# Chemistry 423 Fall 2016
Assignment 3 Key

1 (a) $\Delta\delta$ is about -3.5 ppm for the 373 K spectrum, so these alkene protons are far upfield of the 'normal' position. The most likely explanation is rehybridization of the alkene C from sp^2 towards sp^3 with a structure closer to a metallacyclopropane than an alkene:

Since Rh is electron rich (as Rh(I)) and Cp is primarily a donor, most of the back donation should go to the ethylenes.
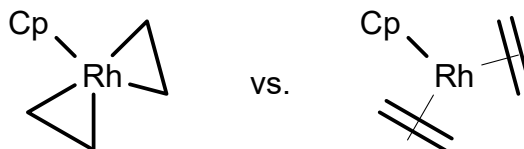
(b) At 233 K, the low T limit has probably been reached since we can clearly see fine coupling on each resonance. The 'inside' (*i*) and 'outside' (*o*) protons of each ethylene are chemically inequivalent so we expect two resonances. The two ethylene units are related to each other by a mirror plane and are therefore equivalent. At the very least, we should expect each inequivalent ethylene resonance (*o* or *i*) to show a large coupling to ^{103}Rh (100%, I = ½) giving rise to a basic doublet pattern as observed. Fine coupling can then be expected between the inequivalent *o* and *i* protons ($^2J_{Ho-Hi}$, *geminal*). In fact, the two *i* (and two *o*) protons are actually magnetically inequivalent so this is an AA'BB'X spin system (for those of you familiar with these descriptors).
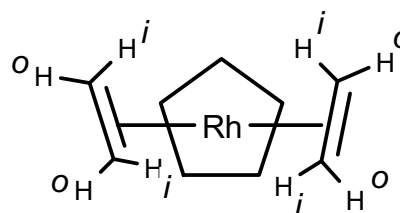
(c) We have probably not reached the high T limit yet as the peak is still very broad. What we see at the high T limit depends on the process that is exchanging the proton resonances of the ethylene unit. If this involves ethylene dissociation then a sharp singlet will be observed with no ^{103}Rh coupling. If the process actually involves ethylene rotation about the Rh-alkene bond (exchanges *o* and *i*), then a sharp doublet with an average $^2J_{Rh-H}$ coupling constant (average of that seen for the δ 2.9 and 1.1 ppm resonance in the 233 K spectrum) will be observed. The latter is actually the case here.
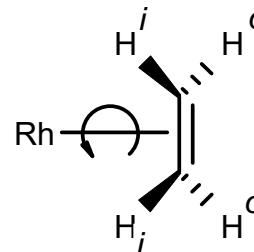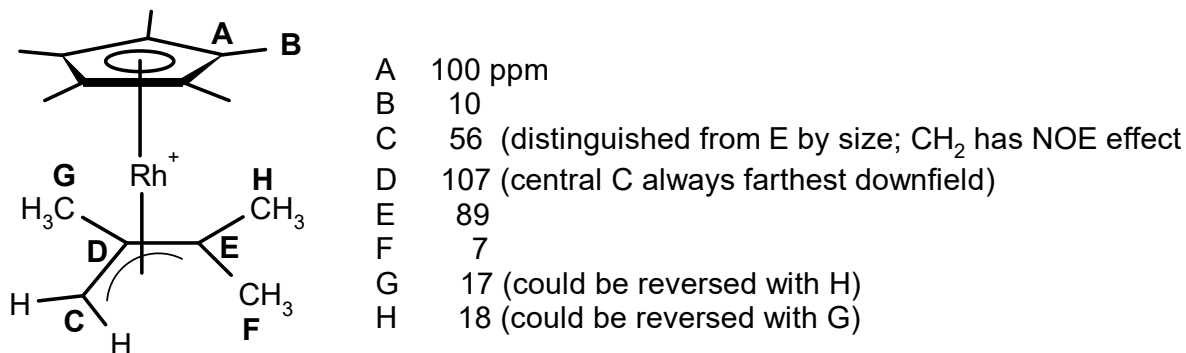

(d) ΔG^* can be calculated from the T_c value and δv in the 233 K spectrum.

