**423/523 Organometallic Chemistry**
**Problem set 4**

1. Strained alkenes such as cyclopropene or norbornene bind unusually strongly to metals. Suggest a reason why.

   Rehybridisation ($sp^2 \rightarrow sp^3$) upon binding leads to relief of strain.

2. Alkynes readily bridge M-M bonds, in which case they act as 2e donors to each metal. Sketch the product of the reaction below, indicating the hybridization of the C atoms.

$$PhCCPh \ + \ Co_2(CO)_8 \ \rightarrow \ (\mu_2\text{-}PhCCPh)Co_2(CO)_6 \ + \ 2CO$$
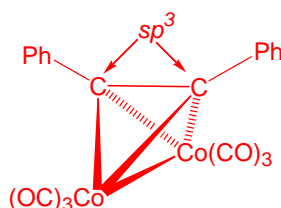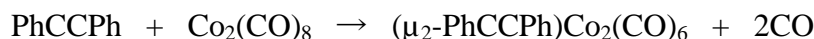


3. Draw as many bonding modes for cyclooctatetraene as you can think of.

   Lots! Don't forget bridging modes…
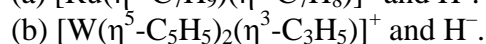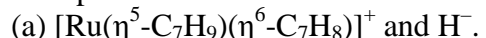
4. Sketch the three π-MOs of the allyl anion, $[C_3H_5]^-$. Draw metal $d$-orbitals that can interact with these MOs, and name the type of bonding (e.g. M→L π-acceptor).



M to L
π-acceptor

L to M
π-donor

L to M
σ-donor
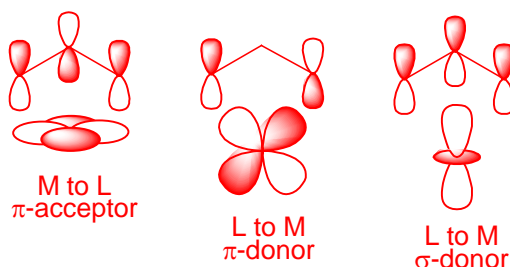
5. The M-P distance in ($\eta^5$-$C_5H_5$)Co(PEt$_3$)$_2$ is 221.8 pm and the P-C distance is 184.6 pm. The corresponding distances in $[(\eta^5$-$C_5H_5)Co(PEt_3)_2]^+$ are 223 pm and 182.9 pm. Account for the changes in these distances as the former complex is oxidised.

   The oxidised complex is less able to donate electron density into σ* PEt$_3$ antibonding orbitals, so P-C bonds become shorter. Weakening of π-back bonding will also lengthen the Co-P bond. However... the better energy match between metal and ligand orbitals upon oxidation of the metal would make the M-P bond become shorter due to stronger σ-bonding, and given that σ-bonding is much more important for phosphines than π-back bonding, I would have thought it would be the more important effect. Apparently not…

6. Predict the product of the reactions between:  Work out the structures and then use DGM rules.
   (a) $[Ru(\eta^5$-$C_7H_9)(\eta^6$-$C_7H_8)]^+$ and H⁻.  $Ru(\eta^5$-$C_7H_9)_2$
   (b) $[W(\eta^5$-$C_5H_5)_2(\eta^3$-$C_3H_5)]^+$ and H⁻.  $W(\eta^5$-$C_5H_5)_2(\eta^2$-*cyclo*-$CH_2CH_2CH_2$)

7. Ligands of type X–Y only give 3c-2e "agostic" bonds to transition metals if X = H and Y lacks lone pairs. Why do you think this is so (consider alternative structures if X and Y are not H)?

Lone pairs always compete better than an agostic bond (both donate a pair of electrons to the metal). If X ≠ H, the σ* orbital is no longer spherical (it is, for example, a combination of two $sp^3$ orbitals out of phase rather than an $sp^3$ and a H $1s$) and is much less accessible to a metal $d$-orbital.

8. $[IrH_2(H_2O)_2(PPh_3)_2]^+$ reacts with indene to give $[Ir(C_9H_{10})(PPh_3)_2]^+$ (**A**). On heating, this species rearranges with $H_2$ loss to give $[IrH(C_9H_7)(PPh_3)_2]^+$ (**B**). Only **A** reacts with ligands such as CO to displace $C_9H_7$. What do you think are the structures of **A** and **B**?



indene



**A**          **B**
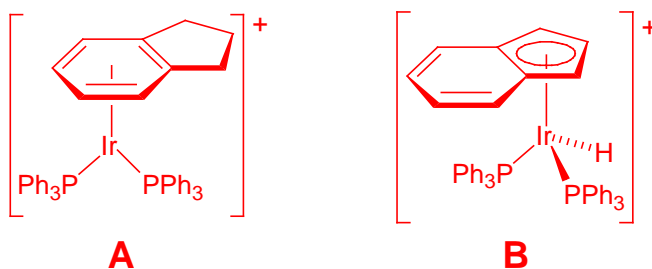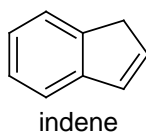
These structures obey the 18e rule and fit the empirical data. The reactivity described should probably read "Only **A** reacts with ligands such as CO to displace $C_9H_{10}$; **B** does not react to displace $C_9H_7$". However, you don't really need this to solve the structural question.
The Cp-like indenyl ligand is difficult to displace as it is formally anionic, whereas the neutral arene can be replaced relatively easily by 3 COs.