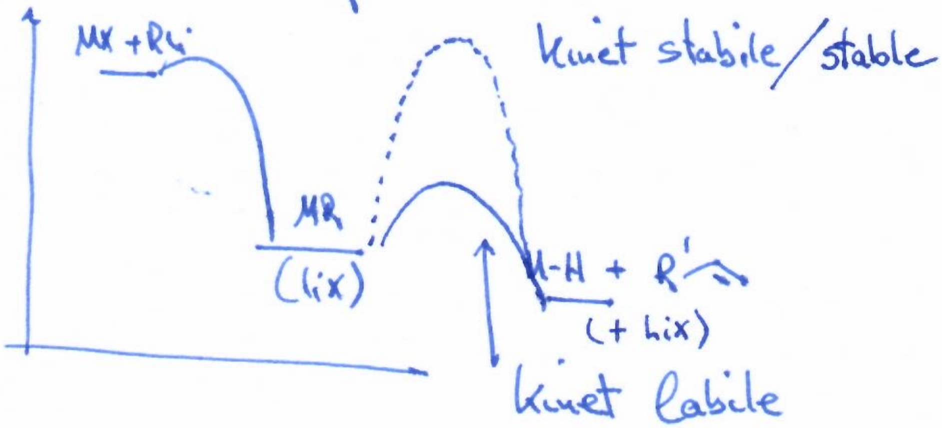
Kinetic stability



read Ch 10.x

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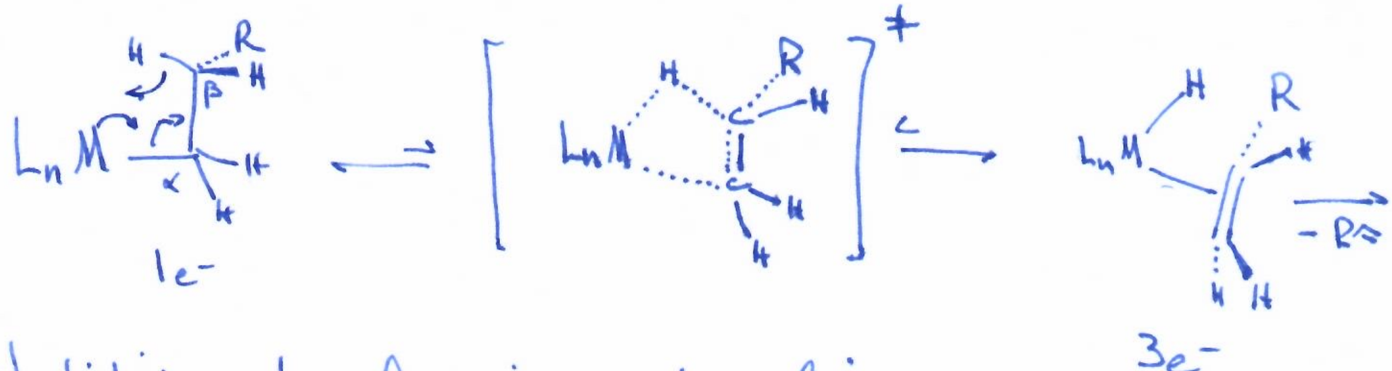
lecture 4 p. 1

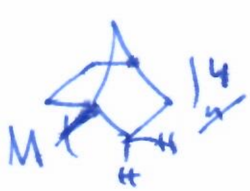
common decomposition pathway:
β-hydrogen elimination



⇒ stabilizing role of ancillary donor ligands
strategies for preventing β-elimination

$-CH_3$, $-CH_2Ph$, $-CH_2CMe_3$, $-CH_2SiMe_3$, Ph
Me, Bn, neopentyl Np, trimethylsilylmethyl

special alkyls
1-norbornyl
(adamantyl)



M: Ti → G

prohibition of bridgehead olefins!

metallacycles

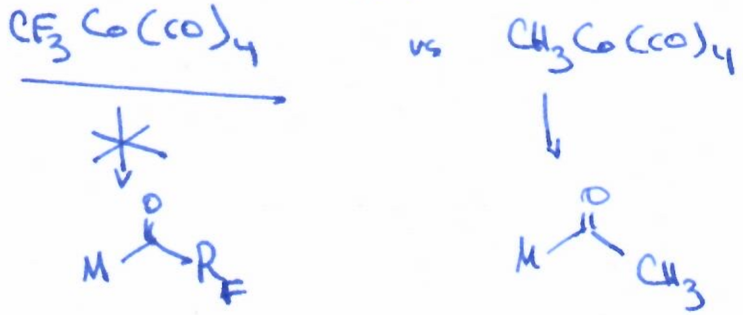
Compare:

hard to get to coplanar TS !

at 120°C $t_{1/2} \sim 0.7$ s $t_{1/2} \sim 22$ min !

perfluoroalkyls much more stable !

