Olefin Metathesis Schrock, Grubbs, Chauvin 2005 Nobel

1956 H.S. Eleuterio (→ copolymer → + !)

2 R–R' ⇌ R–R + R'–R'

Catalysis! Chs. 9, 12 Lecture 20 1

in industry: SHOP process: C_2H_4 → C_{10}–C_{18} olefins, alcohols p. 239 ff

$\Delta H \approx 0$ but very fast, originally only good for hydrocarbons

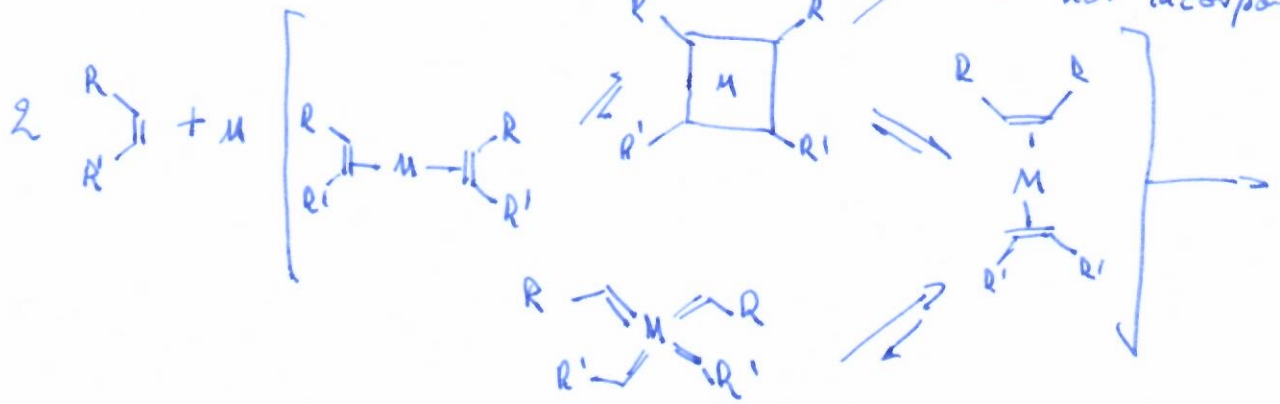
Mo, W, Re halides plus main group alkyls

mechanism?

1)

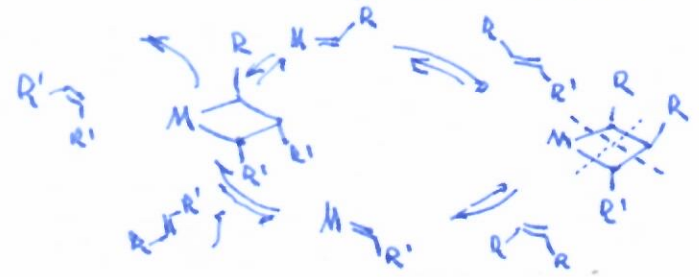
$$H_3C-CH=CH-CH_3 + D_3C-CD=CD-CD_3 \rightleftharpoons CH_3-CH=CD-CD_3 \quad !$$

