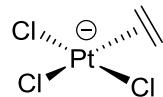
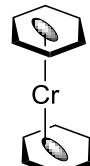
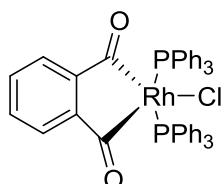
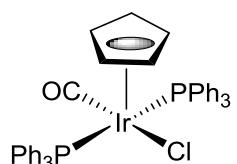
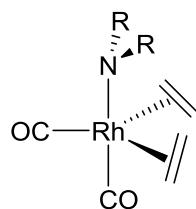
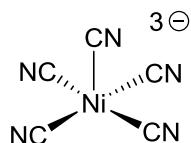
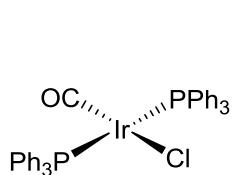


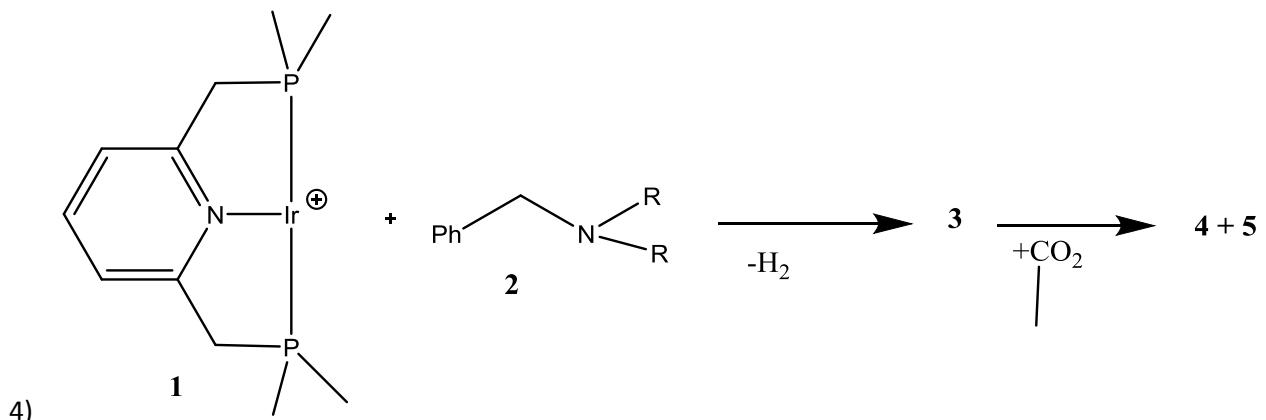
1. Determine the oxidation state of the metal centre and count the number of electrons.



meant to be aromatic ring!

2. The metal fragment **1** reacts with the amine to give a carbene complex **3**.

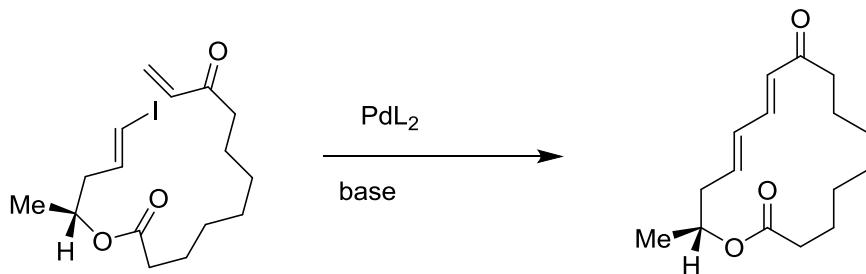
- 1) Count the electrons and determine the oxidation state of the metal centre of **1**.
- 2) Propose a mechanism for the formation of **3**. Count the electrons and determine the oxidation state for the product and every intermediate.
- 3) Justify if **3** is a Fischer or Schrock carbene.



