

**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?

Transmetalation requires the transfer of  $R^+$ , so doesn't work for  $F_3CI$ . However, the acyl complex forms without difficulty and can lose the CO by alkyl migration.

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

(a) explain why  $-O^tBu$  is a common ligand in metal alkoxide chemistry.

No  $\beta$ -hydrogens.

(b) what are the products of decomposition of primary and secondary alkoxide ligands?

Aldehydes and ketones.

(c) why are alcohols, in the presence of a base, used as reducing agents for metal complexes?

The base converts the alcohol to an alkoxide, which after coordinating can  $\beta$ -eliminate an aldehyde (or ketone) to give M-H.

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.

CO is strongly *trans*-directing, so *fac*- is favoured. Once 3 CO ligands are substituted, the remaining COs are bound very tightly. Also, steric factors disfavour tetra-substitution. A *mer*-arrangement of ligands is sterically less crowded, hence favoured for bulky phosphines despite the electronic disadvantage.

4.  $CpRe(NO)(CO)Me$  reacts with two equivalents of  $PMe_3$  to provide a product in which six ligands are bound to Re. The reaction has a large negative  $\Delta S^\ddagger$ . Draw the product and suggest a plausible mechanism.

$Re(\eta^1-C_5H_5)(NO)(CO)(PMe_3)_2(Me)$ . Associative; the NO and Cp can both change bonding modes, delocalizing electrons onto the ligand and generating a 16e complex.

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?

Suggests an associative reaction (the rds involves the incoming nucleophile); reasonable since  $V(CO)_6$  is 17e. Trend in reaction rate seems to suggest both steric and electronic factors at play: small, electron-rich (good  $\sigma$ -donor) phosphines react fastest.

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.