M–F >> M–H



Spectroscopy : NMR (for diamagnets)

^1H, ^{13}C, ^{31}P, metal ions

^{103}Rh 100% $I = 1/2$

^{183}W (14.4%) "

$Pt-CH_3$ ⇐ ^{195}Pt (33.8%) " ^{59}Co (100%), $I = 7/2$ quadrupolar

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NMR of paramagnets

— broad resonances, extreme shifts

$\delta_{para} - \delta_{dia}$ = 'isotropic shift' 2 contributions: Fermi contact shift, dipolar shift

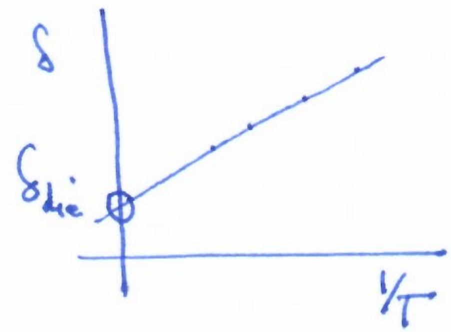
can improve broadness by ^2H-substitution.

refs La Mar, Horrocks, Holm NMR of Paramagnetic Molecules

Bertini, Luchinat NMR of Paramagnetic Molecules in Biological Systems

isotropic shift is T-dependent

$$\chi_m = \frac{C}{T}$$ Curie Law

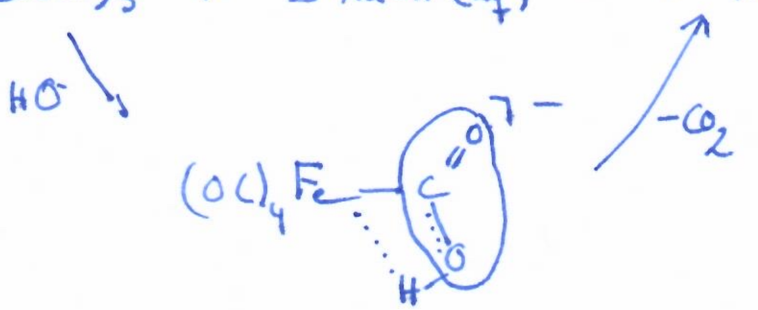


$TpMn^{II}R$

Hydrides

$H_2Fe(CO)_4$ W. Hieber, 1931

$Fe(CO)_5 + 3\ NaOH(aq) \longrightarrow Na[HFe(CO)_4]$



$\downarrow H^+$

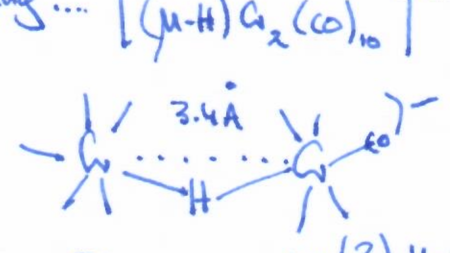
$H_2Fe(CO)_4$ carbonyl hydride

$HCo(CO)_4$

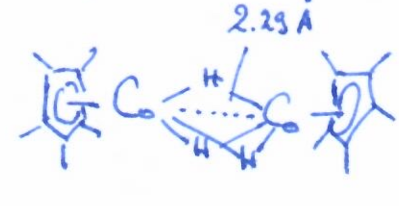
$HMn(CO)_5$

& others: $[Re^{VII}H_9]^{2-}$, $WH_6(PR_3)_3$, Cp_2ZrH_2, $Pt^{II}(H)Cl(PR_3)_2$

bridging.... $[(\mu\text{-}H)Cr_2(CO)_{10}]^-$



34e no(?) M-M bond



$Cp^*Co{=}CoCp^*$

paramagnetic