

The Fischer-Tropsch Process

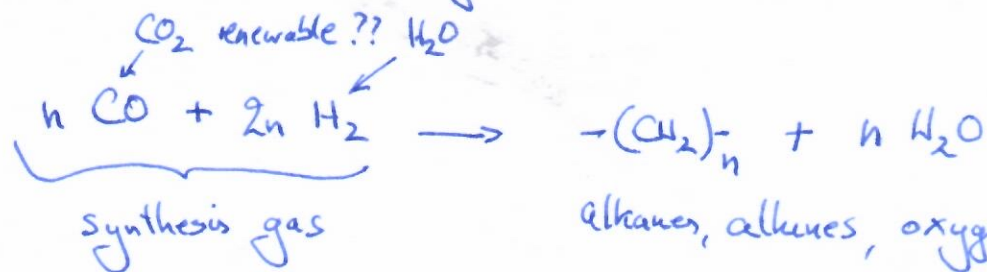
lecture 21

heterogeneous catalysis

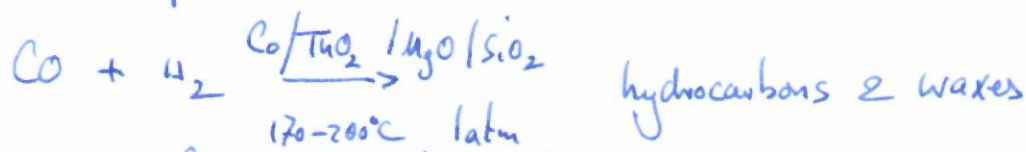
a homogeneous - more selective - analog?

$CH_4 + H_2O$
steam reforming

'C' + H_2O
Coal gasification

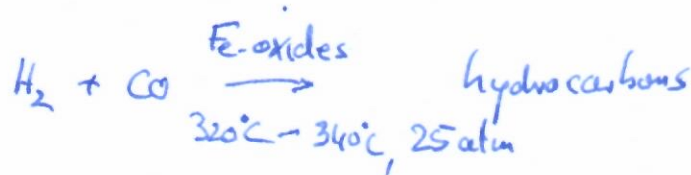


1925 Fischer & Tropsch

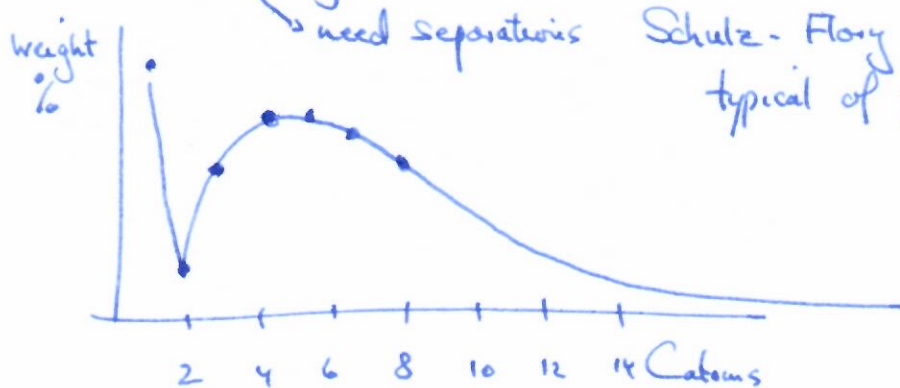


WWII fuels for German war effort - now disc.

