27.09.

M-H cont'd

Recap:

$M\text{-}H \rightleftharpoons M^- + H^+$ (pK_a)

$M\text{-}H \rightleftharpoons M^\bullet + H^\bullet$ (BDFE)

$M\text{-}H \rightleftharpoons M^+ + H^-$ ($\Delta G^\circ_{H^-}$) — Hydricity

Square scheme:

$L_nM\text{-}H \xrightarrow{\Delta G^\circ_{H^-}} L_nM^+ + H^-$

$L_nM\text{-}H \downarrow pK_a$

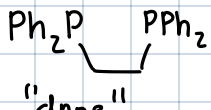
$L_nM^+ + H^- \uparrow E^\circ(L_nM/L_nM^+) + E^\circ(H/H^-)$

$L_nM^- + H^+ \longrightarrow L_nM^\bullet + H^\bullet$

$E^\circ(L_nM^-/L_nM) + E^\circ(H^+/H)$

$\Rightarrow$ NET: $\Delta G^\circ_{H^-} = 1.37\, pK_a(L_nM\text{-}H) + 96.12\left(E^\circ(L_nM^-/L_nM^+) + E^\circ(H^+/H^-)\right)$

Some values



"dppe"

$(dppe)_2Ni\text{-}H^\oplus$ $(dppe)_2Pd\text{-}H^\oplus$

$\Delta G^\circ_{H^-}$	$\Delta G^\circ_{H^+}$
62.8	76.7
52.8	

↓ more hydritic, less acidic

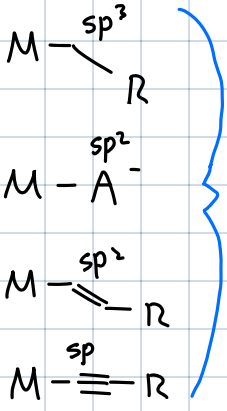
much more likely to give up H^+, as already cat.

$\Rightarrow$ just the inverse trend as for acidity

↳ most hydritic are 3rd row, e^- donating L, low ch.

↳ (in same group)

M-C (organometallics)



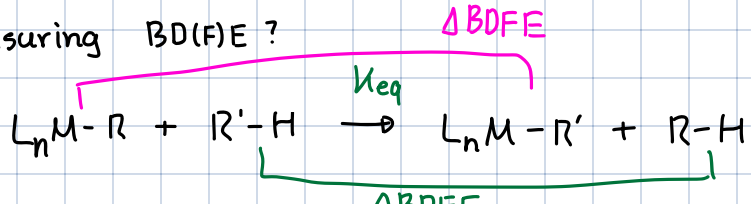
X-type

↝ Gen. trends:

i) $BD(F)E_{M\text{-}R} \approx \frac{1}{2} BD(F)E_{C\text{-}H}$

ii) 1:1 correlation in trends

↝ Measuring BD(F)E?



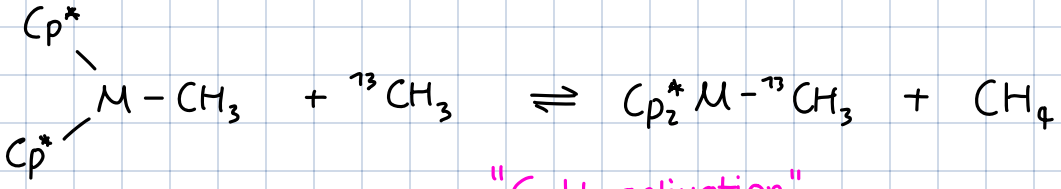
unknown $\Rightarrow$ can be calc.

known

⇒ But how do we exchange these two X-type ligands?

↳ σ-bond methatesis (σ-BM)

Not easy to do, only few examples:



"C-H activation"

M(III), d°, 14e⁻

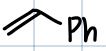
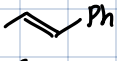
M = Y, Lu

Rate Study k_{rel}

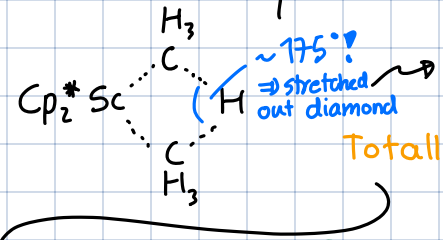
					k / $M^{-1}sec^{-1}$
$Cp^*_2Sc^{III}-CH_3$	+ $^{13}CH_4$	⇌	$Cp^*_2Sc^{III}-^{13}CH_3$	+ CH_4	10^{-5}
"	+ H_2	⇌	" – H	+ CH_4	10
" – H	+ D_2	⇌	" – D	+ H-D	10^3

