

# C-H activation

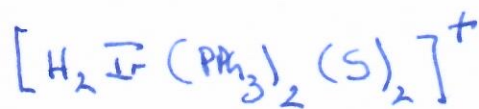
Lecture 25  
(the last one)

for overviews see:

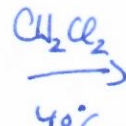
J. Bercaw, Nature 2002, 417, 507

& R. Crabtree, Dalton Trans 2001, 2437

Crabtree:



H acceptor



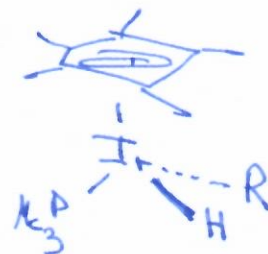
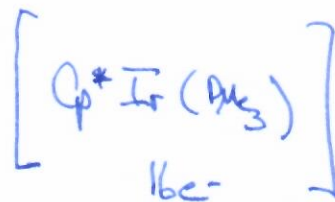
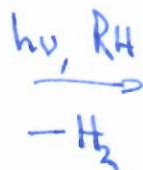
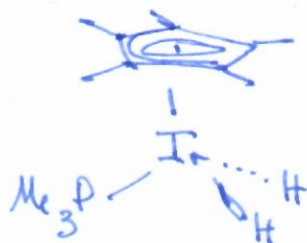
7+



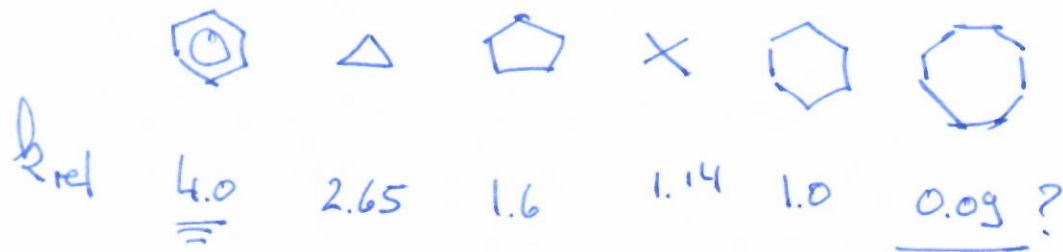
A. Janowicz & R.G. Bergman

JACS 1982, 104, 352

(Graham, Jones...)

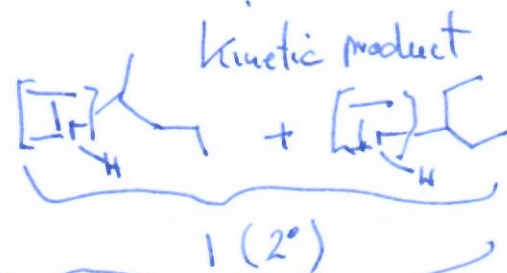
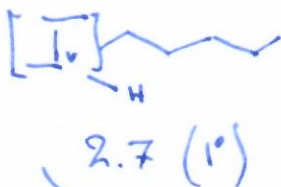


Competition expts:



$$\frac{k_{RH}}{k_{RD}} = 1.38$$

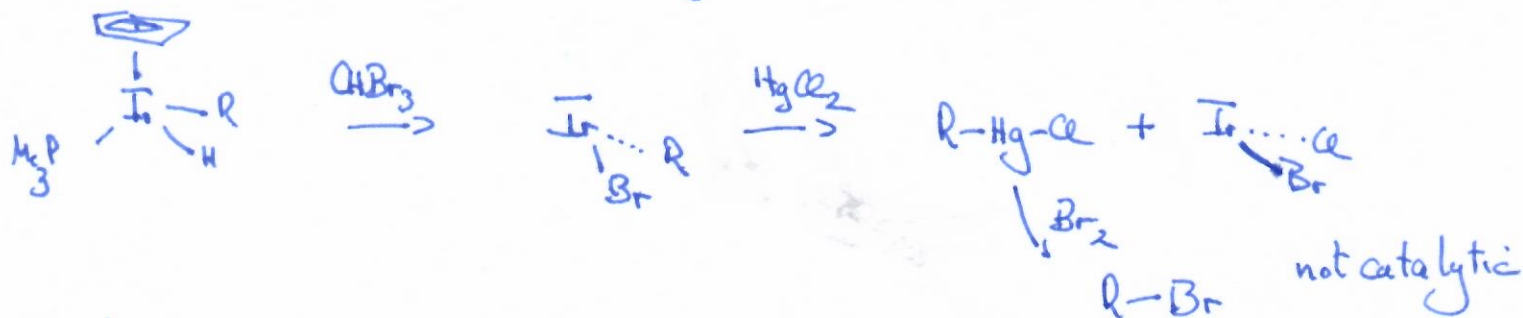
Selectivity:



1° Ir-R > 2° Ir-R  
by 5.5 kcal/mol

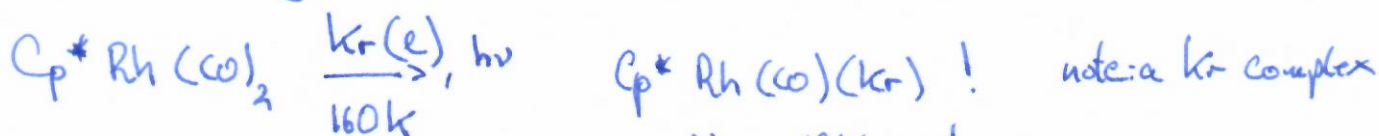


functionalization? external ligands induce red elim of R-H 2



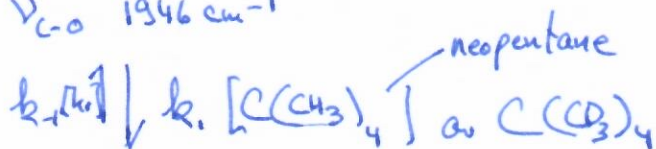
Mechanism:

Moore & Bergman JACS 1994, 116, 9585 → liquid noble gases



Kr b.p. ~ 120 K

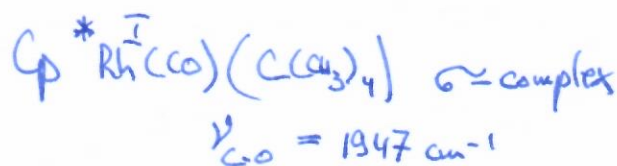
$\nu_{\text{C-O}} 1946 \text{ cm}^{-1}$



Surprise: large eq. isotope effect

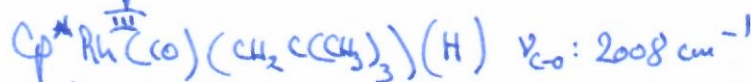
$$\text{C}(\text{CO})_4 \text{ is more strongly bound}$$

$$k_{\text{eq}} \sim 14 !$$



at 165K

$$k_{\text{H}}(\text{C}(\text{CO})_4) = 3.9 \times 10^4 \text{ s}^{-1} !$$



$$\Delta H^\ddagger = 4.1 \text{ kcal/mol} \leftarrow \text{very low barriers!}$$

$$\Delta S^\ddagger = -11.2 \text{ e.u.}$$

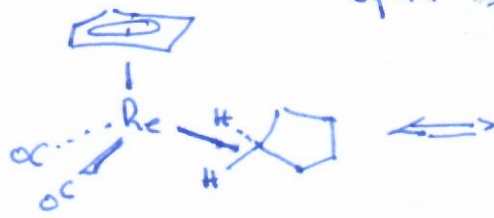
$$k_{\text{H}} / k_{\text{D}} \sim 16 !$$

Exptl. evidence for 'σ-Complexes'

Hall & Perutz Chem. Rev. 1996, 96, 3125

Geffakis & Ball JACS 1998, 120, 9953

equil isotope effect favors C-H  
 $k = 0.75$



$^1\text{H-NMR } \delta: -2.32 \text{ ppm (q, 2H)}$

$^{13}\text{C-NMR } \delta = -31.2 \text{ ppm}$

$J_{\text{C-H}} = 112.9 \text{ Hz}$  (free  $\text{C}_5\text{H}_5$  129 Hz)

recent spectroscopy:

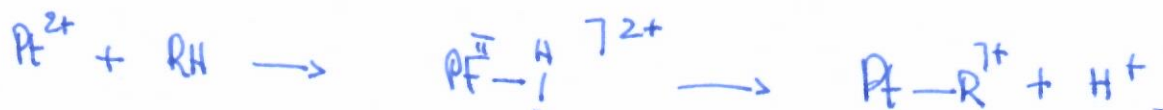
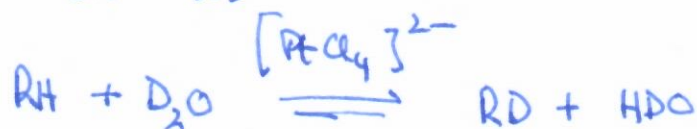
Bernskoetter et al. Science 2009, 326, 553



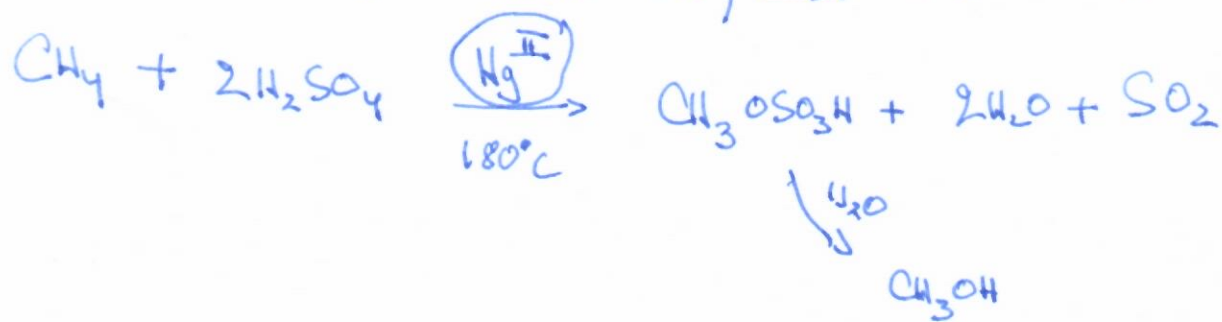
Crystal structures? ✓

### Electrophilic C-H activation

A. Sklar 1969



→ R. Periana Science 1993, 259, 340 ← look this up!



The end!