today: Sasol

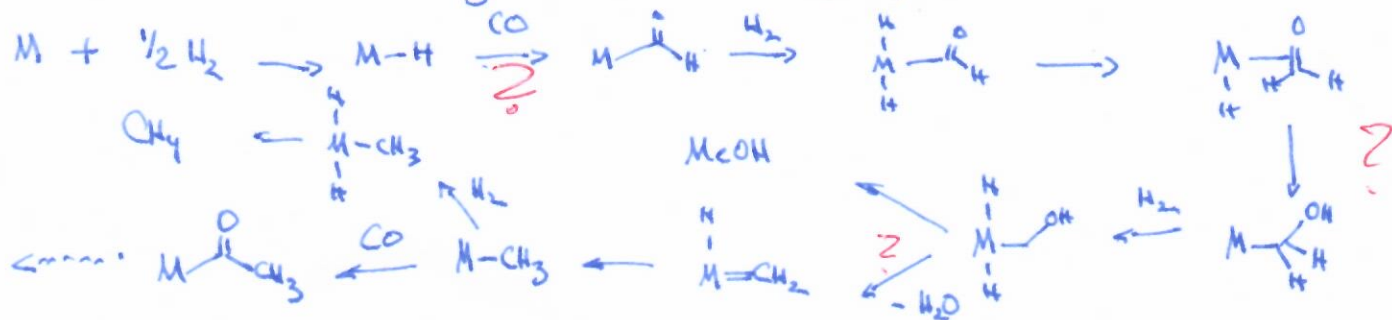


Lack of selectivity



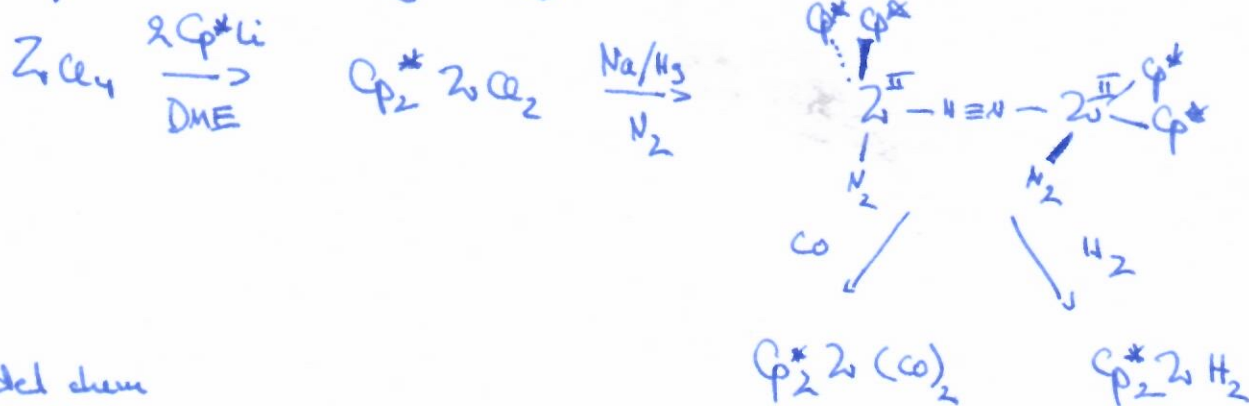
Schulz-Flory distribution
typical of polymerizations → monomers??