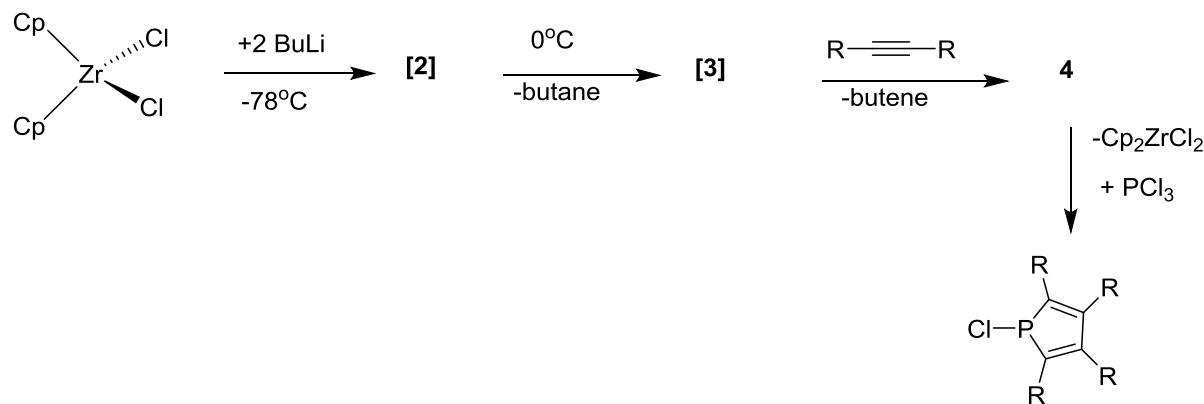
The carbene complex **3** reacts with  $\text{CO}_2$  to yield complex **4** and an organic derivative. Using the ligand field scheme of a square planar  $\text{ML}_4$  complex determine which orbital can interact with  $\text{CO}_2$ . Propose a mechanism to explain the transformation of **3** +  $\text{CO}_2$  into **4** + **5**. (Note: the complex **4** contains the metal fragment and an L type ligand.)

5) Bearing in mind that the reaction is designed as a catalytic process, why might it be advantageous to heat the reaction under a partial vacuum.

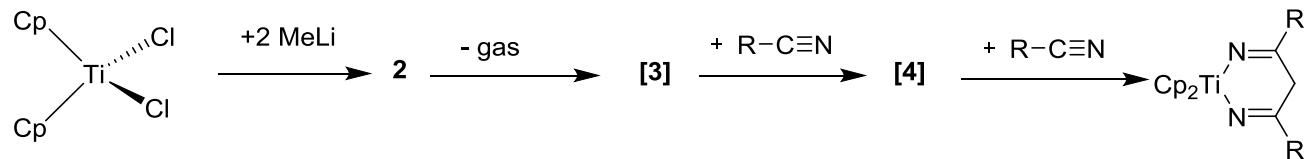
3. Give a mechanism for this Heck reaction. Determine the oxidation states of Pd and name the elementary reaction steps.



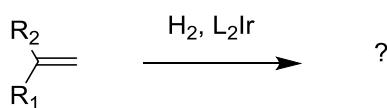
4. The chemistry of the elements of group IV allow the synthesis of phosphorus containing heterocycles. Determine the compounds **2,3,4** and the oxidation state of Zr for each intermediate. Name the elementary reaction types. What are A and B?



5. What are the compounds **2,3,4**? Determine the oxidation state of Ti for every intermediate. The nature of compound **3** is crucial for the regioselectivity of the reaction with the nitrile.



6. Propose a catalytic cycle for the Ir-catalysed hydrogenation of an alkene that involves Ir(I) and Ir(III) complexes as intermediates. Assume that the starting point of the cycle is a cationic Ir(I) complex which is bonded to a general aminophosphine ligand and solvent molecules as needed to form a square planar complex. Ox. Add. of H2 is followed by displacement of solvent by alkene. Which step introduces a stereogenic centre?

