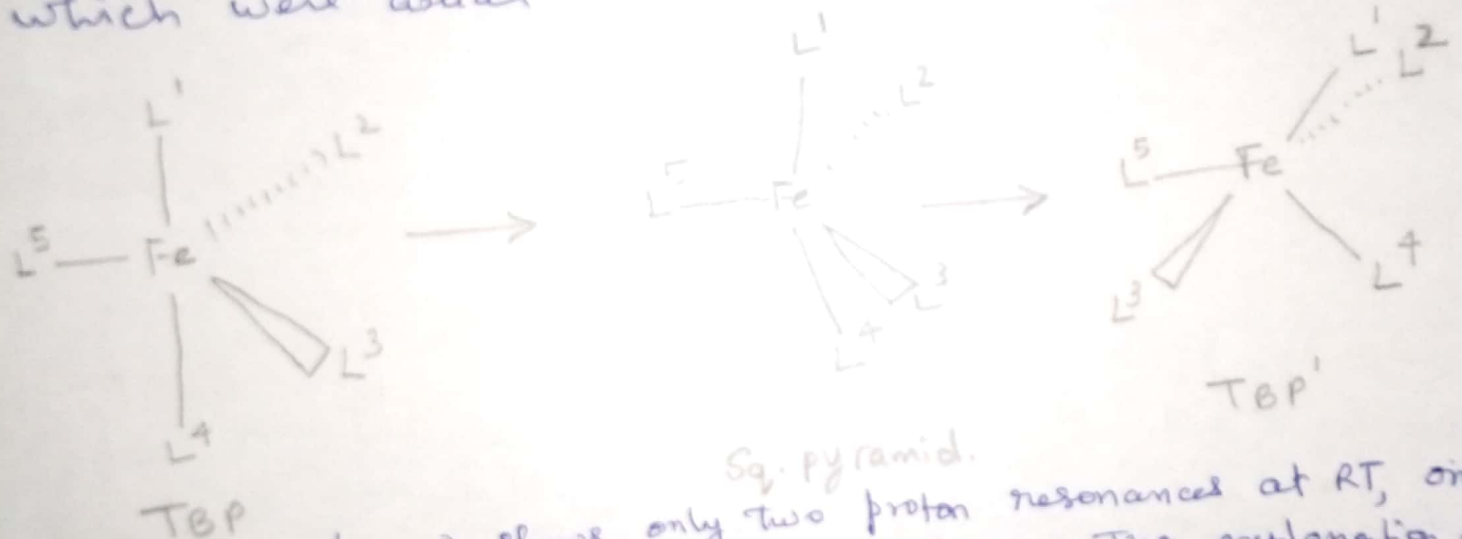
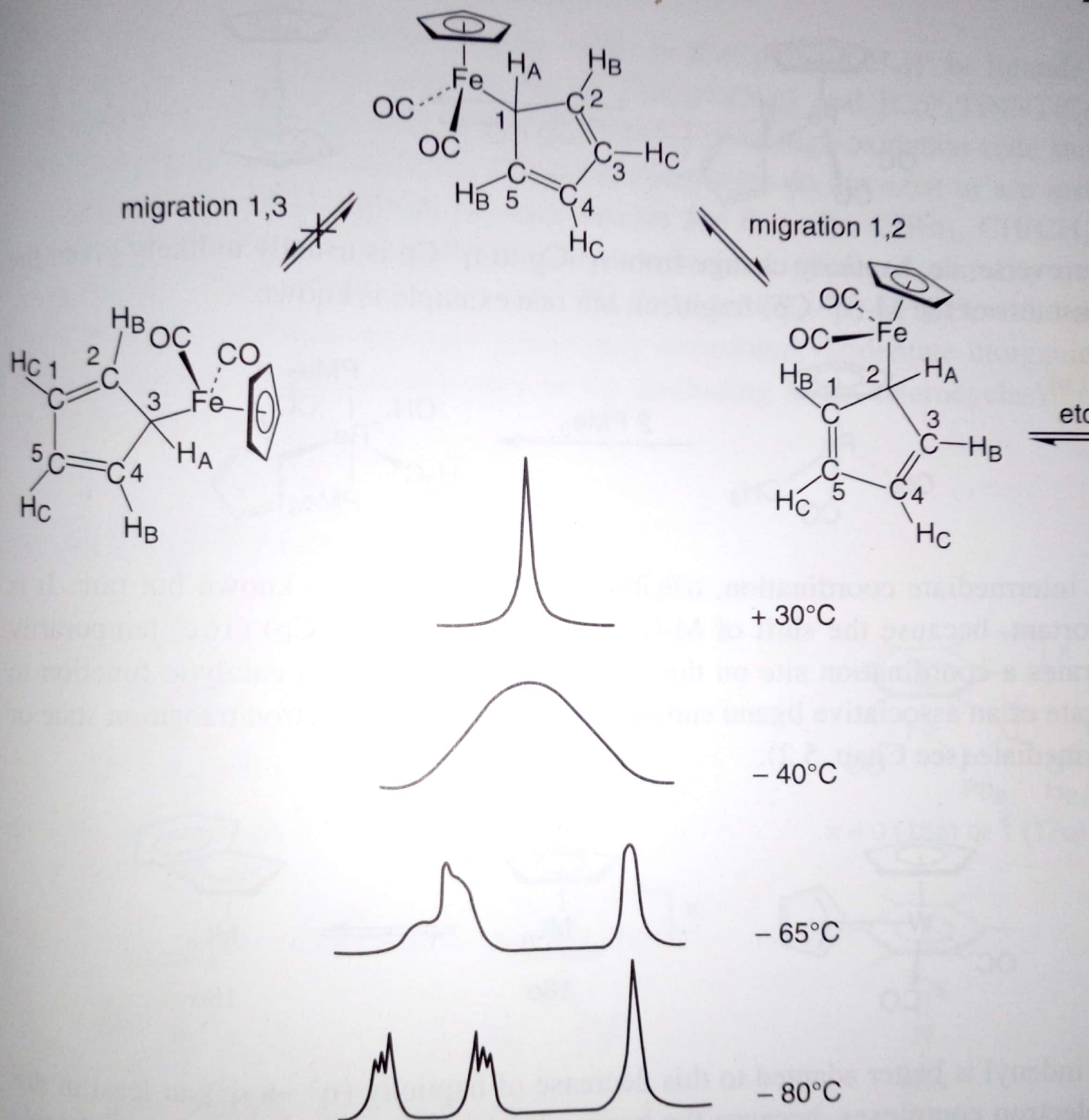