mechanism Olive' *Ang. Chem. Int. Ed.* 1976, 15, 136

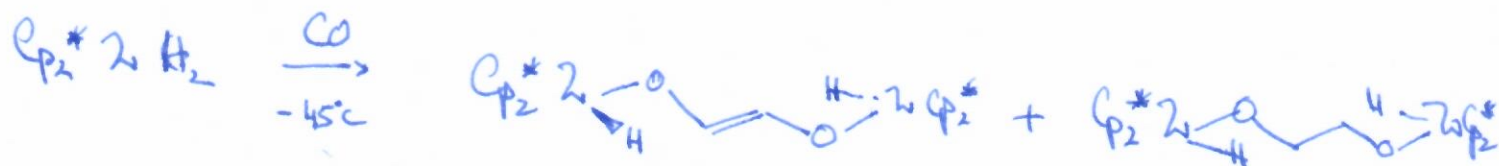


homogeneous model chemistry

early metal chemistry: J. Bergan & P. Wolczanski Acc. Chem. Res. 1980, 13, 121



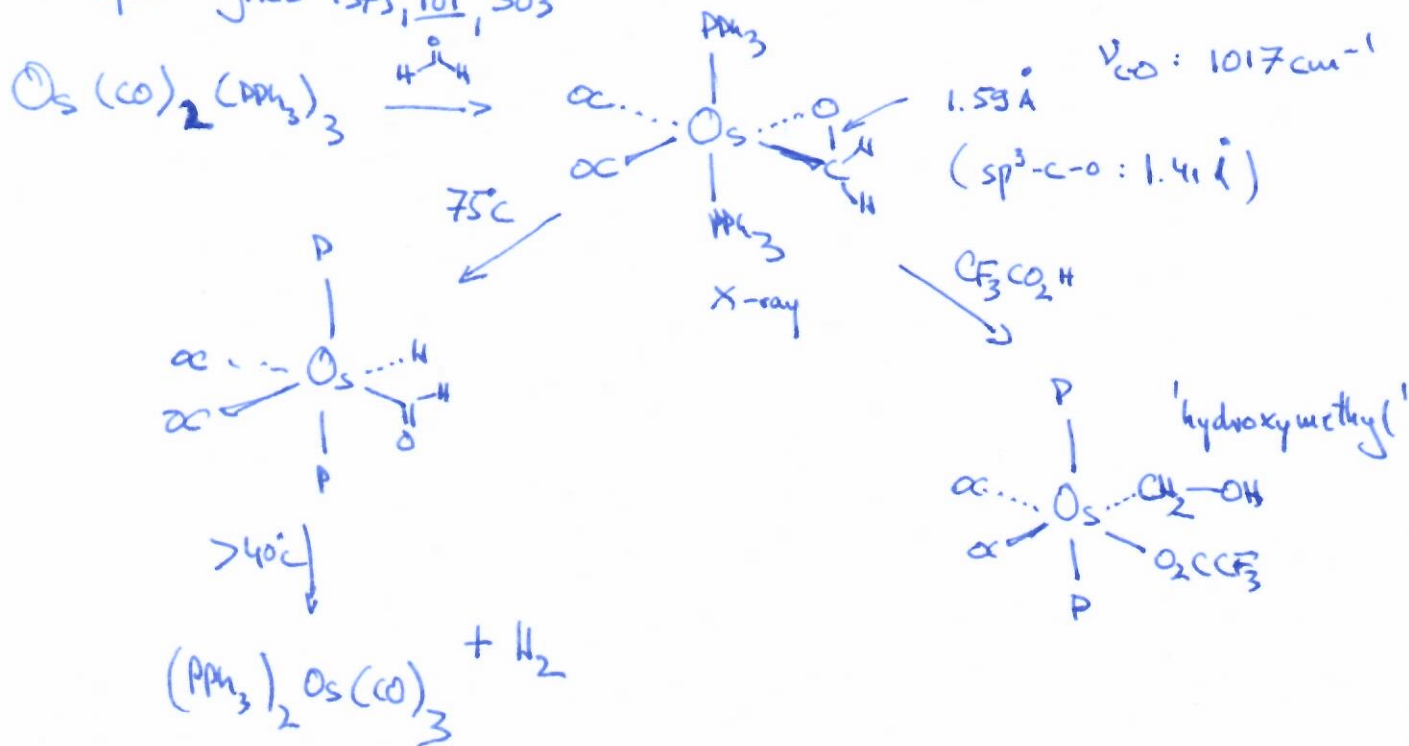
model chem

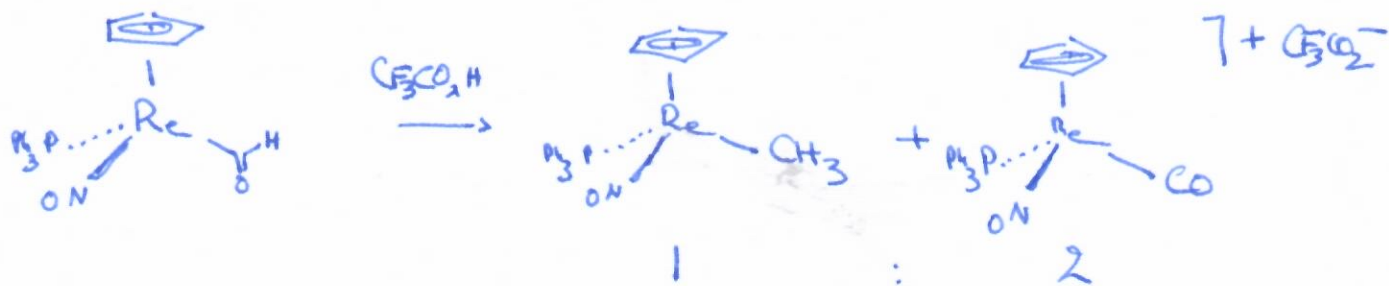


remembers Marks oxycarbene!