a) pairwise

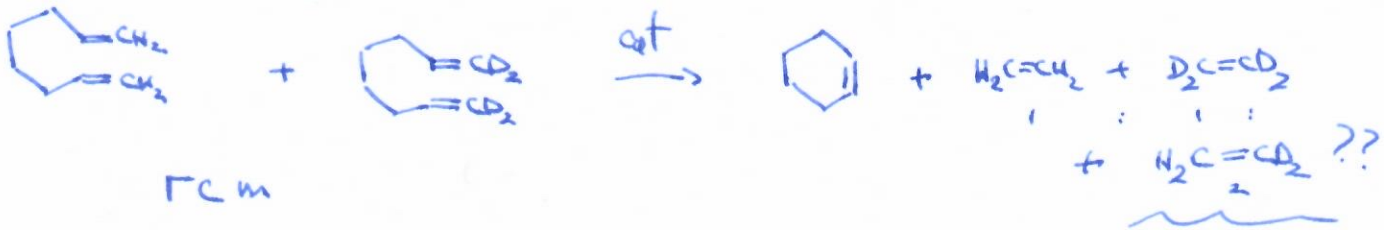


extremely high formal ox state

b) non-pairwise: Y. Chauvin in 1971 (Makromol. Chem. 1971, 141, 161



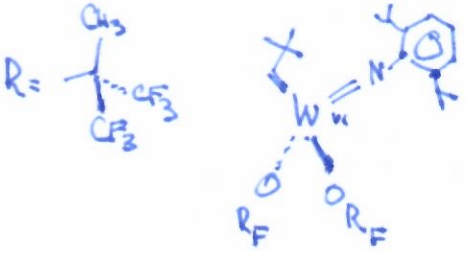
expt'l. test



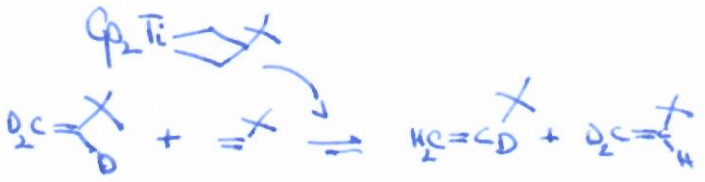
expt: 1 : 1 : 2 !
‖
Chauvin mech.

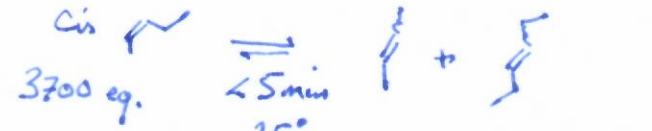
model chemistry:

1) Schrock et al JACS 1986, 108, 2771

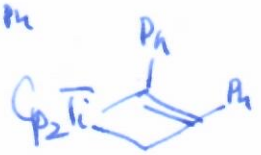


4) Grubbs JACS 1982, 104, 7491

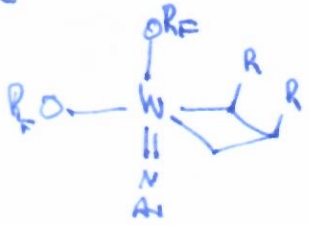




' Cp2Ti=CH2 '



isolate



Ring opening metathesis polymerization (ROMP)

living polymerization !

=> block copolymers !

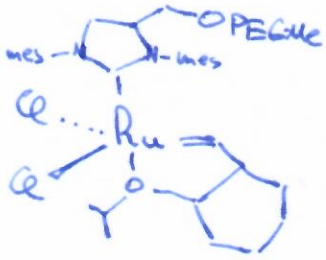
Grubbs: Science 1989, 243, 907

Schrock: Acc. Chem. Res. 1990, 23, 158

functional group tolerance?

Grubbs JACS 2006, 128, 3508

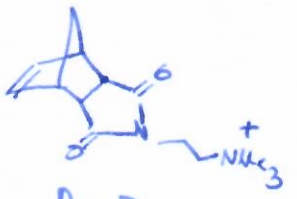
all in H_2O!



NHC

water soluble

1)



ROMP

2)

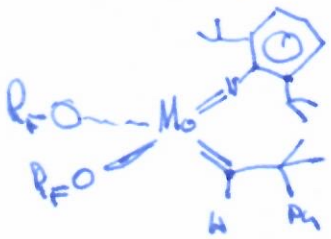
RCM

3)

Cross metathesis + C_2H_4

2nd generation Grubbs cat.

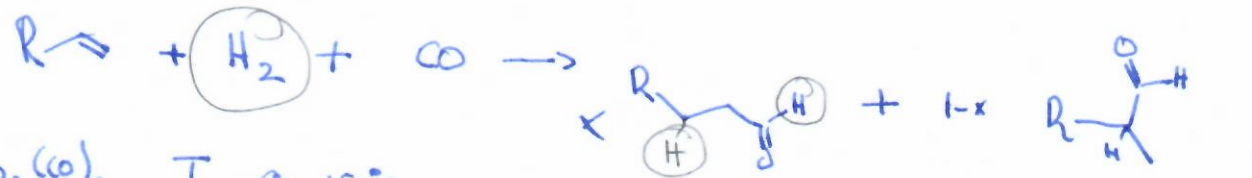
Schrock:



CO-chemistry: homogeneous (& heterogeneous - FT)

1) Hydroformylation (oxo-process)

