

5.4: Concerted Oxidative Addition

Concerted oxidative addition is a more general reaction than polar addition, in the sense that it is not restricted to compounds that can undergo aliphatic nucleophilic substitution. It could also be thought of as non-polar oxidative addition, because it does not involve charged intermediates as seen in the polar mechanism.

Aryl halides, for example, do not undergo nucleophilic substitution, but they do undergo concerted oxidative addition.

Instead of proceeding step by step, the addition of both fragments is synchronized. They add to the metal at the same time.



Figure 5.4.1

At first, it's difficult to understand this mechanism in terms of nucleophiles and electrophiles. The reaction is generally explained in terms of molecular orbital interactions, however, that can be thought of as nucleophile-electrophile interactions.

There are interactions involved in a concerted or non-polar oxidative addition.

- There is sigma bond donation from a bonding orbital in the substrate into a metal p orbital. This interaction is shown on the left of figure OA4.2.
- There is donation from a metal d orbital into an antibonding orbital on the substrate. This interaction is shown in the middle of figure OA4.2.
- Overall, a pair of electrons are donated from the substrate to the metal, and a pair of electrons are donated from the metal to the substrate.

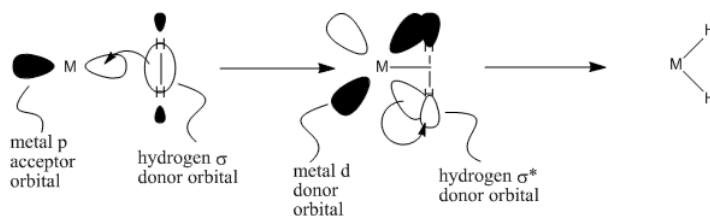


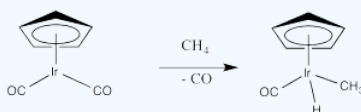
Figure 5.4.2: Molecular orbital interactions in a non-polar oxidative addition.



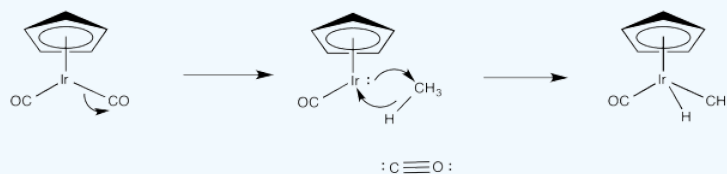
Figure 5.4.3: A curved arrow representation of non-polar oxidative addition.

? Exercise 5.4.1

Provide a mechanism, with curved arrows, for the following reaction.

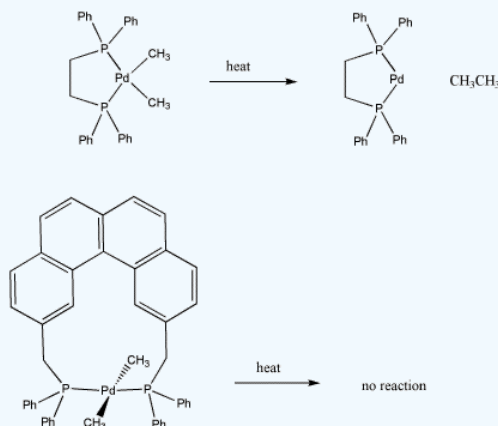


Answer



? Exercise 5.4.2

Propose a reason for the fact that one of the following dimethyl palladium compounds undergoes reductive elimination, but the other one does not.



Answer

Concerted oxidative addition is the mechanism that occurs when a polar mechanism ($\text{S}_{\text{N}}2$) is not possible. It is sometimes called "cis" oxidative addition. Because the two fragments added to the metal form bonds to the metal at the same time, they must be cis to each other.

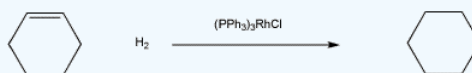
By the principle of microscopic reversibility, reductive elimination works the same way. The ligands have to be cis to each other in order to reductively eliminate, unless they are eliminating via a polar mechanism. Since both alkyl groups would have the same charge, a polar mechanism is unlikely.

Both of these platinum(II) complexes are d^8 and they would adopt square planar geometry. In the second case, the alkyls would be trans to each other and would be unable to undergo reductive elimination.

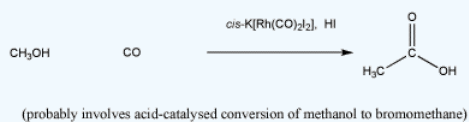
? Exercise 5.4.3

Frequently, oxidative addition and reductive elimination are combined with other reactions into catalytic cycles. These cycles form the basis of important processes used to make valuable materials. Propose catalytic cycles for the following reactions. You don't need to draw curved arrows; just provide the intermediate formed after each reaction step.

a) catalytic hydrogenation



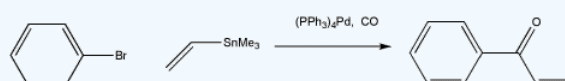
b) Monsanto Acetic Acid Process



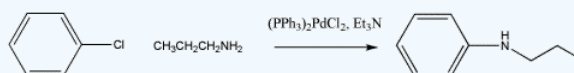
c) Suzuki Coupling



d) Stille Coupling (Carbonylative Variation)



e) Buchwald-Hartwig Coupling



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