  T_c = ca. 333 K, δv = (2.90-1.05 ppm)(200 Hz/ppm) = 370 Hz

  $\Delta G^* = (1.912E-2)(333)[9.972 + \log(333/370)] = 63.2$ kJ mol^{-1} = 15.1 kcal mol^{-1}

2 (a)

A	100 ppm	
B	10	
C	56	(distinguished from E by size; CH_2 has NOE effect
D	107	(central C always farthest downfield)
E	89	
F	7	
G	17	(could be reversed with H)
H	18	(could be reversed with G)

(b) Coupling between a metal and a π-bound ligand C is usually quite small (low s character). In this case, the coupling constant is so small that it is close to the spectral resolution.

(c) At this temperature we only see the Cp* carbons and a peak coresponding to **G/H** (at an averaged position). All other peaks are missing. From this we can assume that we are near coalescence for a dynamic process that exchanges **C** with **F** and **D** with **E**. The reason we already see a sharp peak for **G/H** is because the $\delta\nu_{G/H}$ is very small in the low T limit; *i.e.*, we are already well above T_c for this pair of resonances.

(d) We can't measure ΔG* very accurately from the information given but we can get a range of values representing the probable maximum and minimum. We can do this by noting that the 203 K spectrum shows no peaks for the **C/F** and **D/E** pairs and is reasonably assumed to be close to T_c for both sets:

$\delta\nu_{CF} = 49\ (100.8) = 4939$ Hz
$\Delta G^*_{CF} = (1.912E\text{-}2)(203)[9.972 + \log(203/4939)] = 33$ kJ mol^{-1}

$\delta\nu_{DE} = 18\ (100.8) = 1814$ Hz
$\Delta G^*_{DE} = (1.912E\text{-}2)(203)[9.972 + \log(203/1814)] = 35$ kJ mol^{-1}

So ΔG* is likely in the range 33-35 kJ mol^{-1}

NB: Using a value of 34 kJ mol^{-1} we can solve for T_c related to coalescence of **G** and **H**. This gives a T_c value of 173 K for **G/H** exchange, so as expected we are well above T_c for this process at 203 K.

(e) Since **C/F**, **D/E** and **G/H** exchange in pair wise fashion, the position of the η^3-allyl must be shifting. In other words, a proton shift from the methyl group **F** to allyl carbon **C** must be occurring. Note also that **I** and **II** are enantiomers so this process causes racemization.

(f) The two invariant resonances are those of the Cp* group. The Cp* group must be rotating rapidly at all temperatures.

(g) CD_2Cl_2 — D has I = 1 so the number of lines in the ^{13}C NMR will be 2nI+1 = 5.

I ⇌ II
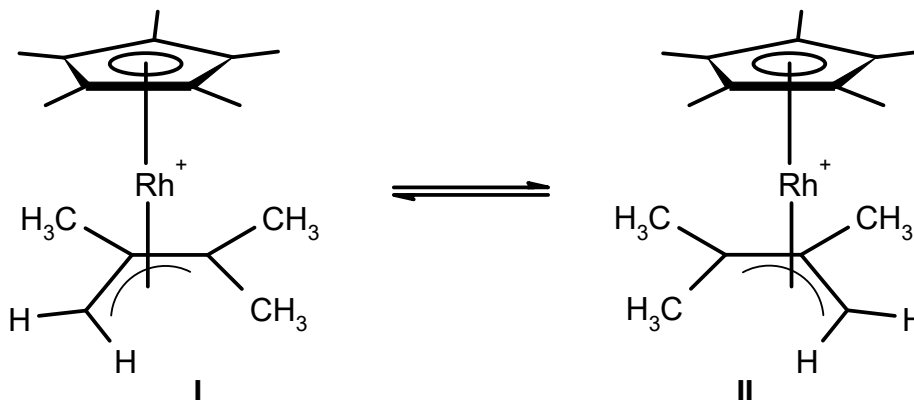
3 (a) This 16 e- complex is very likely to add a donor such as $P(OMe)_3$ and give an 18 e- octahedral species. The question is: where does the $P(OMe)_3$ enter the equatorial plane of the trigonal bipyramid? Consider the three options:
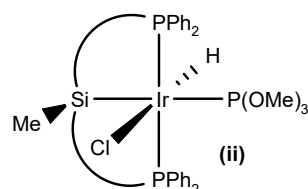
(i) between Si and Cl gives:

Hydride should be a dt with a large $^2J_{PH}$ coupling to $P(OMe)_3$ (*trans*) and a small $^2J_{PH}$ coupling to PPh_2 (*cis*)
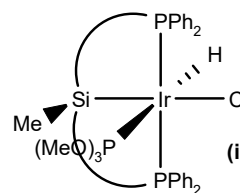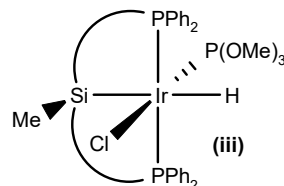

(ii) between H and Cl gives:

Hydride should only show small $^2J_{PH}$ couplings to two equivalent PPh_2 and one $P(OMe)_3$ (*all cis*)


(iii) between Si and H gives:

Hydride should again only show small $^2J_{PH}$ couplings to two equivalent PPh_2 and one $P(OMe)_3$ (*all cis*)


The initial compound shows a quartet at –20 ppm. This is inconsistent with **(i)** but could be consistent with either **(ii)** or **(iii)** if $^2J_{PH}$ is the same (or very close) for both coupling to PPh_2 and $P(OMe)_3$. This is quite reasonable given the fact that all three P are *cis* to H and trivalent. The observation of a doublet for the SiMe group is unusual and implies coupling with a unique P. Most likely this P is the $P(OMe)_3$ group

located in a position *trans* to the Si. In other words, the kinetic product is **(ii)**. The thermodynamic product shows a clear dt pattern and is consistent with **(i)** only.
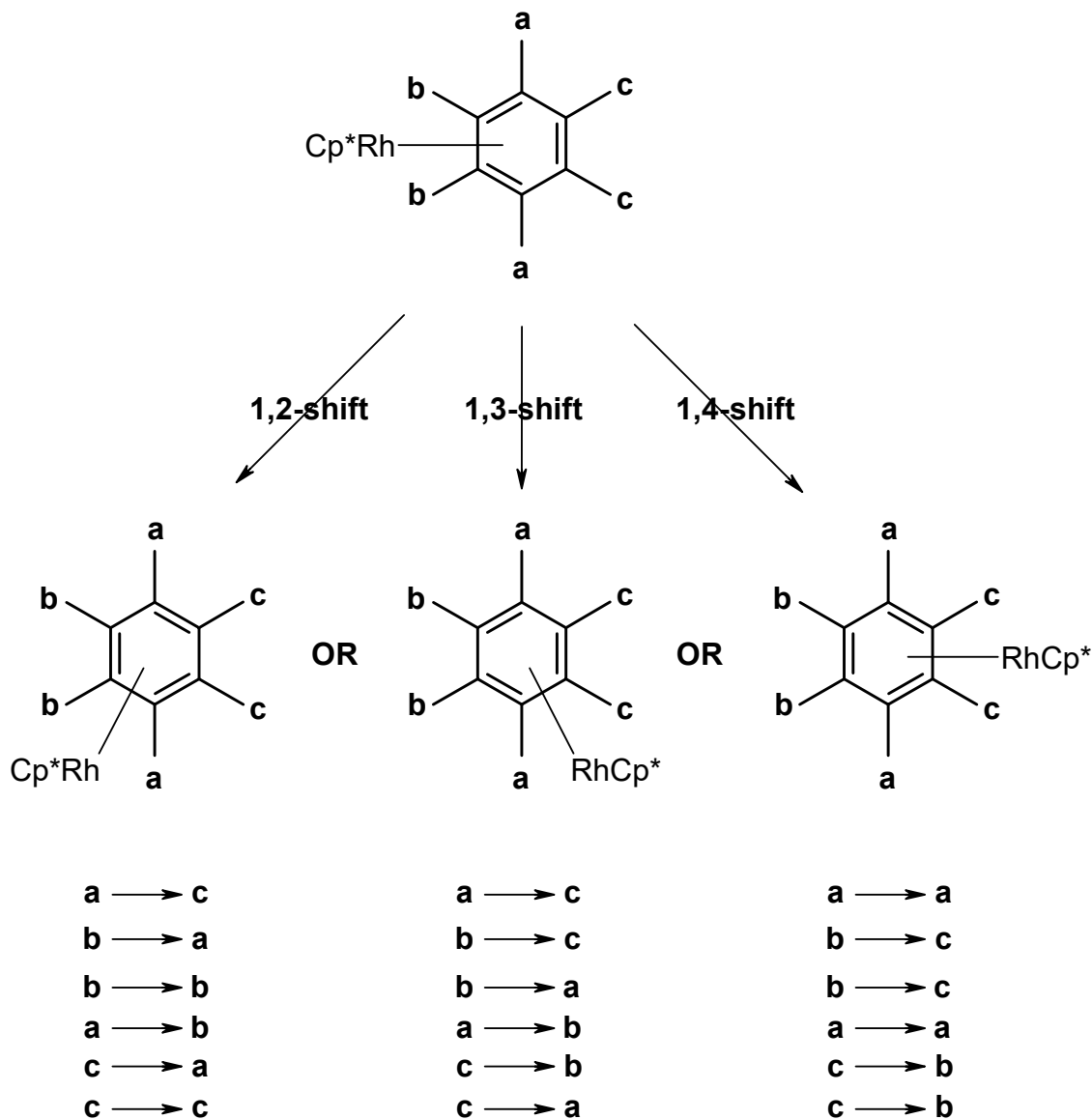
(b) The ligand set contains several powerful *trans effect* (and *trans influence*) ligands: R_3Si^-, H^-, $RPPh_2$. This results in increased lability of the 6th ligand and provides stabilization (in a relative sense anyway) of the 5-coordinate precursor complex.

