

5.3: Polar Oxidative Addition

The polar oxidative addition mechanism is very similar to an aliphatic nucleophilic substitution (S_N1 or S_N2) reaction.



Figure 5.3.1: An example of a polar oxidative addition.

In an oxidative addition, the metal can act as a nucleophile in the first step in an S_N2 process. In the second step, the liberated halide binds to the metal. That doesn't happen in a normal nucleophilic substitution. In this case, the metal has donated its electrons and is able to accept another pair from the halide.



Figure 5.3.2: Mechanistic steps in a polar oxidative addition.

Polar oxidative addition has some requirements similar to a regular S_N1 or S_N2 reaction:

- Requires good leaving group
- Requires tetrahedral carbon (or a proton) as electrophile

? Exercise 5.3.1

- What do you think is the most difficult step (i.e. the rate-determining step) for the reaction in Figure 5.3.2 (OA3.2)? Why?
- Suggest the probable rate law for this reaction.

Answer a

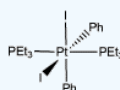
Probably the first step is the hardest (slowest) step, involving bond breaking in the alkyl halide. The donation of the resulting anion to the cation should be pretty fast.

Answer b

$$Rate = k_1 [ML_n][CH_3Br]$$

? Exercise 5.3.2

The platinum compound shown below is capable of reductively eliminating a molecule of iodobenzene.



- Show the products of this reaction.

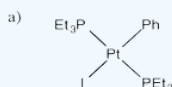
The starting platinum compound is completely stable in benzene; no reaction occurs in that solvent. However, reductive elimination occurs quickly when the compound is dissolved in methanol instead.

- Explain why the solvents may play a role in how easily this compound reacts.

The reaction in methanol is inhibited by added iodide salts, such as sodium iodide.

- Provide a mechanism for the reductive elimination of iodobenzene from the platinum complex, taking into account the solvent dependence and the inhibition by iodide ion.

Answer a

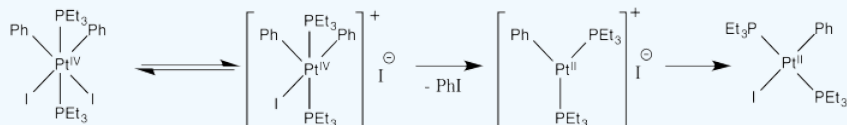


Answer b

Methanol is more polar than benzene. The acceleration of the reaction in methanol suggests that there is increasing polarity in the transition state, or polar intermediates.

Answer c

Inhibition by iodide ion suggests that iodide is a product of a reversible step during this reaction. Adding iodide pushes that step backward, decreasing the rate of product formation. The mechanism below is consistent with these observations:



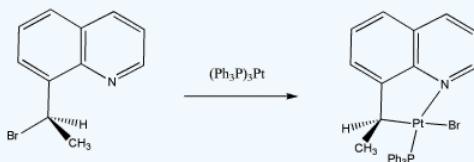
Thus reductive elimination occurs as we go from the second to the third intermediate.

Presumably, the increased positive charge (and general decrease in electron density, owing to loss of a ligand) results in reductive elimination because of destabilization of the Pt(IV).

Alternatively, we might suppose that after loss of iodide, the iodide ion donates directly to a phenyl ligand, displacing the platinum as a leaving group in an S_N2 reaction. That would lead directly to the product from the first intermediate, which is a simpler route. However, the precedent for aliphatic nucleophilic substitution involves nucleophilic donation to tetrahedral carbons, not to trigonal planar ones. That mechanism is unlikely.

? Exercise 5.3.3

For the following reaction,



- Identify the oxidation state at platinum in the reactant and the products.
- Assign stereochemical configuration in the product and the reactant.
- Explain the stereochemistry of the reaction.

Answer a

Pt(0) to Pt(II)

Answer b

Changes from (*R*) to (*S*)

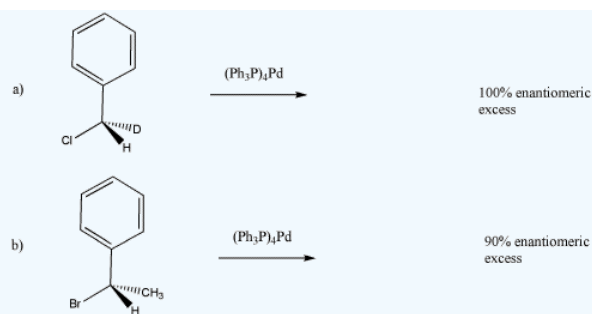
Answer c

This is an S_N2 reaction, so the platinum displaces the bromide from the opposite side.

? Exercise 5.3.4

Reaction of the following deuterium-labeled alkyl chloride with tetrakis(triphenylphosphine) palladium produces an enantiomerically pure product (equation a). Draw the expected product.

However, reaction of a very similar alkyl halide produces a compound that is only 90% enantiomerically pure. Draw the major product and explain the reason that there is some racemization

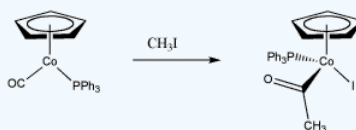


Answer

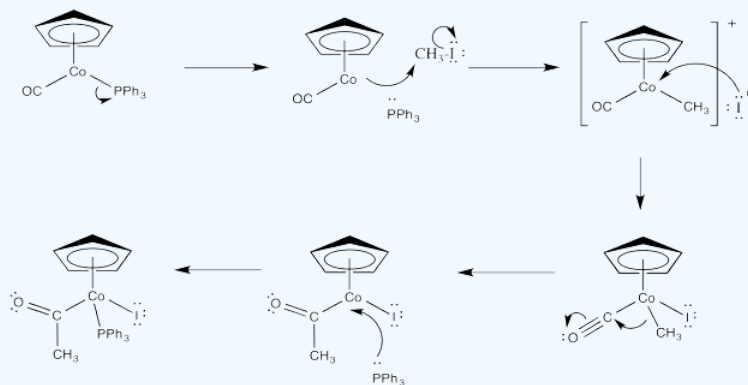
In case (a), the reaction appears to be S_N2 , presumably with complete inversion of configuration from (*S*) to (*R*). In case (b), there is probably a competing S_N1 pathway because the resulting cation is both benzylic and secondary, so it is pretty stable. On the other hand, if the reaction proceeded entirely through an S_N1 pathway, the reaction would result in nearly complete racemization, with 0% ee.

? Exercise 5.3.5

Frequently, oxidative additions and reductive eliminations are preceded or followed by other reactions. Draw a mechanism for the following transformation.



Answer



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