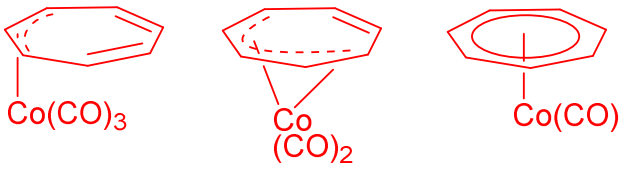
1. Draw the structure of the three complexes (cyclo-C_7H_7)$Co(CO)_n$ (n = 1, 2 and 3). Give three ways of forming n = 2 and/or n = 3 from n = 1.

[6 marks]

η^3, η^5, η^7 generate 18 electron complexes for n = 1, 2 and 3 respectively:



I worded the second part of this question backwards, my apologies - it should have been ways of forming n = 1 from n = 2 or 3.
As such, I assigned all 6 marks for the structures, and any plausible attempt at the second part (e.g. "add CO" or other reasonable suggestions) got bonus marks. So it was possible to score >6 for this question (max = 9).

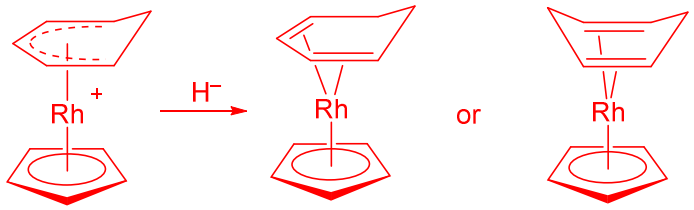
2. Draw the structures of starting materials and products of the following reactions, and account for the selectivity you chose:

$[Rh(\eta^5\text{-}C_5H_5)(\textit{cyclo}\text{-}\eta^5\text{-}C_6H_7)]^+ \quad + \quad H^- \quad \rightarrow$

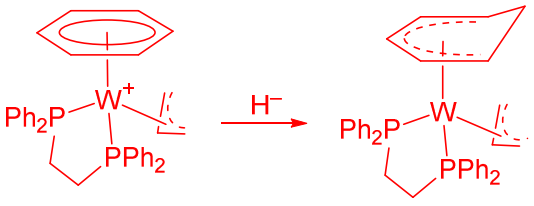
$[Mo(\eta^6\text{-}C_6H_6)(\eta^3\text{-}C_3H_5)(\kappa^2\text{-}Ph_2PCH_2CH_2PPh_2)]^+ \quad + \quad H^- \quad \rightarrow$

[8 marks]

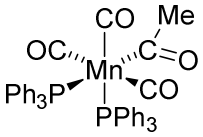
Rule 2, open before closed. I accepted either answer for application of rule 3:



Rule 1, even before odd:

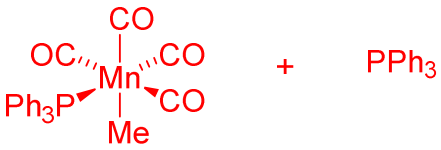


3. Sketch the products of the reaction when the following complex loses (a) one PPh_3 or (b) one CO. If more than one product if formed in a given reaction, draw all products and estimate their relative abundance.

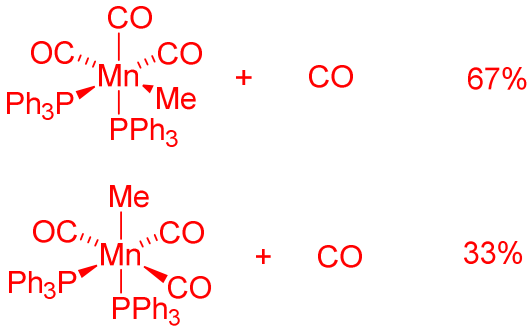


[7 marks]

Loss of PPh_3 from the *trans* position will not result in reaction (recoordination of PPh_3 is faster than isomerization). Loss of PPh_3 in *cis* position leads to migration of Me to that position:



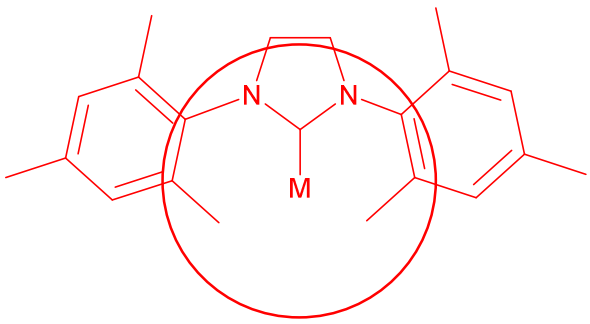
Loss of CO can happen either *cis* to both PPh_3 ligands or *trans* to one and *cis* to the other:



4. Draw a sketch to explain the concept of "buried volume" when it comes to assessing the steric influence of certain types of ligand. Explain why the cone angle concept is not useful for these ligands.

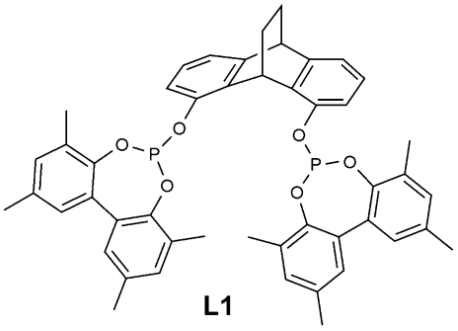
[7 marks]

How much of a sphere of a certain radius about the metal is occupied by the ligand:



NHCs are more fan-shaped than cone-shaped, and can twist to reduce steric influence at metal.

5. **L1** is a bulky bisphosphite ligand. Draw as P⌒P in your answers.



$Rh(acac)(CO)_2$ was treated with **L1**, and the reaction vessel pressurized with CO and H_2. The product, **A**, exhibited strong IR absorbances at 1980 and 2050 cm^{-1}, and a ^1H NMR signal at δ -9.77 (all other signals were attributable to **L1**), and a ^{31}P NMR signal at δ 165.

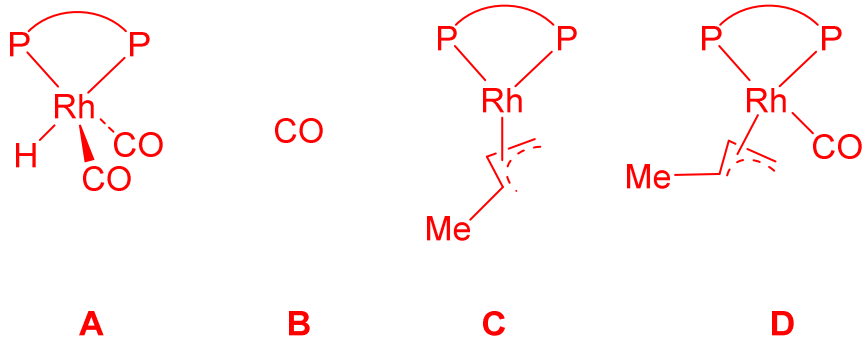
Heating **A** with 1,3-butadiene formed a colourless gas **B** and a different complex **C**, which exhibited no absorbances in the IR spectrum between 1600 and 2800 cm^{-1}. The ^1H NMR spectrum of **C** had no signals at negative δ values, but 5 new signals appeared in addition to peaks attributable to **L1**. Mass spectrometry showed that the overall mass of **C** was 2 amu less than **A**.

C reacted with **B** at low temperature to form **D**, which had a strong absorbance in the IR at 1985 cm^{-1} but other spectroscopic changes were minor.

a. Provide plausible structures for **A**, **B**, **C** and **D**.
b. Account for the observation that the reaction **B** + **C** → **D** was found to be easily reversible.
c. Predict the result of the reaction between **C** and PPh_3, and explain your reasoning.

[12 marks]

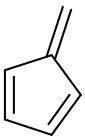
a.



b. Bulk of L1 causes steric crowding and stabilization of 16 e complex

c. None (steric crowding)

6. The six π molecular orbitals of fulvene (see below) have 0, 1, 1, 2, 2 and 3 nodes respectively. Draw plausible π MOs and illustrate how the HOMO and LUMO might interact with metal d-orbitals of matching symmetry.



[10 marks]

Not expected to predict which of the two 1-node and which of the two 2-node orbitals are higher in energy; also OK to say they are the same or to simply not comment.