Otto Roelen 1938, history: JOMC 2014, 754, 5



n-aldehyde

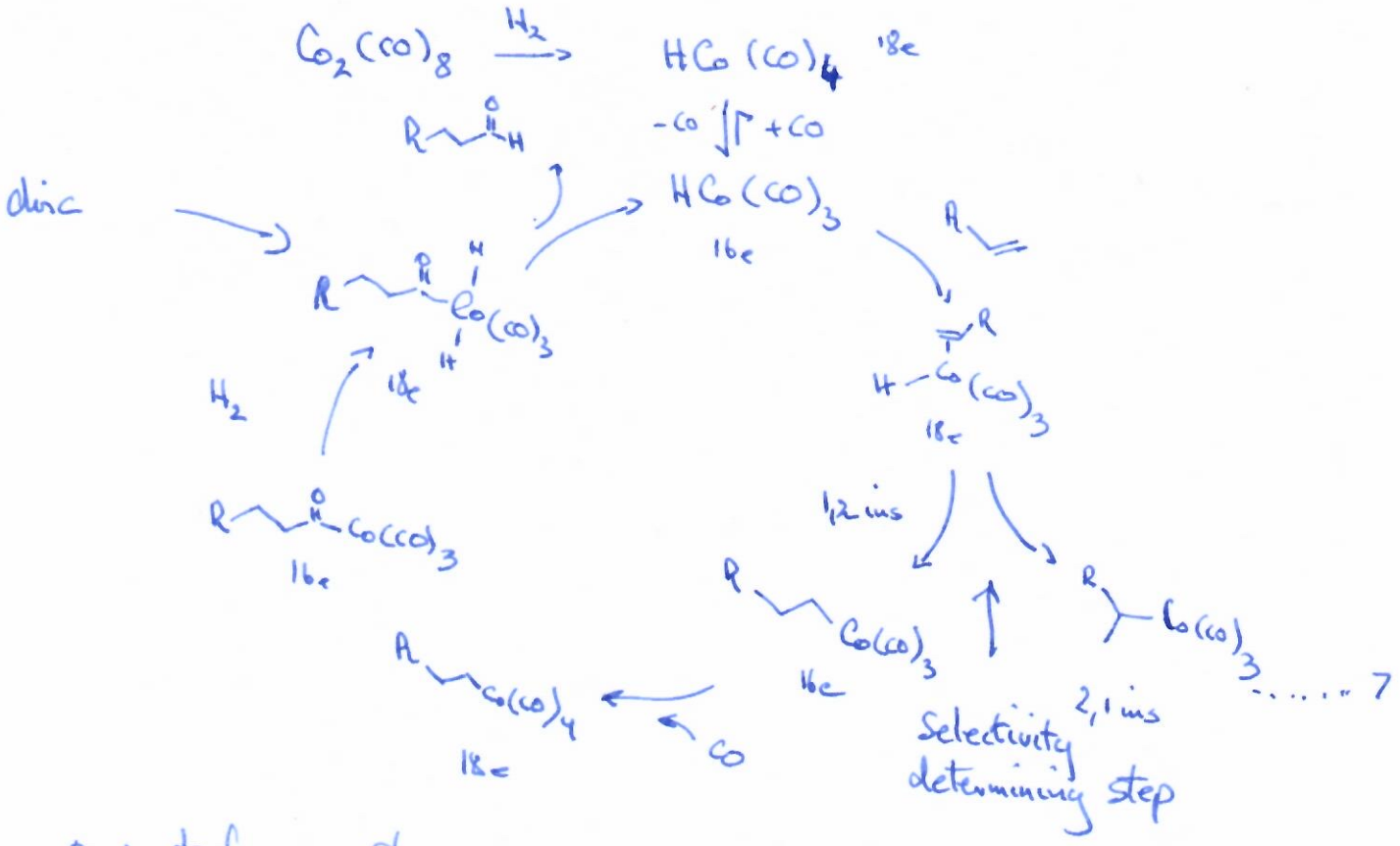
i-aldehyde

catalyst: $Co_2(CO)_8$, T: 90-150°C

P: 60-400 atm

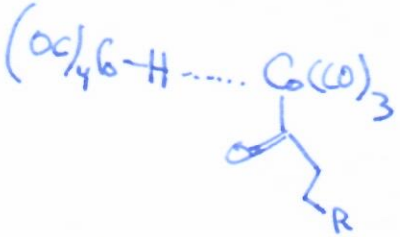
largest homogeneous catalysis 7×10^6 tons/year

mechanism: Heck & Breslow JACS 1961, 83, 4023



product forming Step:

binuclear reductive elimination



heterolytic activation of H_2