonylation Reactions

Industrial synthesis of acetic acid

$$CO + 2\,H_2 \xrightarrow[\text{on alumina}]{\text{CuO/ZnO}} CH_3OH \xrightarrow[\text{[Ir], HI}]{\text{CO}} CH_3COOH$$

Proposed synthesis

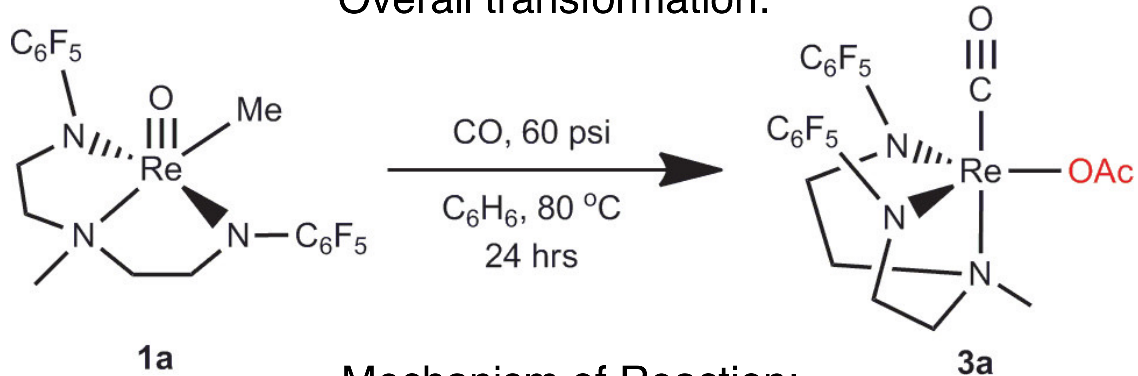
$$2\,CO + 2\,H_2 \dashrightarrow CH_3COOH$$

Can the Monsanto/Cativa Process by Bypassed?

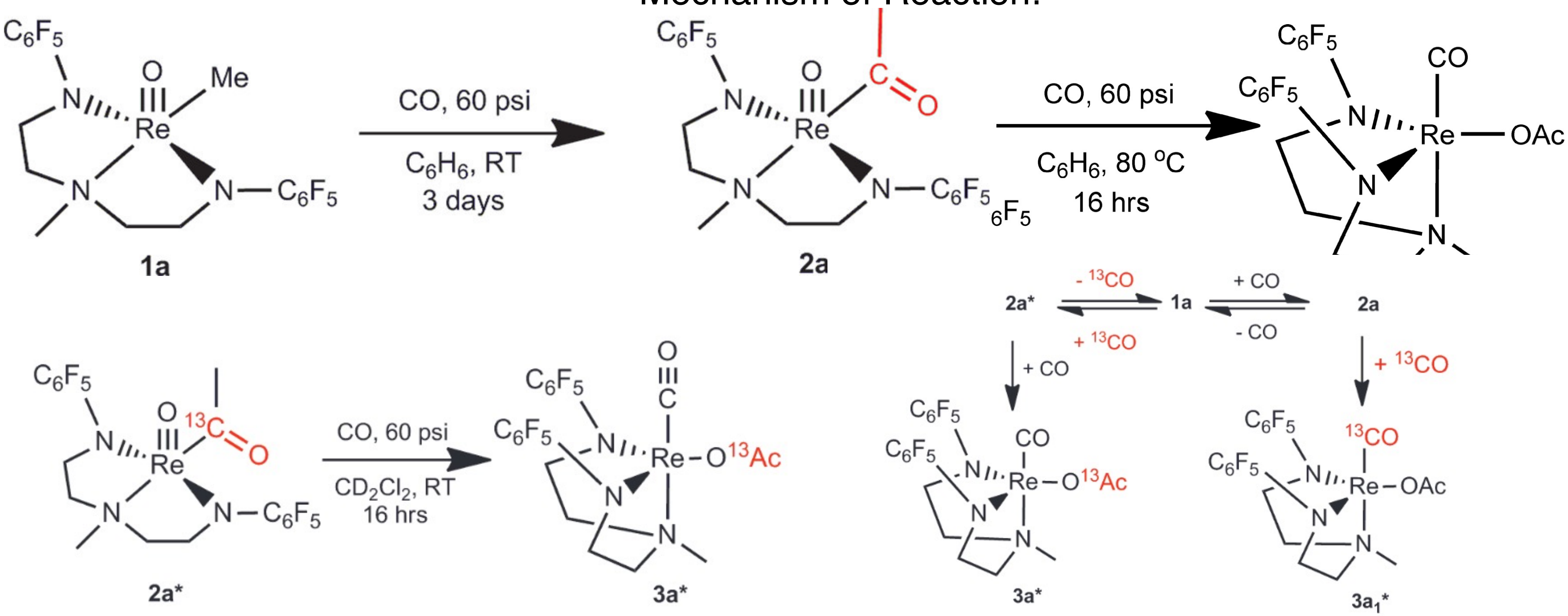
J. L. Smeltz, P. D. Boyle, E. A. Ison *J. Am. Chem. Soc.* **2011,** *133,* 13288-13291

Rhenium Complex for Carbonylation and Oxidation

Overall transformation:



Mechanism of Reaction:

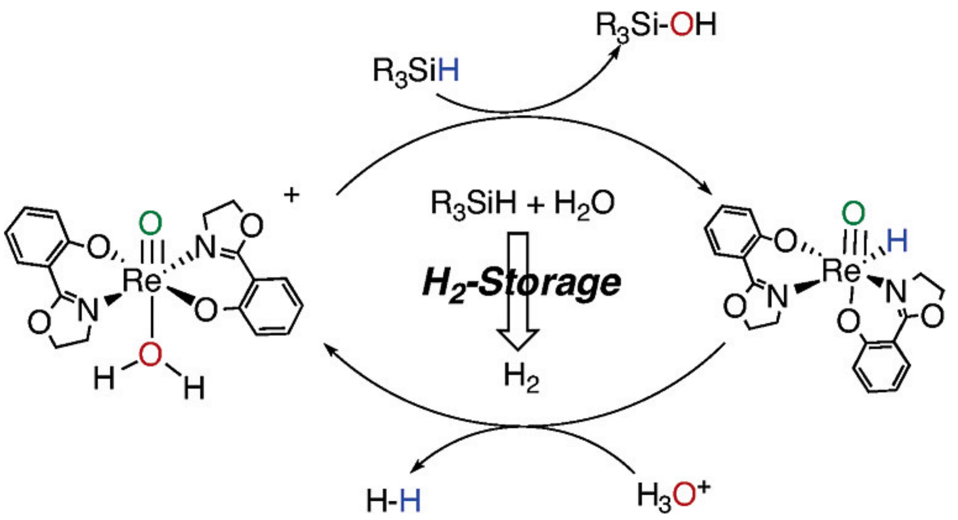


J. L. Smeltz, P. D. Boyle, E. A. Ison *J. Am. Chem. Soc.* **2011,** *133,* 13288-13291

Catalysis and Green Chemistry

Hydrogen production from cationic oxorhenium catalyzed hydrolytic oxidation of organosilanes

- H_2 yields stoichiometric to water
- Low catalyst loading (1 mol %)
- Ambient conditions
- High selectivity for silanols
- Water as the only co-reagent
- Solvent free conditions



New method for storage and production of H_2 for use as fuel:
- Cost of organosilane
- H_2 yield per mass organosilane
    - Polysilyl > 1° > 2° > 3°

Organosilane (mass)	H_2 yield
$HC(SiCH_3)_3$ (18 kg)	3.0 kg
$PhSi_3$ (54 kg)	3.0 kg
Et_2SiH_2 (66 kg)	3.0 kg
Et_3SiH (173 kg)	3.0 kg

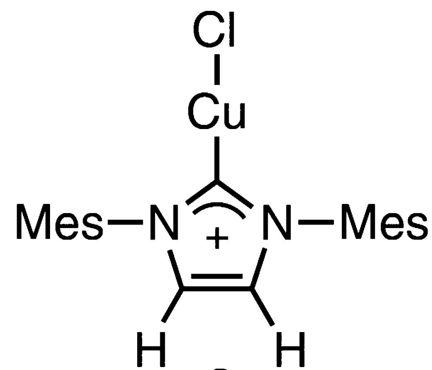
Ison, E. A.; Corbin, R. A.; Abu-Omar, M. M. *J. Am. Chem. Soc.* **2005**, *127, 34*, 11938–11939

Designing Undergraduate Labs

Experiments focused on catalysis and green chemistry

Synthesis of copper *N*-heterocyclic carbene complexes and click azide-alkyne cycloaddition

- sustainable synthesis of catalysts: solvent-free, alternative use of H_2O as benign solvent, non-chromatographic purification



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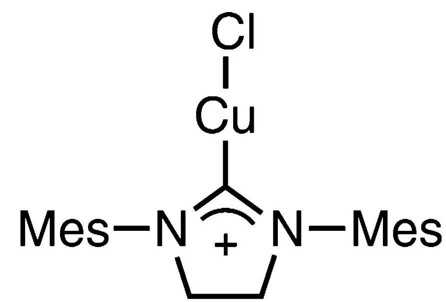

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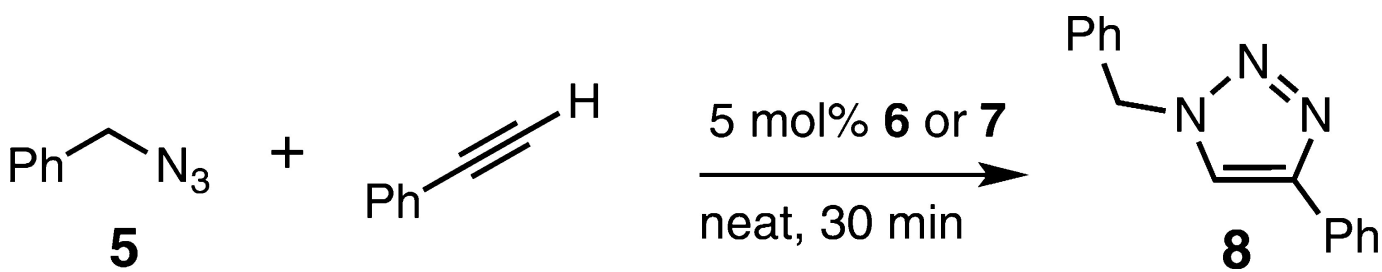

90–93% yield

CuAAC reaction: solvent-free, ambient conditions, high atom economy, high yielding, non-chromatographic purification

E. A. Ison and A. Ison, *J. Chem. Ed.* **2012**, *89*, 1575–1577