(c) The rearrangement can be rationalized by reversible dissociation of $P(OMe)_3$ (favoured by the strong trans effect ligands).

$$\Delta G^*(i) > \Delta G^*(ii) \quad \text{but} \quad \Delta G^\circ(ii) > \Delta G^\circ(i)$$
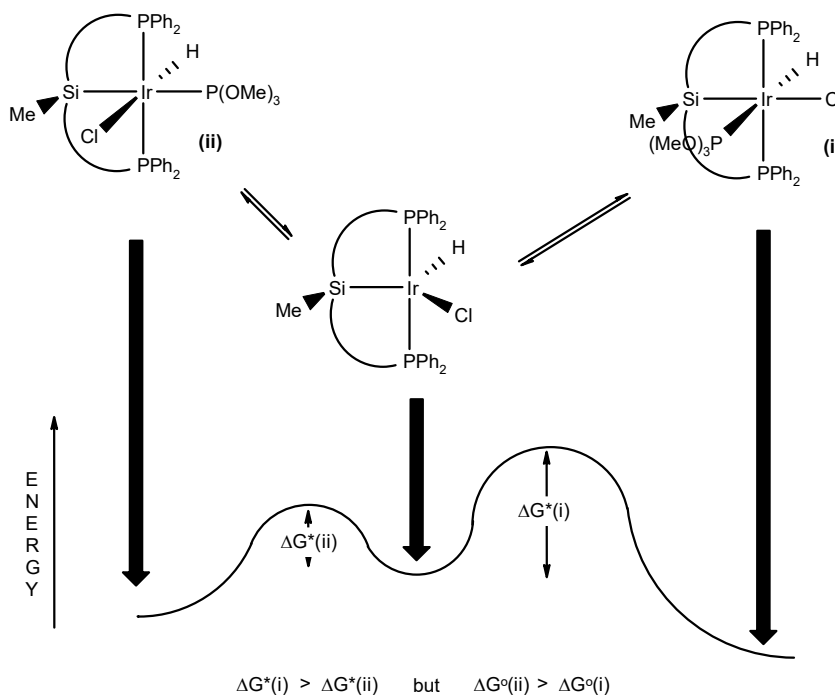
4 (a) The electron count in this complex is 20e$^-$ if it contains a η^5-Cp* and a η^6-C$_6$(CO$_2$Me)$_6$ ring. Since there are obviously inequivalent ester methyl groups, it makes sense to assume that the arene is bound η^4 rather than η^6. A structure that accommodates the electron count and NMR spectrum is shown below:
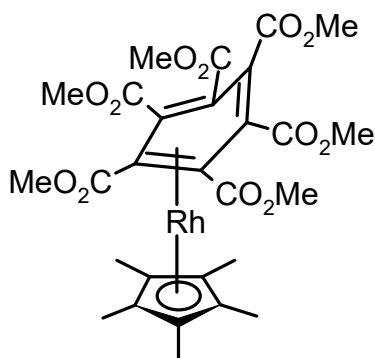
(b) The methyl groups on the Cp* ring remain unchanged with temperature while the ester groups exchange. This observation can be explained by the Cp*Rh group moving about the face of the benzene ring. This shift could occur randomly or it could occur by a **1,2-** (one bond), **1,3-** (two bond) or **1,4**-shift (three bond) as shown below:

1,2-shift   **1,3-shift**   **1,4-shift**

OR   OR

| a ⟶ c	a ⟶ c	a ⟶ a
b ⟶ a	b ⟶ c	b ⟶ c
b ⟶ b	b ⟶ a	b ⟶ c
a ⟶ b	a ⟶ b	a ⟶ a
c ⟶ a	c ⟶ b	c ⟶ b
c ⟶ c	c ⟶ a	c ⟶ b

(c) If the scrambling were occurring via a random process, each signal would broaden at an equal rate. This is not observed so a random process is ruled out. A **1,4**-shift does not exchange '**a**' resonances at all so this can also be ruled out. A **1,3**-shift broadens all methyls at the same rate as shown by the transformation table above; this is not observed so a **1,3**-shift is ruled out. A **1,2**-shift exchanges '**a**' resonances at twice the rate of the '**b**' and '**c**' signals consistent with the observed broadening behaviour.

5   The NMR spectrum of the static (low T) structure should show three types of carbonyls, one terminal and two bridging. Note that the bridging carbonyls are not equivalent: one is cis to Cp and the other is cis to CO. The terminal CO should appear as a doublet since it is coupled to only one [103]Rh (100% nat. abundance). The two bridging CO's will be triplets due to coupling with two [103]Rh:
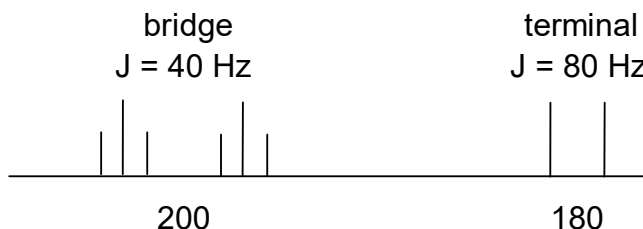
The fluxional process scrambles the three CO's over all three Rh centres but does not exchange CO across the face. This can be accommodated by a transient non-bridged structure between different edge-bridged carbonyl isomers:
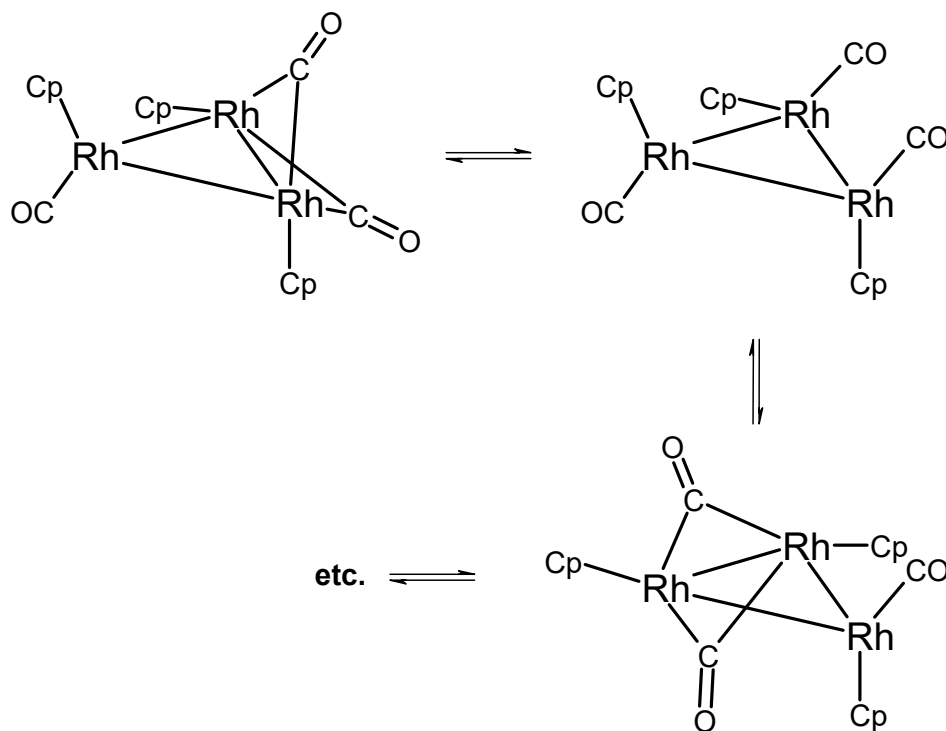
By this mechanism, the unique CO on the bottom face of the Rh_3 triangle is always bridging in the ground state structures while one CO is bridging and one CO is terminal for the top face CO's. This process makes all three Rh equivalent in the high temperature limit but the CO's will remain in a 2:1 ratio for the two unique Rh_3 faces. The unique bottom face CO will be at approx. 200 ppm because it is in a bridging position in all

