## 423/523 Organometallic Chemistry Problem set 4

1. Strained alkenes such as cyclopropene or norbornene bind unusually strongly to metals. Suggest a reason why.
2. Alkynes readily bridge $\mathrm{M}-\mathrm{M}$ bonds, in which case they act as 2 e donors to each metal. Sketch the product of the reaction below, indicating the hybridization of the C atoms.

$$
\mathrm{PhCCPh}+\mathrm{Co}_{2}(\mathrm{CO})_{8} \rightarrow\left(\mu_{2}-\mathrm{PhCCPh}\right) \mathrm{Co}_{2}(\mathrm{CO})_{6}+2 \mathrm{CO}
$$

3. Draw as many bonding modes for cyclooctatetraene as you can think of.
4. Sketch the three $\pi$-MOs of the allyl anion, $\left[\mathrm{C}_{3} \mathrm{H}_{5}\right]^{-}$. Draw metal $d$-orbitals that can interact with these MOs, and name the type of bonding (e.g. $\mathrm{M} \rightarrow \mathrm{L} \pi$-acceptor).
5. The M-P distance in $\left(\eta^{5}-\mathrm{C}_{5} \mathrm{H}_{5}\right) \mathrm{Co}\left(\mathrm{PEt}_{3}\right)_{2}$ is 221.8 pm and the $\mathrm{P}-\mathrm{C}$ distance is 184.6 pm . The corresponding distances in $\left[\left(\eta^{5}-\mathrm{C}_{5} \mathrm{H}_{5}\right) \mathrm{Co}\left(\mathrm{PEt}_{3}\right)_{2}\right]^{+}$are 223 pm and 182.9 pm . Account for the changes in these distances as the former complex is oxidised.
6. Predict the product of the reactions between:
(a) $\left[\mathrm{Ru}\left(\eta^{5}-\mathrm{C}_{7} \mathrm{H}_{9}\right)\left(\eta^{6}-\mathrm{C}_{7} \mathrm{H}_{8}\right)\right]^{+}$and $\mathrm{H}^{-}$
(b) $\left[\mathrm{W}\left(\eta^{5}-\mathrm{C}_{5} \mathrm{H}_{5}\right)_{2}\left(\eta^{3}-\mathrm{C}_{3} \mathrm{H}_{5}\right)\right]^{+}$and $\mathrm{H}^{-}$.
7. Ligands of type $\mathrm{X}-\mathrm{Y}$ only give $3 \mathrm{c}-2 \mathrm{e}$ "agostic" bonds to transition metals if $\mathrm{X}=\mathrm{H}$ and Y lacks lone pairs. Why do you think this is so (consider alternative structures if X and Y are not H )?
8. $\left[\mathrm{IrH}_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}\left(\mathrm{PPh}_{3}\right)_{2}\right]^{+}$reacts with indene to give $\left[\operatorname{Ir}\left(\mathrm{C}_{9} \mathrm{H}_{10}\right)\left(\mathrm{PPh}_{3}\right)_{2}\right]^{+}(\mathbf{A})$. On heating, this species rearranges with $\mathrm{H}_{2}$ loss to give $\left[\mathrm{IrH}\left(\mathrm{C}_{9} \mathrm{H}_{7}\right)\left(\mathrm{PPh}_{3}\right)_{2}\right]^{+}(\mathbf{B})$. Only $\mathbf{A}$ reacts with ligands such as CO to displace $\mathrm{C}_{9} \mathrm{H}_{7}$. What do you think are the structures of $\mathbf{A}$ and $\mathbf{B}$ ?

indene