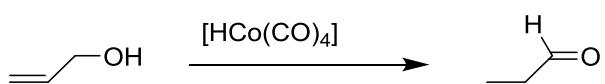


7. Develop a mechanism for the isomerisation below.

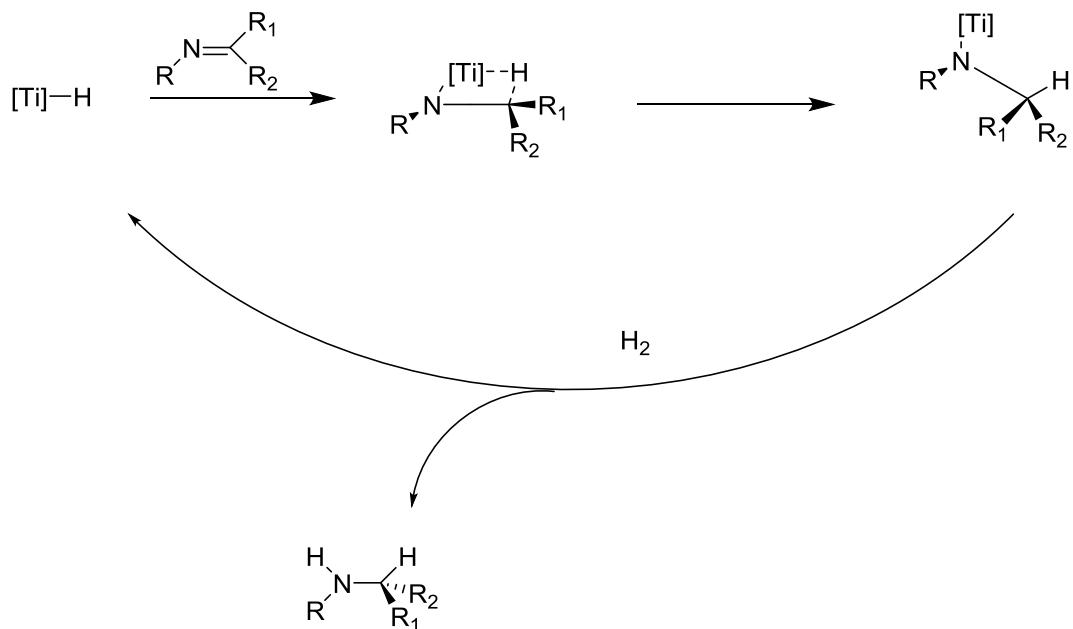
Indications:

- CO is lost in the first step
- the second step allows the formation of an 18 electron complex

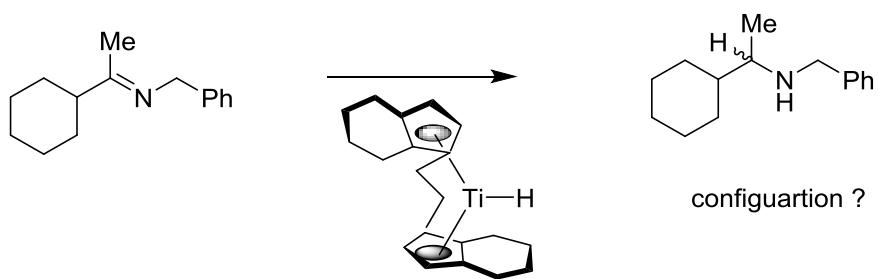
- the third step generates a 16e complex  
 The 4<sup>th</sup> step allows the regeneration of the catalyst



