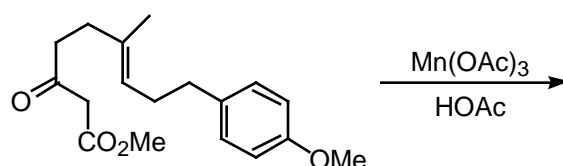


Organic Division

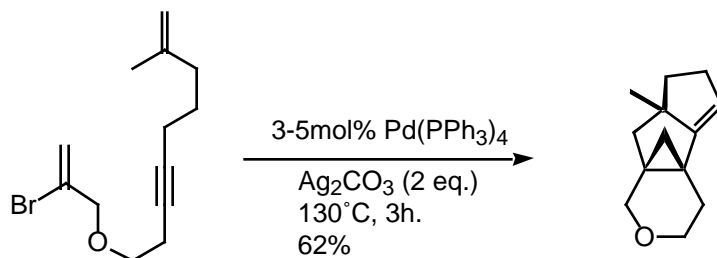
October Cumulative Examination

Metal-Catalyzed Cyclization Reactions

1. $\text{Mn}(\text{OAc})_3$ is an effective one electron oxidant. For the following (Snider, B.B. *Chem.Rev.* **1996**, 96, 339):

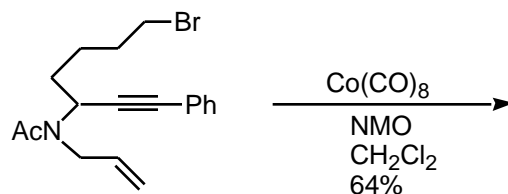


- (5 pts) A. Provide the product of the oxidative cyclization reaction.
- (2 pts) B. Identify the oxidation number of manganese in $\text{Mn}(\text{OAc})_3$ and the oxidation number after the reaction.
- (5 pts) C. Provide the structure of the intermediate that initiates the cyclization.
- (5 pts) D. What Stereochemistry do you expect in the product you gave in part A.
2. (10 pts) Provide a mechanism for the following (Ojima, I.; *et. al. Chem. Rev.* **1996**, 96, 635):



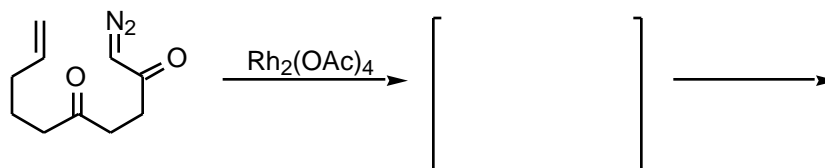
- (10 pts) Identify the three fundamental organometallic reaction mechanisms involved in the above reaction.

3. The Pauson-Khand reaction is a method to form cyclopentenones. Provide the product of the following reaction (**5pts**) and provide the structure of the alkyne complex postulated in the mechanism of the Pauson-Khand (**5 pts**). (Ojima, I.; *et. al. Chem. Rev.* **1996**, *96*, 635):

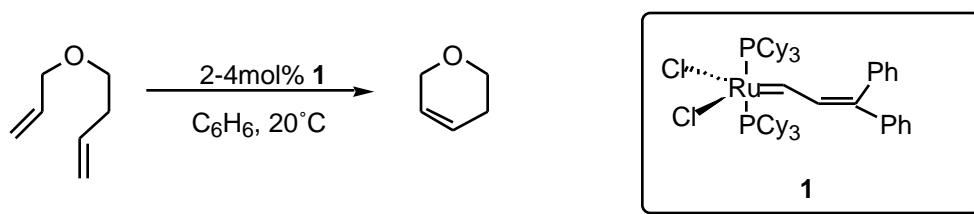


$\text{Co}_2(\text{CO})_8$ is coordinatively saturated. What must happen to the cobalt complex before any reaction will occur? (**5 pts**).

4. Rhodium(II) carboxylates catalyze the cyclization of carbenoids with carbonyls to give carbonyl ylides. Provide the product of the following reaction (**5 pts**) and identify the intermediate that undergoes cycloaddition to the final product (**5pts**). (Padwa, A.; Weingarten, M.D. *Chem. Rev.* **1996**, *96*, 223)



5. Ruthenium-catalyzed “ring-closing metathesis” reactions provide an efficient route to carbonyl and heterocyclic compounds. Given the Ru-catalyst shown provide a mechanism for the following: (Ojima, I.; *et. al. Chem. Rev.* **1996**, *96*, 635):(**15 pts**)



hint: ethylene is the byproduct