This literature discussion is based upon the article

Robbins, L.K; Lilly, C.P.; Smeltz, J.L.; Boyle, P.D.; Ison, E.A. *Organometallics* **2015**, *34*, 3152-3158.

1. What is/are the goal(s) of the study in this article?
2. Find the thesis statement in the paper and write it down. Compare this to the goal you stated above in your own words.
3. Consider the term “direct insertion”.
   1. What is a “direct insertion” of CO?

* 1. What might “indirect” CO insertion look like?

1. Carbon-carbon bond formation in organometallics are generally considered to proceed through one of two generally accepted pathways. Draw these two reaction pathways using the pentacarbonyl alkyl manganese complex. Examples of these can be found in your textbook or Noack, K; Calderazzo, F. *J. Organomet. Chem.* **1967**, *10*, 101-4 or organometallic hypertext.
2. For the complexes shown in Scheme 3, choose a ligand set **a**, **b**, or **c**. Indicate your choice by circling.
   1. Characterize each ligand as L, X or Z. Determine the valence number, ligand bond number, electron number, and dn count for example compounds **3** and **5** for your chosen ligand set.
   2. Why is the oxygen shown with a triple bond? How many electrons does it contribute to the electron number?
   3. Consider the ligand set in compound **d**. Should your answers for (a) change? Explain.
3. In Scheme 4, why are kobs and k1 not equal? (Hint: what does the term pseudo-first order mean?)
4. Find equation 2 in Scheme 4. Describe how you could graphically determine the second-order rate constant (OR: k1)? *What experiments would you need to perform in order to obtain your data?*
5. What is a rate law? What is an integrated rate equation? What is the advantage of an integrated rate equation? What did the authors do to circumvent the need for an integrated rate equation?
6. Find Mechanism B in Scheme 5. Using the steady state approximation, show the derivation of equation 4.
   * 1. If the intermediate **Int** is formed, what is/are the possible reaction(s) that it can undergo?
7. The C=O stretching frequency of acetone is 1715 cm-1. Why are the C=O bond of the acyl ligands in complexes **5a-d** have stretching frequency of 1592 cm-1? For full credit, your answer should include both text and a sketch of any relevant resonance structures.
8. What information did the authors determine from the log/log plot in Figure 5? Why was this type of plot created?
9. The oxo ligand is widely regarded as one of the strongest trans influence ligands.
   1. What is trans influence?
   2. What unique properties are afforded to complexes **3** and **5** by having this strong trans influence ligand?
   3. What makes the oxo ligand a strong trans influence ligand?
10. Activation parameters can sometimes provide clues regarding the reaction mechanism type, whether it is A, D, IA, ID.
    1. What were the activation parameters determined for complex **3a**?
    2. Which thermodynamic term gives you the most information about the mechanism?
    3. *Different version/level of this question:*Based on the DeltaS of activation, is this mechanism more likely to be associative or dissociative in nature? Explain.
11. Which peak(s) in the 1H NMR spectra of the reactant **3a** do you expect to shift the most upon formation of the product **5a**? Why?
12. Consider the concentration plots, expressed as a function of time, in Figure 5.
    1. How were the concentrations of **3a** and **5a** measured?
    2. What was the purpose of showing the sum of **3a** and **5a** concentrations?
13. What are the major findings of this article?
14. Revisit question (1). Were the goals of the article achieved? Explain in 1-2 paragraphs.