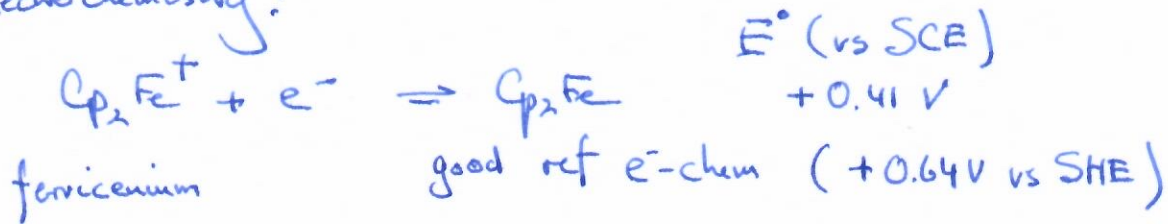


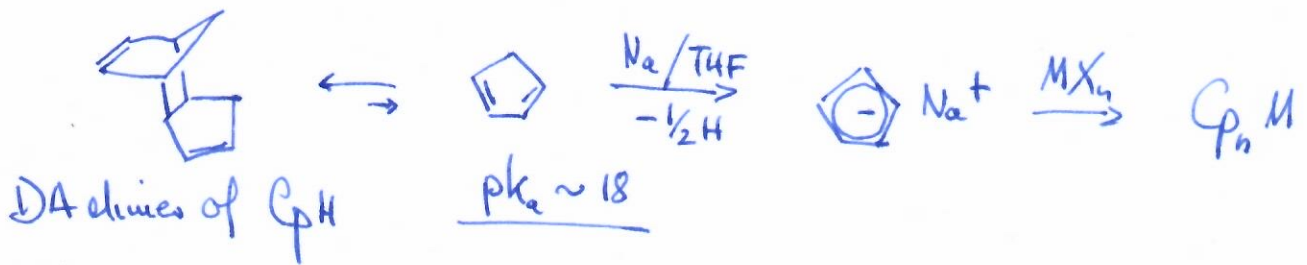
electrochemistry:



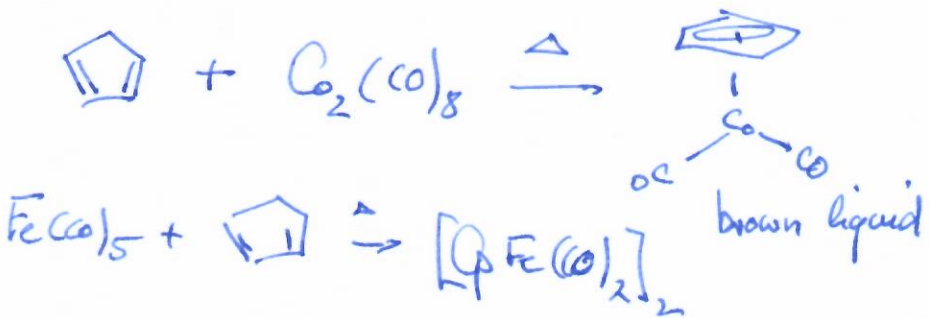
Lecture 11

#1

Synthesis



less reducing alternative: TL Cp



Cp\*

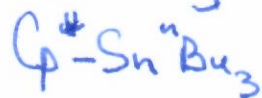
- more steric protection
- better solubility, crystallinity
- better donor  $\left( \text{CpH}-\text{CO} \text{ vs } \text{Cp}^*\text{M}-\text{CO} \quad \Delta\nu_{\text{CO}} \sim 50 \text{ cm}^{-1} \right)$
- $E^\circ \text{ Cp}^*\text{M}^{2+} \text{ vs } \text{Cp}_2\text{M}^{2+} \quad \Delta E^\circ \sim -0.5 \text{ V}$

note:  $\text{Cp}_2^*\text{Fe}^{2+}$  recently made by K. Seppelt Science, 2016, 353, 678

prep of Cp\*H, prep Org. Synth 1987, 65, 42

less reducing alternative to Cp\*Li

pKa of Cp\*H: 26

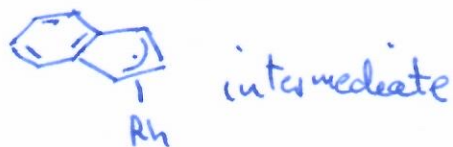
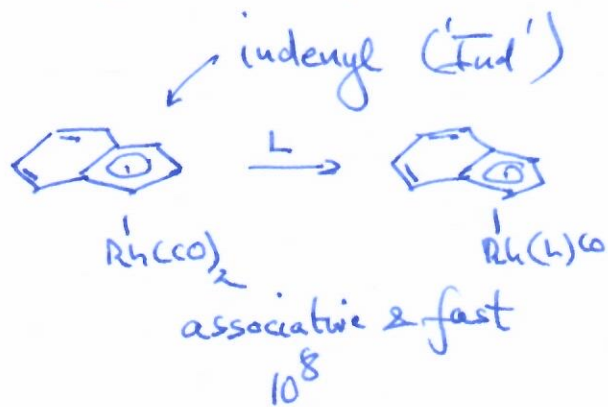
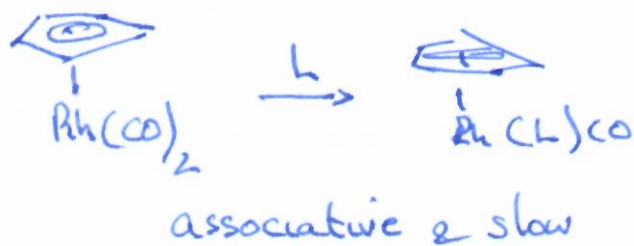


