Oxd. Addn. cont'd   Lecture 13

Radical Chain rxns

$$Pt^0(PEt_3)_3 + {}^nBuBr \longrightarrow$$
'h'

> 95%   < 5%

$+ C_4H_{10} + C_4H_8$
butane   butene

kinetics irreproducible
 (induction period)
radical traps, inhibition
 (2,6-di^{t}butyl phenol)

radical chain:

  initiation: $Q^. + RX \longrightarrow QX + R^.$

  propagation: $\begin{cases} \boxed{R^.} + Pt L_3 \longrightarrow R \overset{I}{Pt}L_3 \\ RPtL_3 + RX \longrightarrow R(X)\overset{II}{Pt}L_3 \xrightarrow{-L} R(X)PtL_2 \\ \quad\quad\quad\quad\quad\quad\quad + \boxed{R^.} \end{cases}$

  termination: $2 R^. \longrightarrow R-H + R'$

———————

Reductive Elimination
   favored by high metal ox. stat. & $M \overset{A}{\underset{B}{<}} \longrightarrow M + A-B$
                                         weak M—A(B) bonds
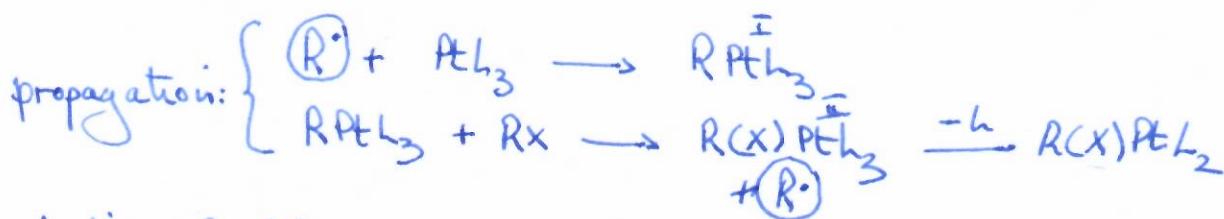
  $L_n M \overset{H}{\underset{H}{<}}$ (microscopic reverse of H_2 ox. addn
                    fast reversible
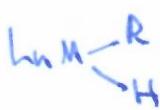
  $L_n M \overset{R}{\underset{H}{<}}$ (mic. rev. of C–H activation, fast & downhill

  $L_n M \overset{R}{\underset{R}{<}}$ (mic. rev. C–C activation,   slow & downhill)

$$R_3 \overset{\text{III}}{Au} L \xrightarrow{\text{DMSO}} R-R + RAuL$$

$L = PPh_3$

crossover exp.

$$(CH_3)_3 AuL + (CD_3)_3 AuL \xrightarrow{\text{DMSO}} CH_3-CH_3 + CD_3-CD_3$$
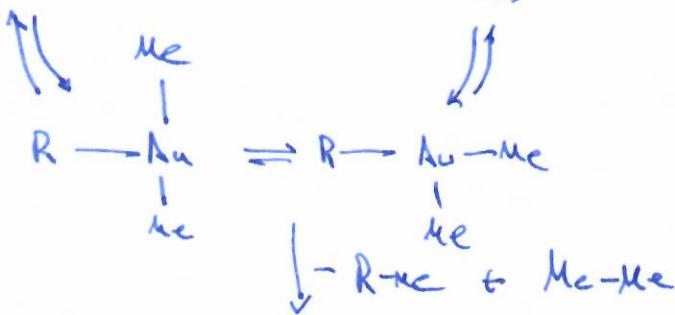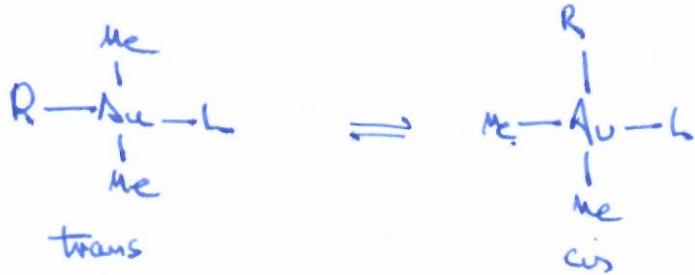
$$\text{no } CH_3-CD_3 \text{ !!}$$

isomerization is faster than red. elim.
and both are inhibited by xs L

elimination of
cis alkyls from
coordinatively unsaturated
intermediate
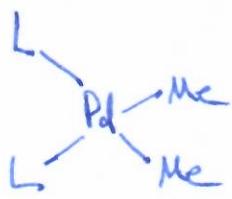
$k = 1 \times 10^{-3} s$
$(60°C)$
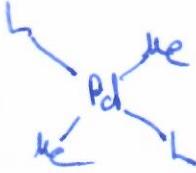
$8 \times 10^{-5} s^{-1}$
$(60°C)$

$5 \times 10^{-7} s^{-1}$
$(90°C)$
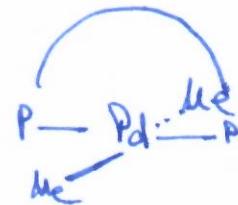
no rxn
at 100°C

Both coordinate unsaturation _and_ cis relationship
seem important

can induce red. elim. by oxidation Kochi

Organomet. 1982, 1, 155

$(bipy)_2 Fe^{II} Et_2$ (18e) $\xrightarrow[t_{1/2} \geq 15d]{\Delta (30°C)}$ $C_2H_6 + C_2H_4 + \text{'Fe'}$ $Fe\overset{\frown}{\frown} \rightarrow Fe-H$

