

**423/523 Organometallic Chemistry**  
**Problem set 7**

1. In 1968, the Shell Oil Company reported that adding tertiary phosphine such as  $\text{PBu}_3$  to the oxo reaction resulted in hydroformylation taking place at less than 100 atm. Though it the new catalyst is a less active hydroformylation catalyst than  $\text{HCo}(\text{CO})_3$ , it is a better hydrogenation catalyst. Separation of catalyst from products is improved. The ratio of linear to branched product is as high as 9 to 1. Studies of the reaction failed to observe alkyl or acyl-containing intermediates.

(a) Explain the greater selectivity of the new catalyst by drawing an appropriate transition state.  
 4-membered TS for the 1,2-insertion of alkene. Branched product causes steric crowding.

(b) What are the advantages and disadvantages of the new catalyst being a good hydrogenation catalyst?

Next step is hydrogenation of aldehyde to alcohol, so doing this all in one pot is advantageous. However, you don't want the alkene hydrogenated, as this will diminish the yield.

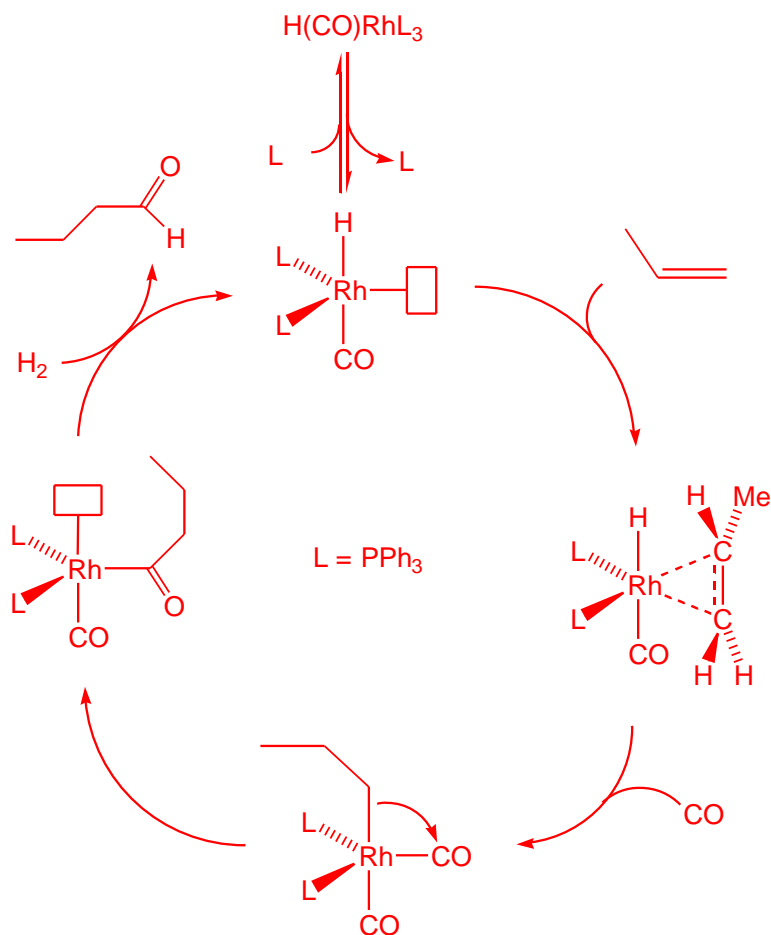
(c) What does the failure to observe intermediates tell you about the likely rate-determining step?

That it is before the alkyl or acyl intermediates form; probably the 1,2-insertion of the alkene.

(d) Why is it easier to remove the products from the catalyst?

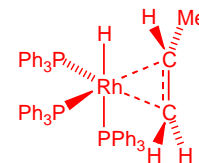
The resting state of the original catalyst,  $\text{HCo}(\text{CO})_4$ , is volatile whereas  $\text{HCo}(\text{CO})_3(\text{PBu}_3)$  is not.

2. Draw a catalytic cycle for phosphine-rhodium-catalysed hydroformylation. The catalyst precursor is  $\text{H}(\text{CO})\text{Rh}(\text{PPh}_3)_3$ .



3. Explain why increasing the concentration of phosphine in the phosphine-rhodium cycle slows the reaction rate, but also raises the linear/branched product ratio.

Excess  $\text{PR}_3$  slows the ligand dissociation that produces the active catalyst, but also probably displaces  $\text{CO}$ , forcing insertion such that the metal is attached to the least substituted carbon.



4. Rate of Rh/HI-catalysed carbonylation of 2-propanol to give a mixture of butanoic and 2-methylpropanoic acids is actually a little faster than that for carbonylation of ethanol and up to seven times more rapid than that for 1-propanol. If OA is still the rds in the pathway, what can be said about the mechanism of that step when 2-propanol is the starting material?

RDS is OA of 1-iodopropane or 2-iodopropane to  $[\text{Rh}(\text{CO})_2\text{I}_2]^-$ . The mechanism of this step is probably not  $\text{S}_{\text{N}}2$ , but one involving alkyl radicals. Since  $\text{II}^\circ$  radicals are more stable than  $\text{I}^\circ$ , 2-iodopropane (derived from 2-propanol) reacts faster than 1-iodopropane.