ground state structures. The top face CO's will appear at the average of a bridging (200 ppm) and a terminal (180 ppm) CO position, i.e. at 190 ppm. Since all CO scramble over three Rh centres, they will all appear as quartets. The coupling constants for each type of CO are calculated as the average of the contributing isomers:

Unique (bottom face) CO:

J_{Rh1-C} = 40 Hz
J_{Rh2-C} = 40 Hz
J_{Rh3-C} = 0 Hz
$J_{Rh(ave)-C}$ = 27 Hz

Equivalent (top face) CO's:

Bridging		Terminal	
J_{Rh1-C} =	40 Hz	J_{Rh1-C} =	0 Hz
J_{Rh2-C} =	40 Hz	J_{Rh2-C} =	0 Hz
J_{Rh3-C} =	0 Hz	J_{Rh3-C} =	80 Hz
$J_{Rh(ave)-C}$ =	27 Hz	$J_{Rh(ave)-C}$ =	27 Hz

Average for the top face CO's is therefore 27 Hz as well.

bottom face   top face
J = 27 Hz   J = 27 Hz

200   180
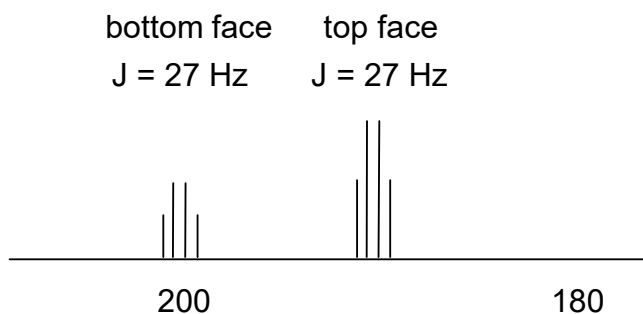
6   Compound **A** is a simple alkyl complex and should not have any resonances upfield of TMS so it can be eliminated as a possibility. Both **B** and **C** could give rise to an upfield (-12.6 ppm) resonance but **C** is highly symmetric and should show only five proton resonances. Since far more than five resonances are clearly observed, we conclude that **B** is the more likely structure. Note also that there is a carbon coupled to the upfield proton with a J value of 85 Hz. This is consistent with an agostic C-H group.

