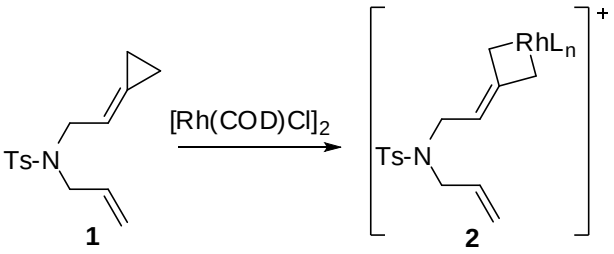
Organometallic Chemistry Name:___Cole Hamels_____
Problem Set #4
Due: Oct. 28, 2008

1. The following mechanistic step was recently reported in the literature to explain a new reaction. (from P. Andrew Evans et al. *JACS* **2008**, *130*, 12838-9)



a) What type of reaction is occurring? Support your answer with a brief explanation. (Note: the authors did not indicate the number of L's on Rh in the intermediate, but assume there are 4, i.e. n=4.) (4 pts.)

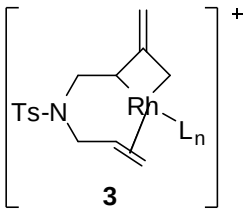
Oxidative addition is occurring. The Rh reagent is oxidized from +1 to +3 and the coordination number increases from 4 to 6.

b) It is unusual for this type of reaction to occur with C-C bonds. Explain why this molecule might be special and therefore allows this type of reaction to occur in this case. (4 pts.)

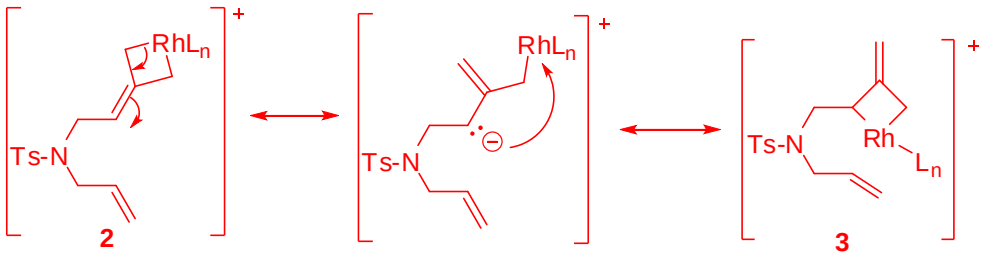
The C-C bond that is cleaved is part of a cyclopropane ring which is highly strained. The strain in the ring encourages cleavage of the C-C bond through Rh d_{π} donation into the C-C σ^{*} bond.

c) The authors propose that compound **2** in question 1 undergoes rearrangement to compound **3** (below). Briefly explain what has happened to **2** in becoming compound **3**. (4 pts.)

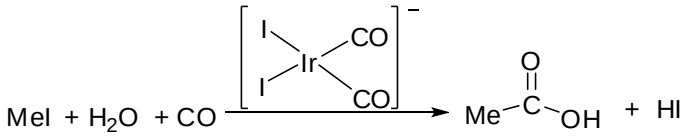
This transformation is simply a rearrangement of the allylic system that the Rh is bonded to. Allylic ligands readily rearrange when bonded to metals and equilibrate through resonance. One possible electron flow mechanism to envision this conversion is shown below. (Note: it is unlikely that the transformation forms an unassociated carbanion in the process. The carbanion intermediate



is shown to simplify the conversion.) Transformation to **3** also allows the Rh to bond to the other alkene in the molecule, thereby generating a tridentate ligand, which is then more strongly bonded to the Rh.



2. The Cativa process is now the most common industrial way to generate acetic acid from methanol. The reaction is shown below.



Suggest a catalytic cycle that performs this transformation. The catalytic cycle should combine three fundamental reaction types. Identify each step by its reaction type. The fourth and final step (which is not technically part of the catalytic cycle) is the hydrolysis of an acyl halide. (8 pts.)