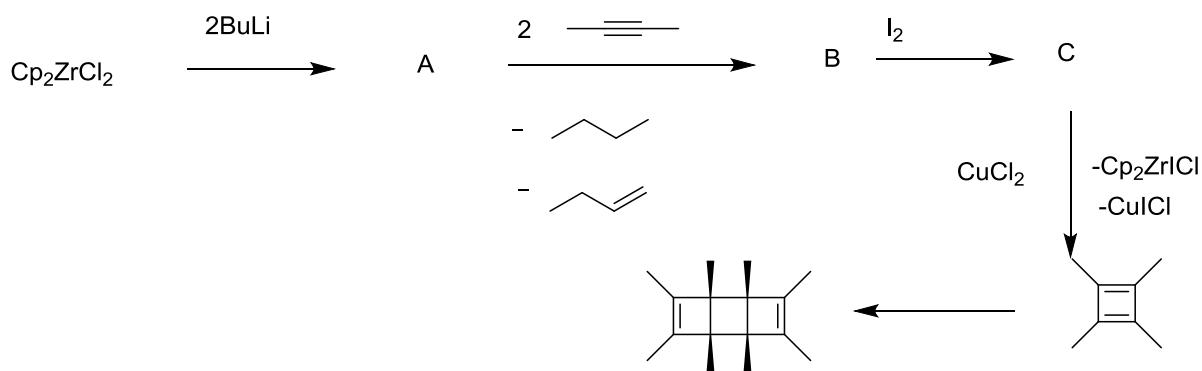
8. The following describes the mechanism of the hydrogenation of imines with Ti(III).



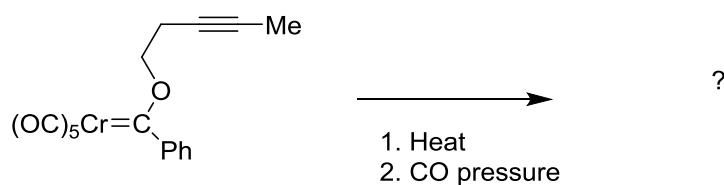
The reaction can also be done enantioselectively with the following catalyst. Based on steric effects what will the configuration of the product be?



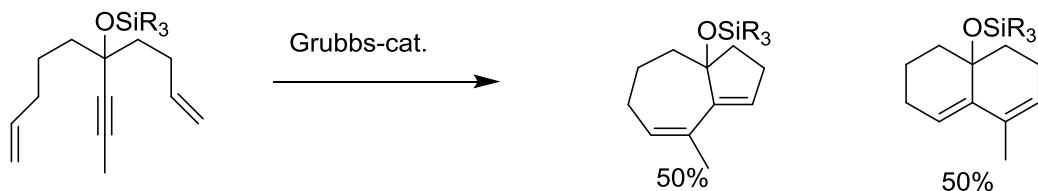
9. Propose a mechanism for the transformation below.



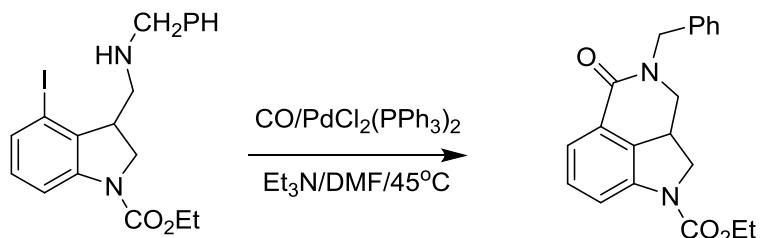
10. The following carbene reacts in a Dötz reaction. What is the structure of the final product and the mechanism?



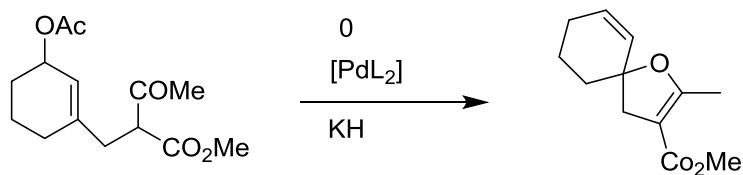
11. Explain the two products formed.



