22.P11 The Mo has an 18e$^-$ count, so a coordination site must be first opened for the PR_3 to associate. The most plausible route is to have the Cp ring slip to η^3 in order to free up a coordination site for association of the phosphine, then the CO dissociates with the Cp returning to η^5. Another potential route is to have a CO undergo migratory insertion into the Mo-CH_3 bond to free up the coordination site. This would be followed by PR3 association, then CO dissociation, then CO reverse migration back out of the C(=O)CH_3 to give the final product.

26.5 There is a step in Wilkinson's catalytic cycle (Figure 26.5) that has a phosphine leaving (the **B** --> **C** step). Naturally, such a step is an equilibrium process: the just-left phosphine will compete with the alkene for the coordination site. If extra free phosphine is added, the equilibrium will shift, causing the coordination of phosphine to be more favourable (or, if there are more phosphines to compete for the free coordination site, there is less chance the alkene will coordinate).

26.6 Alkene coordination gives an octahedral complex, with two triphenylphosphines (relatively bulky ligands) in *cis* positions. The trend in reactivity clearly follows the steric trend, *i.e.* the sizes are: 1-methylcyclohexene > 4-methyl-2-pentene > hexene > cyclohexene (for the latter two, consider that the ring "pulls back" the carbons around the double bond to give a smaller cone angle). If size is hindering the reaction, that usually means the addition of the sterically demanding ligand is the rate-determining step (if the r.d.s. is the loss of the bulky group, size would have the opposite effect, *i.e.* increasing the rate). Therefore, it is the step **C** --> **D** that is affected.

26.8 Remember what the object is: to get the CO into the ester part of the bond, *i.e.*, to perform the reaction CH_3COOCH_3 --> $CH_3COOCOCH_3$. Therefore, the oxidative addition step probably involves addition across the CH_3COO-CH_3 bond. The template Monsanto process is shown in Figure 26.13.