A simple dynamic process exchanging the upfield proton with a resonance in the 1.5 ppm region could involve breaking of the M-agostic H bond on one side of the allyl and reforming it on the other side:

H^b H^b H^b
H^a H^a H^a
$(CO)_3Mn$ $(CO)_3Mn$ $(CO)_3Mn$

18 e⁻   **16 e⁻**   **18 e⁻**
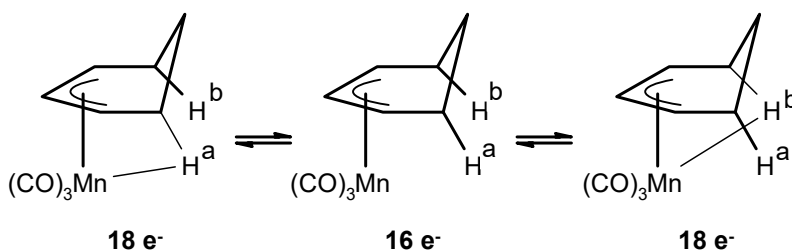
7   a) ^{19}F spectra show one peak that is T invariant. This must be the para-F resonance (*see (b)*). Note this resonance is a sharp triplet at 297 K so this means it is only coupled to two adjacent F, most likely those in the meta position. The implication is that J (ortho-para) is zero. Thus the observation that the other resonance in the 297 K spectrum on the right is not a simple triplet (note broadness of the resonances) implies that it is due to the meta-F. This means the ortho-F are those represented in the lower left 233 K spectrum. This also makes sense intuitively because we might expect a greater distinction between the ortho-F at low T than between the meta-F since they are closer to the metal and any distinguishing ligands.

b) The variable temperature NMR spectra are consistent with restricted rotation about the N-C$_{aryl}$ bond because the para-F resonance remains T invariant. It must do so because it lies on the axis of rotation. If this were a case of two distinct C$_6$F$_5$ groups being inequivalent at low T, then all three aryl F positions would show T dependent resonances.
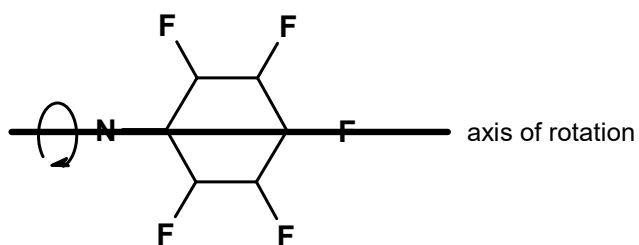
c) $\Delta G^* = (1.912E\text{-}2)(283)[9.972 + \log(283/2169)] = 49$ kJ mol^{-1} using $T_c = 283$ K (ortho-F) and $\delta v = (6.4)(338.86) = 2169$ Hz

d) Calculate rate constants for the upper four temperatures (the lower left 233 K spectrum is the low T limit):
$k(297) = [\pi(2169)2]/[(450\text{-}60)(21/2)] = 26796$ s^{-1}
$k(283) = [\pi(2169)]/(21/2) = 4818$ s^{-1} (this is T_c)
$k(273) = \pi(450\text{-}65) = 1209$ s^{-1}
$k(253) = \pi(120\text{-}65) = 173$ s^{-1}

linear regression on $\ln(k/T)$ vs. $1/T$ gives:

slope = -8342 $\Delta H^* = (\text{-}8.314)(\text{-}8342)(1E\text{-}3 \text{ kJ/J}) = 69$ kJ mol^{-1}

intercept = 32.37 $\Delta S^* = [32.37 + \ln(h/k_b)](8.314) = 72$ J mol^{-1} K^{-1}

as a check: $\Delta G^*(283) = \Delta H^* - T\Delta S^* = 69 - 283(72)(1E\text{-}3) = 49$ kJ mol^{-1} which agrees with the value calculated from T_c.

These values are consistent with rotation about a single bond: ΔH^* is a function of steric effects and can be quite large; ΔS^* is fairly large and positive as expected for increased freedom of rotational motion in the transition state.

The molecule is quite crowded, especially due to the N(SiMe$_3$)$_2$ group so restricted rotation is not a big surprise.