can bind in η<sup>3</sup> or η<sup>1</sup> fashion



η<sup>1</sup>-Cp → fluxional process  
'ring whizzing' equil all 5 H's

η<sup>5</sup> ⇌ η<sup>3</sup> ⇌ η<sup>1</sup> ring slipping creates coord. unsaturation



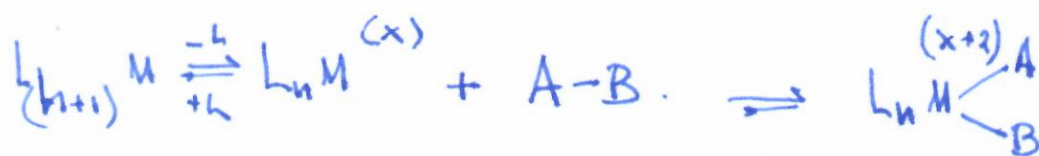
Oxidative Additions & Reductive Eliminations

Tutorial: J. Labinger

OM 2015, 34, 4784

in common: increase / decrease in formal ox. st. ( $\Delta \geq 2$  or 1)  
 " / " in coord. # ( $\Delta = 2$  or 1)

general rxns:



but, also



Principle of Microscopic Reversibility (PMR)

original (R.C. Tolman): In a system at equilibrium, any molecular process and the reverse of that process occur on the average at the same rate.

'principle of detailed balancing'

in mechanistic terms: The lowest energy path in the forward direction must also be the lowest energy path in the reverse direction.



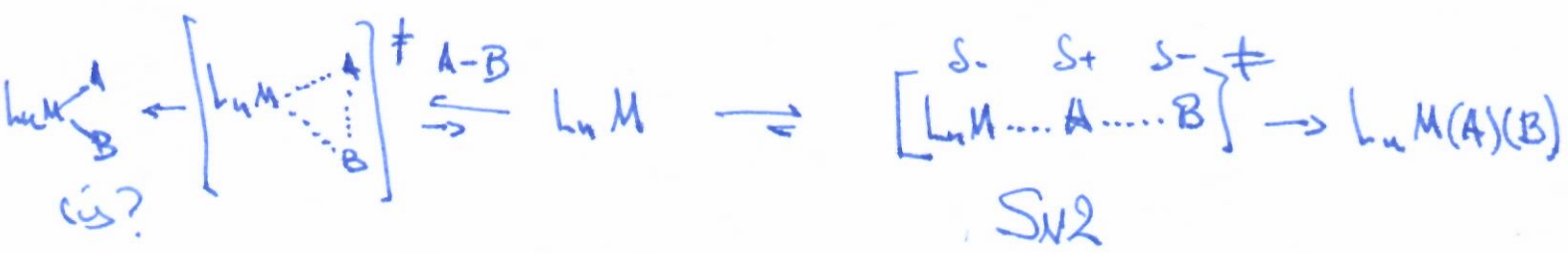
for more: Burrell & Pearson

J. Phys. Chem. 1966, 70, 300

mechanisms

- Concerted  $2e^-$  transformations
- radical processes

even among 'concerted' ones

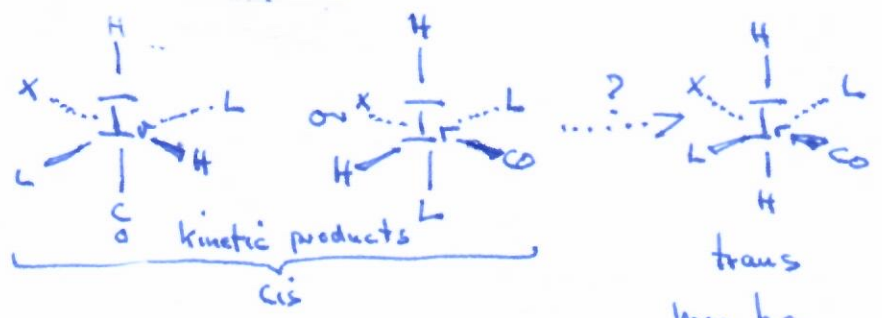


3-center addn.

nonpolar molecules



fast ( $1-100 \text{ M}^{-1} \text{ s}^{-1}$ )  $\Delta H^\ddagger \sim 10-12 \text{ kcal/mol}$   
 $\Delta S^\ddagger \approx -15 - -25 \text{ e.u.}$



favored by:  
 $\text{X} = \text{Cl}, \text{Br}$

favored by  
 $\text{X} = \text{Me}, \text{Ph}$

trans  
 may be  
 thermodynamic  
 product

$\mu-\text{H}^\ddagger$  exists!