① Many organometallic species give fewer NMR resonances than would be predicted from their static structures. This is usually because the molecules are non-rigid and the nuclei concerned are exchanging places at a rate faster than NMR timescale (10^{-1} - 10^{-6} s).

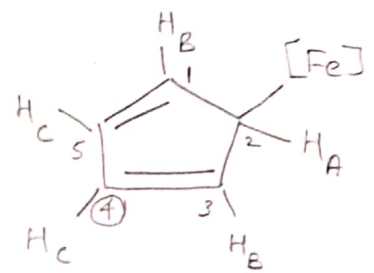
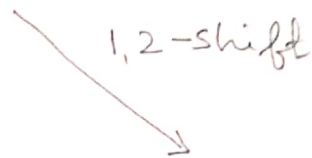
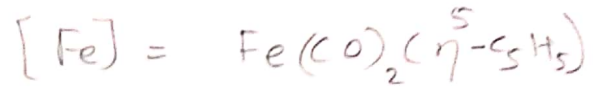
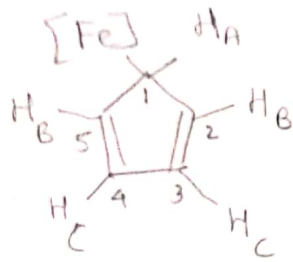
For example, $\text{Fe}(\text{CO})_5$ gives only one carbon resonance at 25°C and yet its IR spectrum (a technique with the much faster timescale of 10^{-12} s) indicates a TBP structure with two types of carbonyl. The reason proposed by Berry, is that the axial and equatorial carbonyls are exchanging by the Berry Pseudorotation mechanism shown below. Ligands 1-4 become equiv. in the square pyramidal intermediate, and 1 and 4, which were axial in TBP, become equatorial in TBP'.



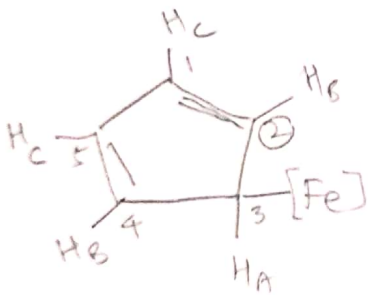
b) $\text{Cp}^*_2\text{Fe}(\text{CO})_2(\eta^1\text{-C}_5\text{H}_5)$ shows only two proton resonances at RT, one for the $\eta^1\text{-C}_5\text{H}_5$, and one for the $\eta^5\text{-C}_5\text{H}_5$. The explanation is that the iron atom is migrating around the $\eta^1\text{-C}_5\text{H}_5$ ring. On going to lower temperature, separate resonances can be distinguished for the three different types of proton in the static $\eta^1\text{-C}_5\text{H}_5$ group. If we warm the sample from the low temp limit, there will be a different degree of initial broadening of the different proton resonances of the $\eta^1\text{-C}_5\text{H}_5$ group if the fluxionality involves 1,2-shifts rather than 1,3-shifts.



Variable-temperature $^1\text{H-NMR}$ spectrum of the fluxional η^1 -Cp ligand of the complex $[\text{Fe}(\text{CO})_2(\eta^5\text{-Cp})(\eta^1\text{-Cp})]$



1,3 Shift



H_B = less initial line broadening

Rate of exchange of $H_C = \frac{1}{2}$ Rate of exchange of H_B

$H_C \Rightarrow$ less initial line broadening

Exptl = 1,2-shift.

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