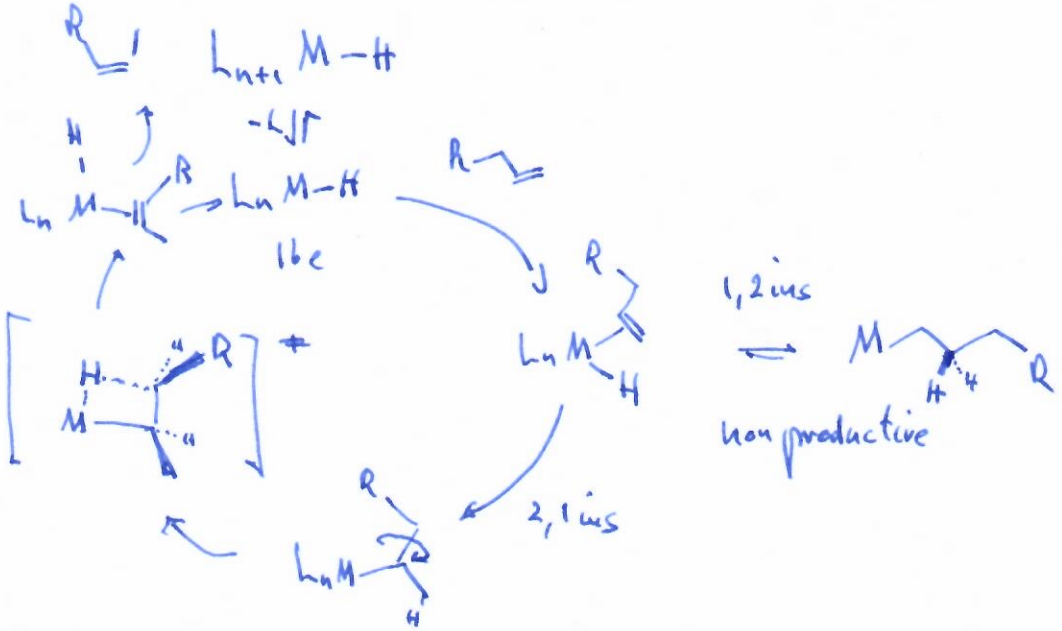
Catalytic Transformations of Olefins — lecture 22

Isomerization:

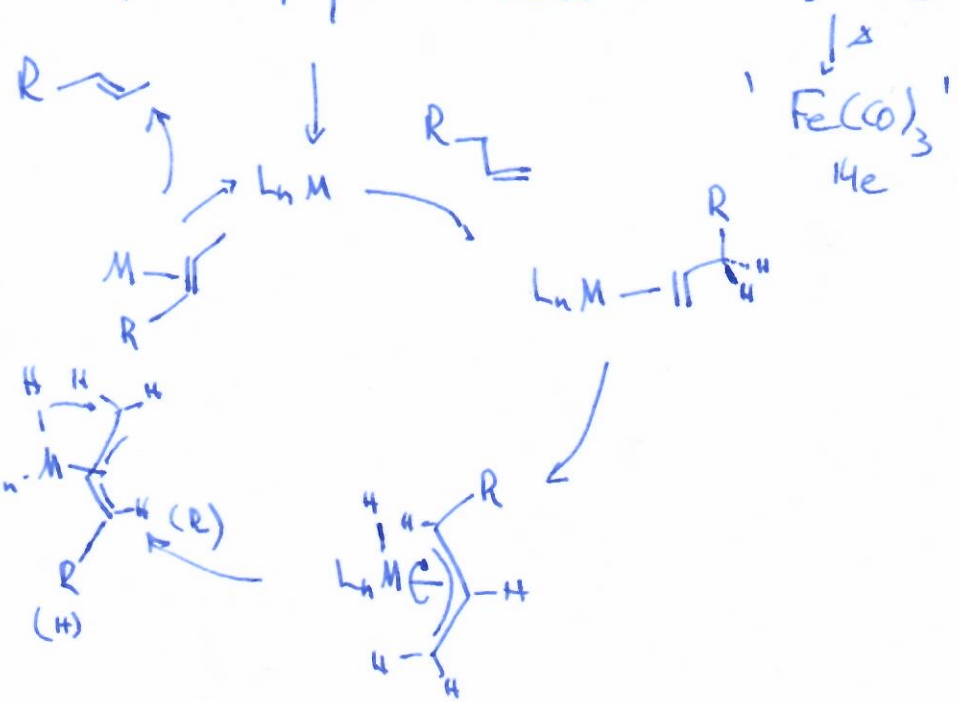
thermodynamic mixture

catalyzed by most TM's, can be unwanted

1) hydride mech

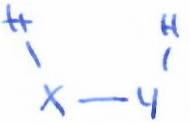


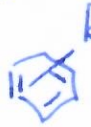
2) allyl mech — req. 2 empty coord sites



η³–η¹ rearrangement of allyls

Hydrogenation

$H_2 + X{=}Y \longrightarrow$ 

X=Y: $R_2C{=}CR_2$, $RC{\equiv}CR$, $R_2C{=}O$, $R_2C{=}NR$, $R{-}N(=O)=O$, 

Thermodynamics:

$\Delta H \sim -27$ kcal/mol

Spontaneous, but requires catalyst!

Best catalysts groups 8, 9, 10

Pd/C (heterogeneous) Syn addition of H_2

Rh/IR (homogeneous)

e.g. Wilkinson's catalyst $Rh^{I}(PPh_3)_3Cl$, - J. Halpern

2 papers:

a) ox. addn of H_2 to Rh^{I}: Chem. Comm. 1973, 629

reaction w/ 'L_2RhCl' is dominant

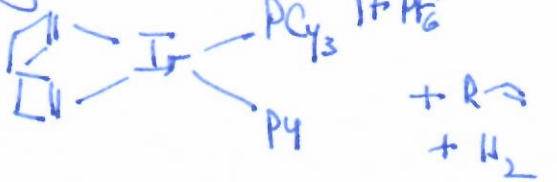
$$\text{rate} = \left(k_2 + \frac{k_1 k_4}{k_{-1}[L] + k_2[H_2]}\right)[H_2][ClRhL_3]$$

b) insertion of  , J. Mol. Cat 1976, 2, 65

$k_6 = 0.2\ s^{-1}$ @ 25°C in benzene

$k_H/k_D = 1.15$

very reactive catalysts? Crabtree Acc. Chem. Res 1979, 12 331



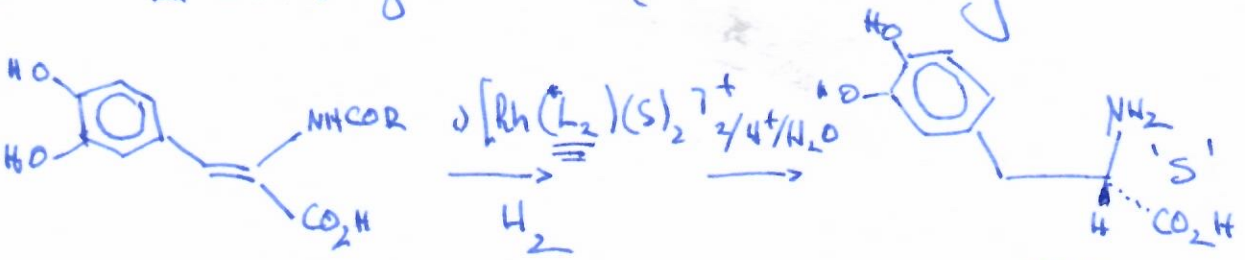
reactivity:

6400 4500 3800 4000 to/h

'asymmetric' hydrogenation

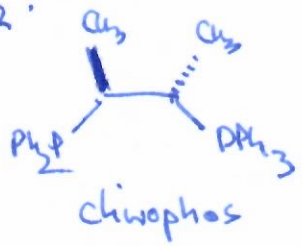
→ enantioselective hydrog... of prochiral olefins

Monsanto L-DOPA synthesis (Parkinson's drug)

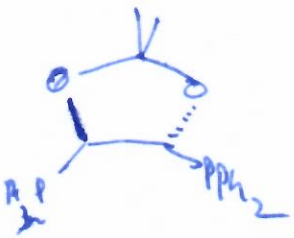


95% e.e.

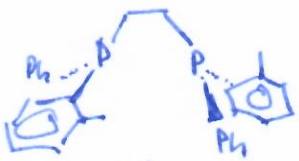
*L2:



chiraphos



'diop'

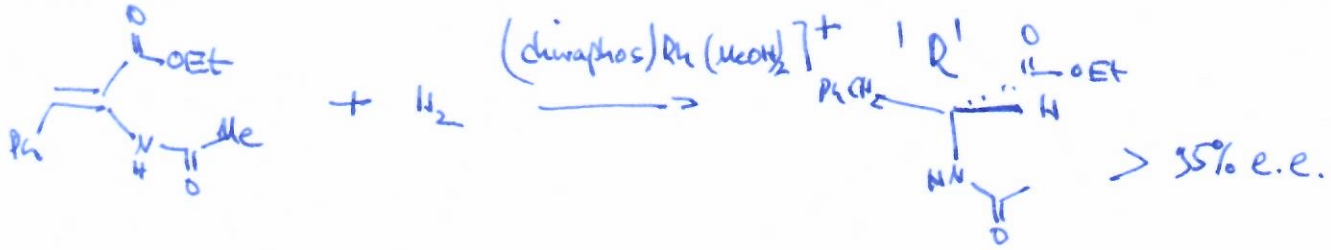


dipamp

2001 Nobel

Knowles, Noyori, Sharpless

J. Halpern JACS 1980, 102, 5952



> 95% e.e.

predicted product!

→ minor diastereomer more reactive?

J. Brown JACS 1980, 102, 3040

detects minor isomer and shows....

a 'Curtin - Hammett' situation