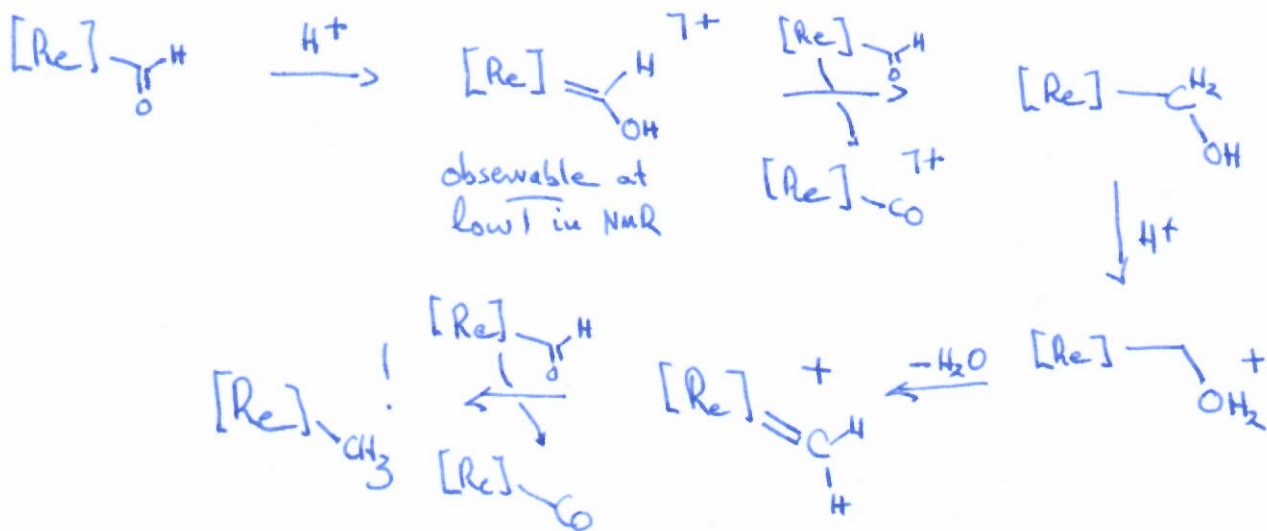
late metal chem

W. Reper JACS 1979, 101, 503





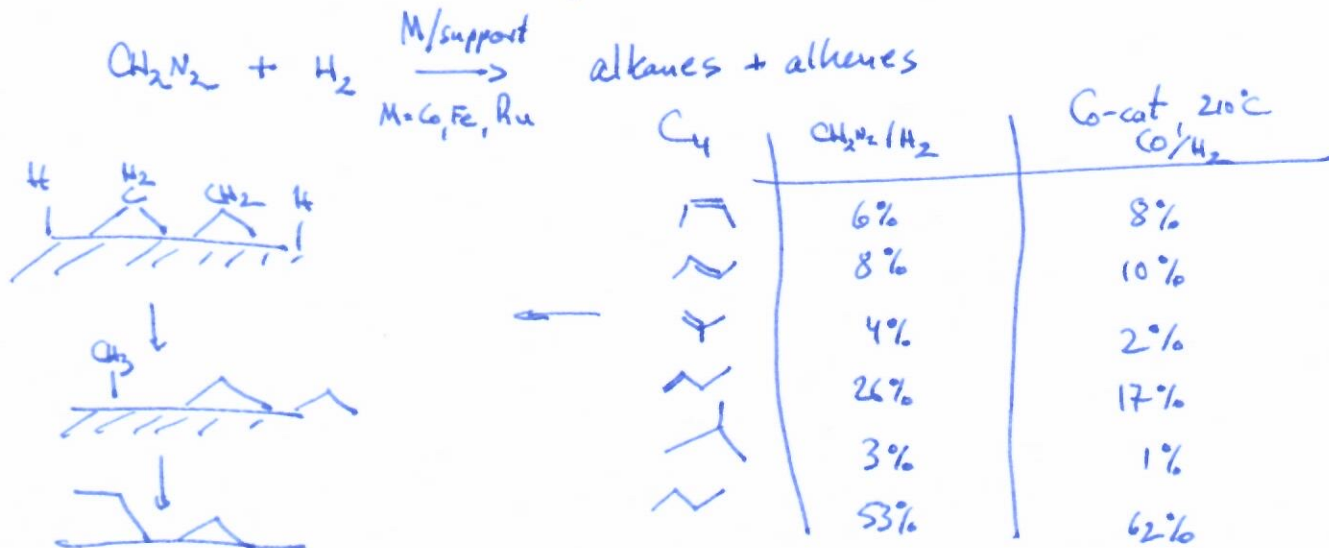
mech.



alternative proposals

F&T: "polymerization of surface bound CH_2 -units derived from the hydrogenation of carbide"...

R. Pettit JACS 1980, 102, 6181



how to form 'CH₂' - dissociative absorption of CO, ...

4



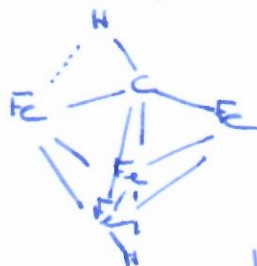
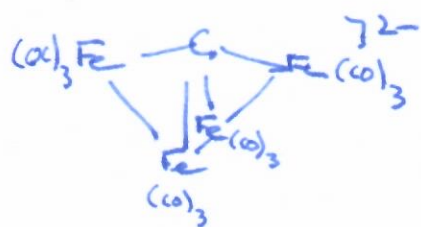
Floriani chemistry (Nb!)
JACS 2000, 122, 538

metal carbide: Cummins

JACS 2001, 123, 5003

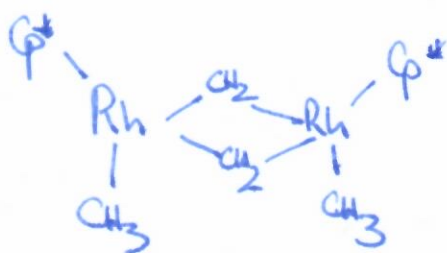
E. Muetterlich JACS 1980, 102, 4541 & 1981, 103, 1485

hydrogenation of carbide



It's exchange
by spin sat transfer

P. Maitlis Chem Commun 1981, 809



C-C bond formation!



Some reviews of homogeneous F-T model chemistry:

- 1) J.R. Moss . Coord. Chem. Rev. 2000, 206-207, 581
- 2) West et al. Coord. Chem. Rev 2011, 255, 881
- 3) James & Maity RSC Advances, 2012, 2, 7342