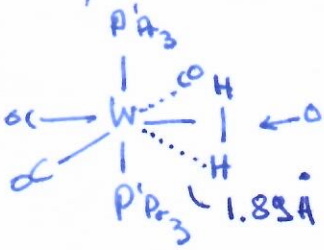
'dihydrogen complexes'

recent review:
R.H. Crabtree Chem Rev 2016, 116, 8750

1984, G. Kubas JACS 1984, 106, 451

book: G. Kubas - Metal Dihydrogen .... Kluwer 2001



← 0.84 Å neutron diff (0.80 – 1.00 Å)

a 'σ-complex'

Lecture 6

^{1}H-NMR: δ 0 → −10 ppm (J_{H-D}: 20 – 34 Hz

43 Hz for free HD

< 2 Hz for M(H)(D)

$T_{1,min}$ < 100 msec !

IR: ν_{H-H} ~ 2300 – 2900 cm^{-1} (4342 cm^{-1}, free H_2)

$M(\eta^2\text{-}H_2) \rightleftharpoons M\text{-}H^- + H^+$

pK_a ~ 0 – 15 free H_2 ~ 35

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agostic interactions!

M. Brookhart / M. Green

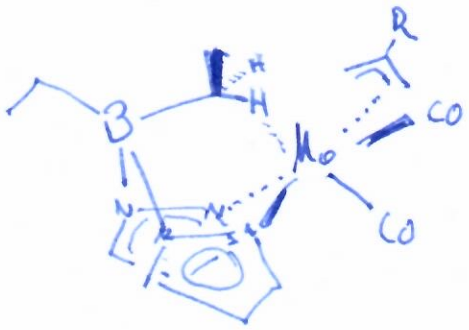
M···H···C 3c-2e bond

typically intramolecular

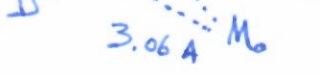
PNAS 2007, 104, 6908 intro & history

Prog. Inorg. Chem 1988, 36, 1

first example: F.A. Cotton JACS 1974, 76, 754 & 5074 made by J. Trofimenko



close M-H interaction



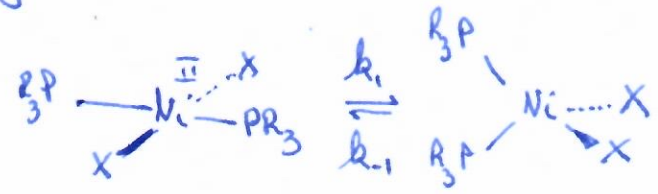
^{1}H-NMR: −3.8 ppm (br)

upon cooling splits into two !?

Fluxional Processes / Dynamic NMR

Kap 10.5

J. Sandström 'Dynamic NMR spectroscopy'



Heisenberg $\delta\nu = \frac{1}{2\pi\delta t}$ lifetime broadening

lifetime $\hat{=}$ $\delta t = \frac{1}{k_1}$

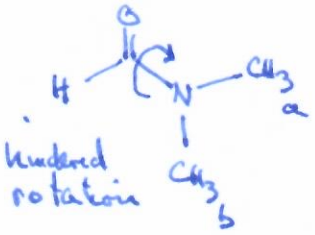
width of ^{1}H-NMR signal ~ 1–2 Hz = 1–2 s^{-1} $\Rightarrow \delta t$: 1 – 0.5 s

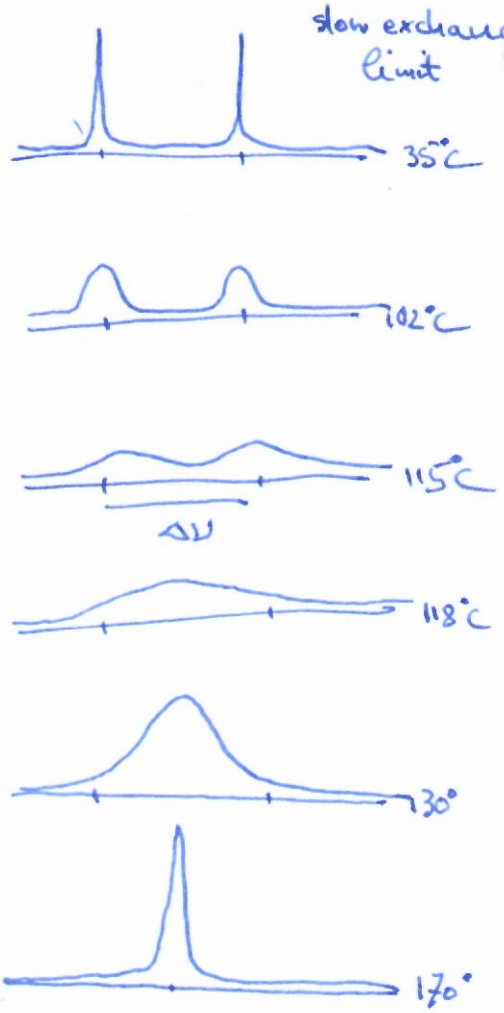
$\Rightarrow$ for processes w/ shorter lifetimes

δt: 10^{-1} – 10^{-3} s

~ rates of 10 – 10^3 s^{-1}

phenomenon: Coalescence of resonances





temperature of Coalescence, T_c

at high T rotation is fast on the NMR timescale

simulate line shapes to get rate constants

→ Eyring analysis, $\Delta H^{\neq}$, $\Delta S^{\neq}$

rules of thumb:

a) $k_c = \frac{\pi}{\sqrt{2}} \cdot \Delta\nu = 2.22 \cdot \Delta\nu$ at T_c!

b) $\Delta G^{\neq} = 50 \cdot T_c$ (in K!)

$\Delta G^{\neq} = 50 \cdot (118 + 273.15)$

$= 19550$ cal/mol

$= 19.6$ kcal/mol

Compare to $\Delta G^{\neq} = 20.2$ kcal/mol from full line shape analysis

$\Delta G^{\neq} = 10.5$ kcal/mol

IR: ν_{C-H} 2704, 2664 cm^{-1}

^{1}H-NMR: