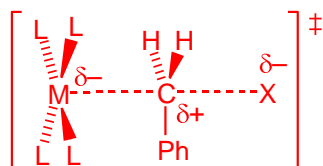


423/523 Organometallic Chemistry
 Problem set 6

1. Sketch the transition state for the first step in the oxidative addition of a benzyl halide and a square planar complex ML_4 .



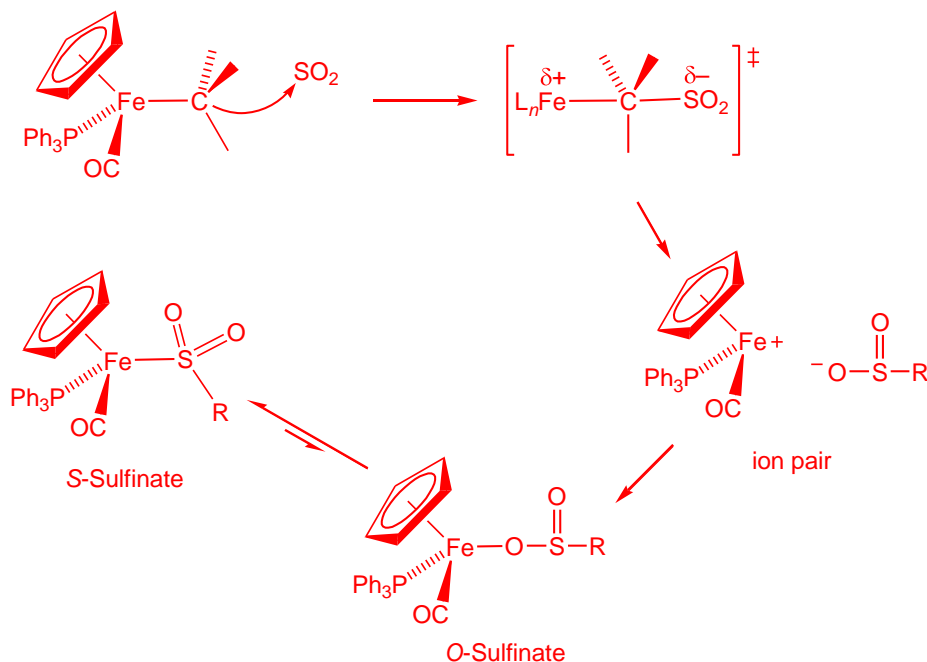
2. Explain the following. The *cis* isomer of $L_2Pd(Et)_2$ decomposes immediately to give butane, but the *trans* isomer produces a 1:1 mixture of ethene and ethane.

RE occurs when groups are *cis*, so this is facile for the *cis* isomer. The *trans* isomer undergoes β -elimination, forming ethene and *cis*- $L_2Pd(Et)(H)$, which reductively eliminates ethane.

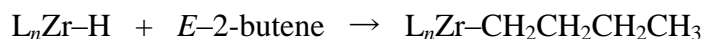
3. The reaction of $L_2Pd(Me)_2$ with PhC^*HDBr produced PhC^*HDMe . What is the other product, and do you expect retention or inversion at the chiral carbon?

$L_2Pd(Me)(Br)$. S_N2 -type OA of R_3C-Br bond (inversion), followed by RE of R_3C-Me (retention). Overall, inversion.

4. SO_2 can insert into an L_nM-CR_3 bond. The reaction is thought to proceed by an S_E2 pathway to form an ion pair, $[L_nM]^+[OS(O)R]^-$. Collapse of the ion pair generates the *O*-sulfinate (formally a 1,2-insertion of SO_2), which can rearrange to the *S*-sulfinate (formally a 1,1-insertion of SO_2). Draw the transition state, the ion pair, and the *O*- and *S*-sulfinates.

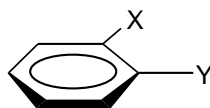


5. Provide a mechanism for the reaction:

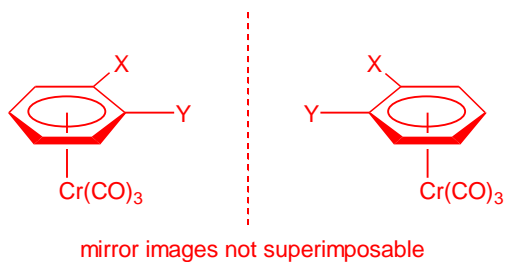


Coordination of alkene, 1,2-insertion, β -elimination, coordination of new alkene, 1,2-insertion.

6. Binding of $\text{Cr}(\text{CO})_3$ to an achiral arene:



gives a chiral complex. Illustrate this. What about for *meta*- and *para*- substituted arenes? How might this be useful?



Binding of metal removes the only plane of symmetry present in the free arene. Also true for *meta*- but not *para*-substituted arenes. If the arene substrate is chiral, coordination of $\text{Cr}(\text{CO})_3$ will give a mixture of diastereomers, which are separable; removal of the metal fragment regenerates the free, resolved arenes.