↳ greater s-character ⇒ faster

↳ Can go even further

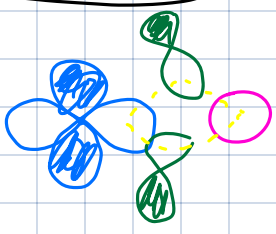
					k
$Cp^*_2Sc-CH_3$	+ 	⇌	Cp^*_2Sc  + CH_4		$10^{-3}\ M^{-1}s^{-1}$
"	+ H–≡–CH_3	⇌	Cp^*_2Sc–≡–CH_3 + CH_4 (sp)		$10^{-2}\ M^{-1}s^{-1}$

So we want to find the explanation:



Totally sym. disallowed BUT avail. d-orb.

Orb. view:



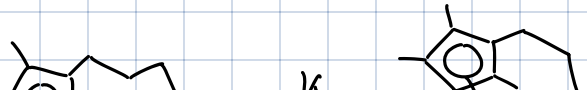
orbitally continuous

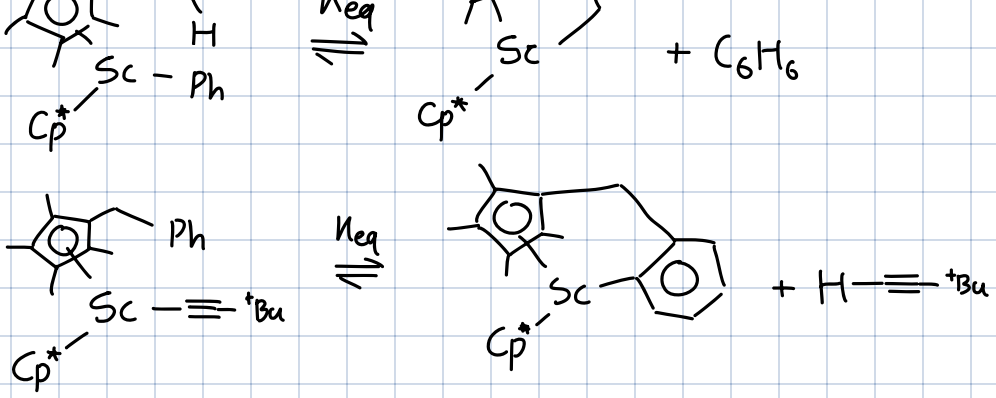
↳ What do we need?

- d° metal

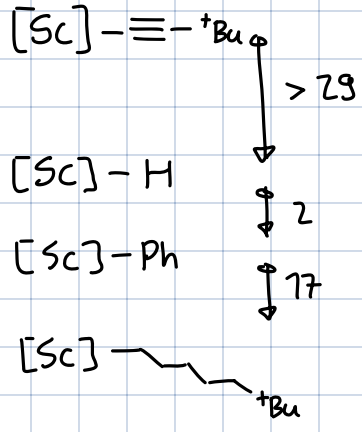
Problem: $Cp^*_2Sc-Ph + R-H \rightleftharpoons Cp^*_2Sc-R + C_6H_6$

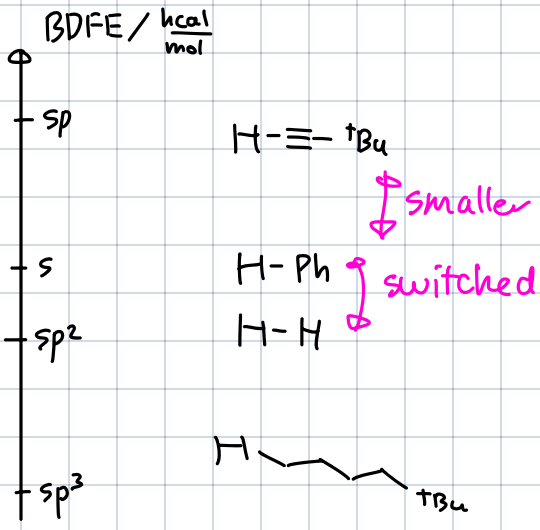
↳ Approach:





⇒ Can get a BDFE ladder:





⇒ Why are metal hydrides so strong?

→ Because $M^+ H^-$ ⇒ strengthens the bond and differences are magnified