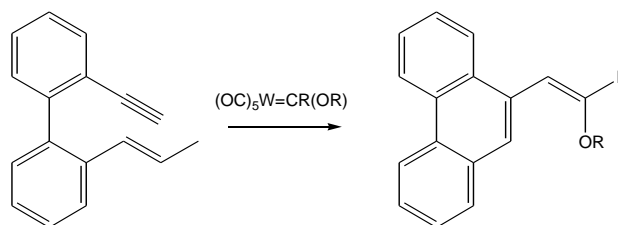


423/523 Organometallic Chemistry
Problem set 8

1. Propose a mechanism for:



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?

3. 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 ?

4. Two chemically inequivalent hydrides, H_A and H_B , in a metal dihydride complex at 50°C , resonate at $\delta -5$ 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?

5. Allyl complexes are characteristically fluxional, the principle pathway being an $\eta^3-\eta^1-\eta^3$ process. Illustrate this process, and sketch the ^1H spectra for the low and high T limits of the complex.

6. The variable temperature ^{13}C NMR of $(\text{cyclooctatetraene})\text{Ru}(\text{CO})_3$ 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).