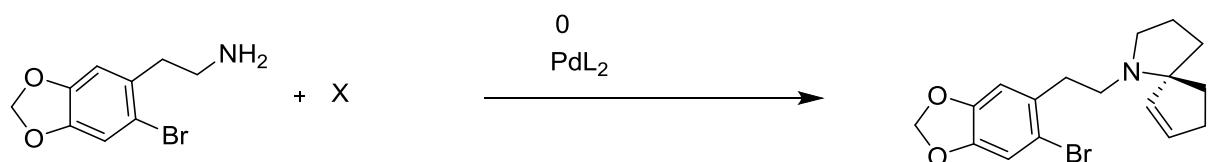
12. Propose a stepwise mechanism for the transformation below.



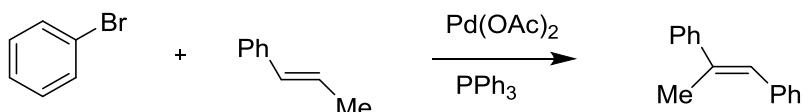
13. Explain the transformation. (Tsuji-Trost)



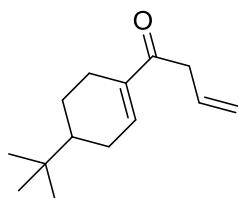
14. How would you synthesise the following product using the same reaction as in 13. The second reagent contains a halogen and good leaving group. The first step of the reaction does not need the catalyst. In the second step a base is needed to deprotonate a secondary amine.



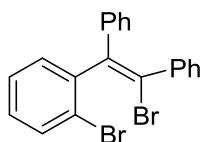
15. Consider the mechanistic pathway of the Heck reaction and show that (E)-1,2-diphenyl-propene ought to result as the major product, if the starting material is (E)-1-phenyl-propene.



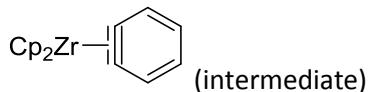
16. What are the starting materials required to synthesize this following compound using a Stille cross-coupling?



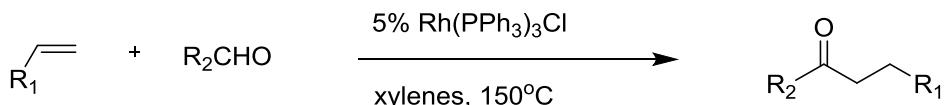
17. Propose a synthetic route for the following compound using only Phenyllithium, methyl lithium, diphenylacetylene, Br<sub>2</sub> and ZrCp<sub>2</sub>Cl<sub>2</sub>.



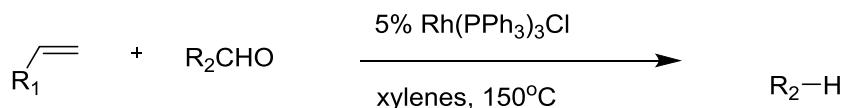
Help: Initially the Zr-complex reacts with Ph-Li and Me-Li to form an aryne ligand.



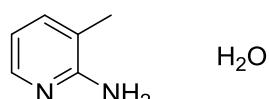
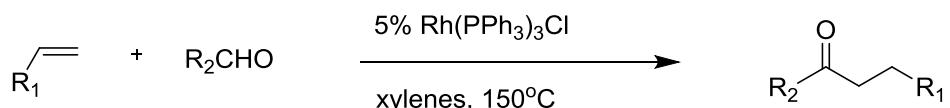
18. Propose a mechanism for the hydroacylation of alkenes using Wilkinson cat.



Unfortunately a 2<sup>nd</sup> reaction consumes most of the aldehyde. Propose a mechanism for this reaction as well.



The use of a co-catalyst has been introduced to prevent this 2nd reaction. Propose a mechanism to justify the use of the co-catalyst.



19. Based on the energy difference in the ligand field scheme decide if a strong pi-acceptor ligand such as CO will prefer to coordinate in equatorial or axial position on a bipyramidal  $\text{ML}_5$  complex. The relevant orbitals and their energy levels of the  $\text{ML}_5$  complex are shown below

