423/523 Organometallic Chemistry Problem set 5

1. F_3CI has a $\delta^- CF_3$ group and a $\delta^+ I$. Because of this, to make trifluoromethyl complexes of transition metals, $F_3CC(O)Cl$ is often used. How does this approach work?

2. Metal alkoxides, like metal alkyls, can also β -eliminate. With this in mind:

- (a) explain why –O^tBu is a common ligand in metal alkoxide chemistry.
- (b) what are the products of decomposition of primary and secondary alkoxide ligands?
- (c) how can alcohols, in the presence of a base, be used as reducing agents for metal complexes?

3. $Mo(CO)_6$ undergoes substitution reactions with phosphine ligands, but the reaction never proceeds further than the $Mo(CO)_3(PR_3)_3$ stage. If the phosphines are very bulky, the phosphines are arranged *mer*, but otherwise are always *fac*. Explain these two observations.

4. CpRe(NO)(CO)Me reacts with two equivalents of PMe₃ to provide a product in which six ligands are bound to Re. The reaction has a large negative ΔS^{\ddagger} . Draw the product and suggest a plausible mechanism.

5. In the substitution of $V(CO)_6$, the rate of reaction changes with respect to phosphine nucleophile according to the order $PMe_3 > PBu_3 > P(OMe)_3 > PPh_3$. What does this suggest about the mechanism?

6. In the following reaction scheme, name the reaction(s) occurring at each step, and work out the oxidation state and electron count of all metal complexes.