$\downarrow -e^- \ (-0.76V \text{ vs NHE})$

$(bipy)_2 Fe^{III} Et_2 \ ^{+}$ (17e) $\xrightarrow[t_{1/2} \sim 30min]{\Delta}$ $C_2H_6 + C_2H_4 + C_4H_{10}$ typical product mix of Et• radicals

  34%   7%   butane 56%

$\downarrow -e^- \ (+0.06V \text{ vs NHE})$

homolysis of Fe–Et bond

$(bipy)_2 Fe^{IV} Et_2 \ ^{2+}$ (16e) $\xrightarrow[t_{1/2} \sim 10^{-3}s]{\Delta}$ C_4H_{10} !
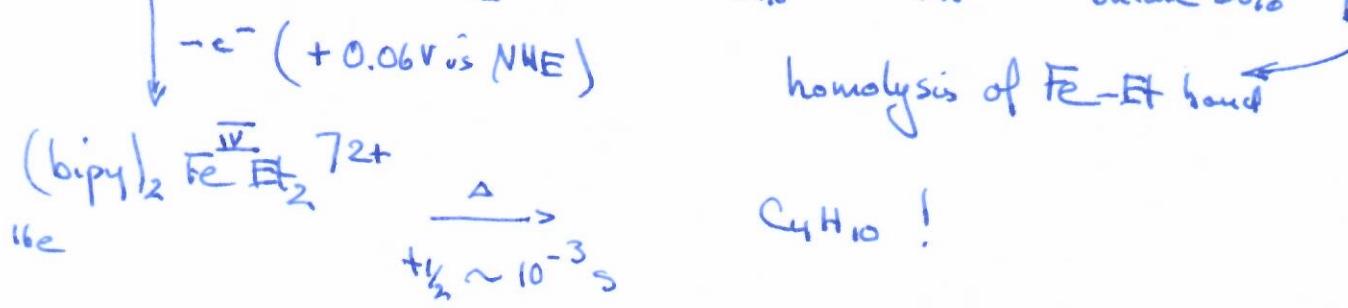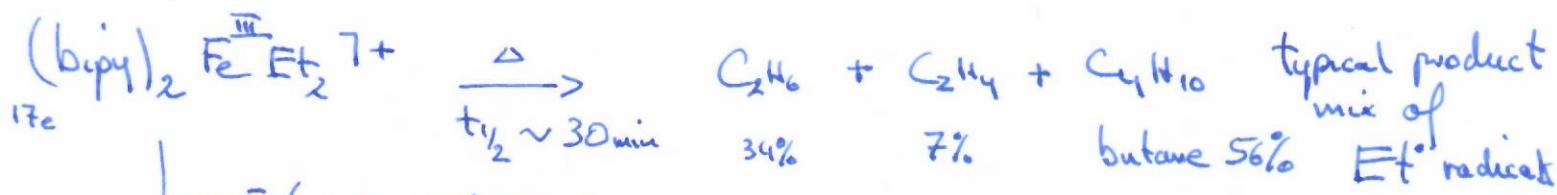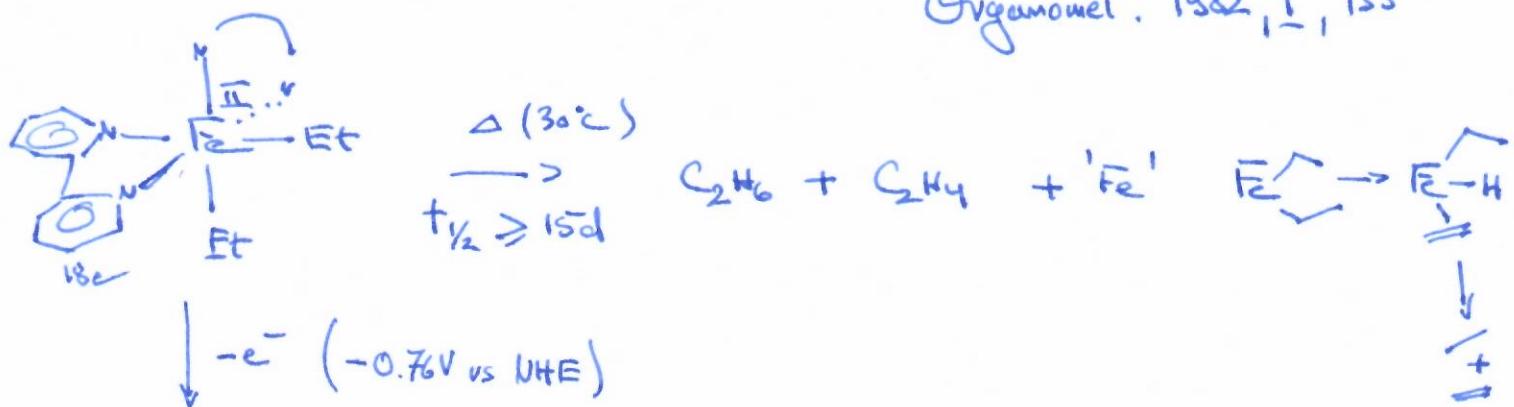
C–H red. elim   classic   J. Halpern   Acc. Chem. Res.

1982, 15, 332

$L = PPh_3$

$Pt(L)_2 H' + CH_4$

$k = 4.5 \times 10^{-4} s^{-1}$

$\dfrac{k_H}{k_D} = 3.3$

crossover : intramolecular !

rate independent of [L]

different!

no coord. unsaturation required

L:

X	Cl	H	Me	OMe
$k \ [\times 10^4 s^{-1}]$	9.2	4.5	1.4	0.47

akin to oxidation

e-withdrawing groups induce red. elim !

$Ph > Et > Me > \searrow$