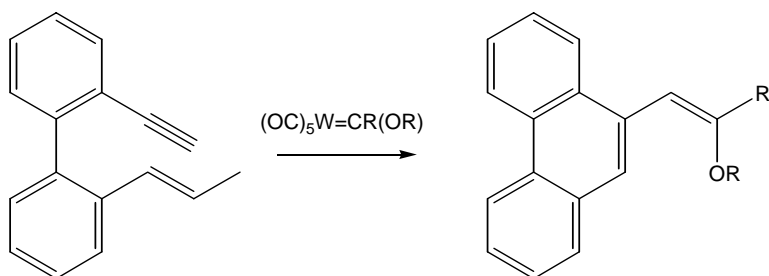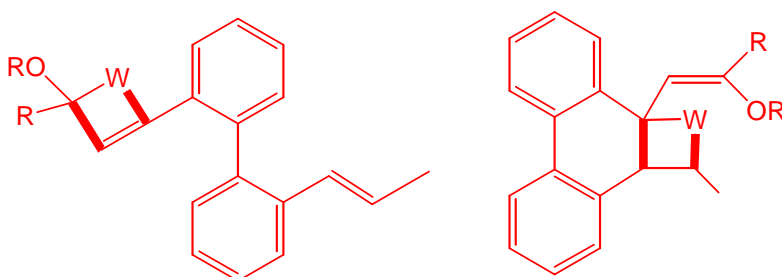**423/523 Organometallic Chemistry**
Problem set 8

1. Propose a mechanism for:

Olefin metathesis. The cyclobutane (or -ene) intermediates are shown below, the bold lines indicating the new bonds forming at each step.

2. In principle, cyclopentene might metathesise to 1,6-cyclodecadiene (cdd). In fact, a polymer is formed. What is the structure of the polymer, and how does its formation, rather than that of cdd, relate to the question of pairwise versus non-pairwise mechanisms?
The polymer is simply $-[HC=CH-(CH_2)_3]_n-$; a pairwise mechanism would predict the formation of cdd, non-pairwise (the correct, Chauvin mechanism) polymer.

2. In some $TiCl_3$-based polymerization catalysts, a small amount of $NiCl_2$ is added to shorten the chain length of the polymer. What is the role of the Ni? What is the structure of the end group when the polymer dissociates from the Ni-doped catalyst? What might be the effect of the additives $FeCl_3$, $HgCl_2$ and VCl_5?
For polymerization, must avoid β-elimination; Ti is d^0 so does this well. If the chain is transferred to a Ni cocatalyst it will β-eliminate and so a shorter chain will result. Fe should work but V is too early and Hg too late.

3. Two chemically inequivalent hydrides, H_A and H_B, in a metal dihydride complex at 50°C, resonate at δ −5 and −10 ppm, respectively, and are exchanging so that each resonance shows an initial broadening of 10 Hz at a field corresponding to 500 MHz. What is the rate of exchange? At 80°C we observe coalescence; what is the new rate of exchange?
$π × 10 = $ **31 s^{-1}**; $π × 2500 / \sqrt{2} = $ **5550 s^{-1}**.

4. Allyl complexes are characteristically fluxional, the principle pathway being an $η^3-η^1-η^3$ process. Illustrate this process, and sketch the ^1H spectra for the low and high T limits of the complex.
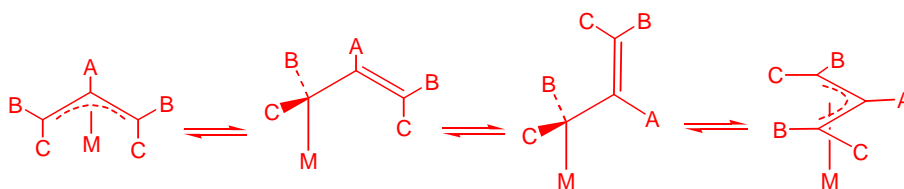
At low T, H_A will couple to $2(H_B)$ and $2(H_C)$ to give a 1H triplet of triplets. H_B will couple to H_C (^2J) and H_A (^3J) to give a 2H doublet of doublets; H_C will also give a 2H doublet of doublets, but at different chemical shift and with a different ^3J. At high T, H_B and H_C will be equivalent, so H_A will couple to four equivalent protons to give a 1H quintet, and there will be a 4H doublet for H_B+H_C.
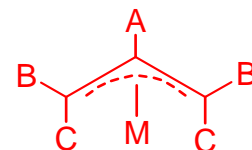
5. The variable temperature ^{13}C NMR of (cyclooctatetraene)Ru(CO)$_3$ is shown below. Suggest a reason for the changes in the spectrum with T, and assign the low T spectrum as best you can (free cyclooctatetraene shows a single resonance at 133 ppm).
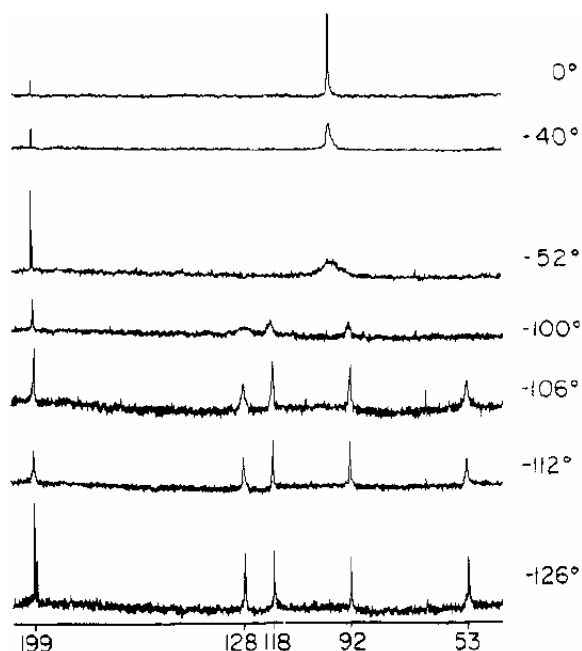
18e rule tells you the COT is η^4. The unchanging peak at 199 ppm is the CO resonance. The remainder correspond to the fluxional cyclooctatetraene, which is a "ring whizzer". The probable mechanism is a series of 1,2-shifts, the intermediate for which is shown below. In the low T limit, we can assign the peaks at 128 and 118 to C/D and those at 92 and 53 to A/B.