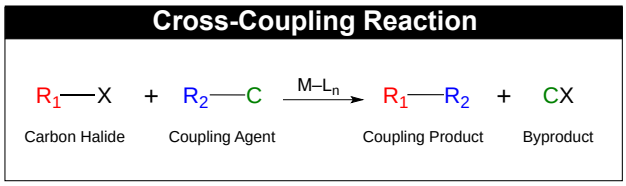
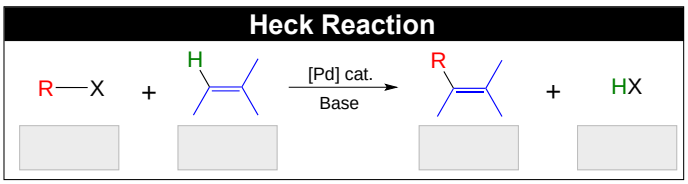
CONCEPT: HECK REACTION

- The Heck Reaction involves the coupling between a carbon halide and an alkene in the presence of a Pd catalyst.
  - □ The **R** group of the carbon halide is substituted for a(n) _____ hydrogen of an alkene.





  - □ The R_1 group of the carbon halide is represented by a(n) *vinyl, aryl* + _____ group.
  - □ The R_2 group is represented by a(n) _____ group.
  - □ The **C** group = _____.
  - □ The **X** leaving group of the carbon halide is represented by a Cl, Br, I or OTf group.
  - □ The Base = _____, _____ or _____.

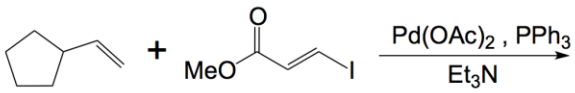
Regioselectivity

- The reaction is highly *regioselective*, with the R_1 group going to the _____ substituted position of the alkene.

Stereoselectivity

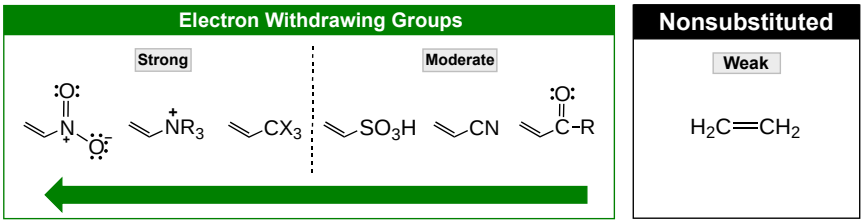
- If an E or Z configuration is possible at the alkene, the reaction is highly stereoselective, often giving _____ as the major.

EXAMPLE: Determine the product from the following Heck Reaction.

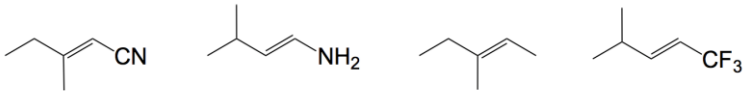


The Alkene

- The reactivity of the alkene (R_2) _____ with increasing substitution.
  - □ Highest yields are obtained for _____ and _____ with *electron withdrawing groups*.



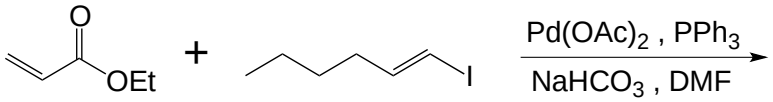
EXAMPLE: Rank the following alkenes in order of increasing reactivity towards the Heck Reaction.



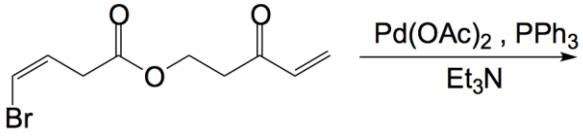
A B C D

CONCEPT: HECK REACTION

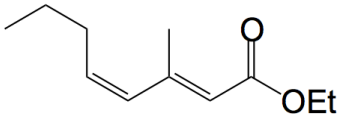
PRACTICE: Determine the product from the following Heck Reaction.



PRACTICE: Predict the product formed from the following intramolecular Heck reaction.

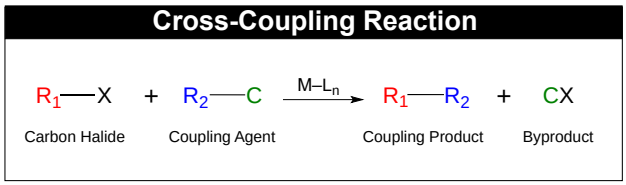


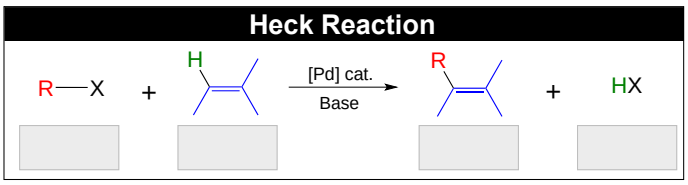
PRACTICE: Using ethyl-2-butenoate as your starting material, prepare the following compound by a Heck reaction.



CONCEPT: HECK REACTION MECHANISM

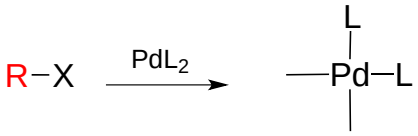
- The Heck Reaction mechanism occurs via a catalytic cycle that is comprised of _____ intermediates.



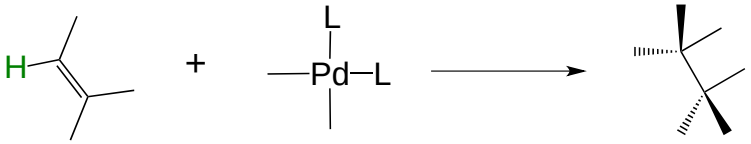


Coupling Mechanism

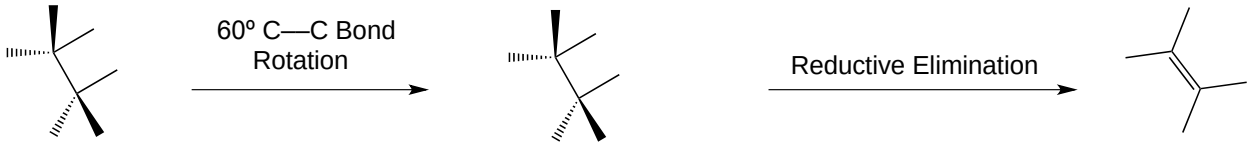
1) **Oxidative Addition**: Involves the addition of the carbon halide to the transition metal complex.



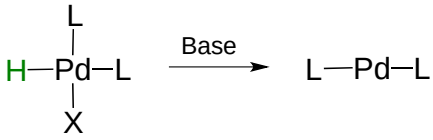
2) **Syn Addition**: The resulting complex reacts with the alkene and adds R_1 and Pd across the pi bond on the same side.



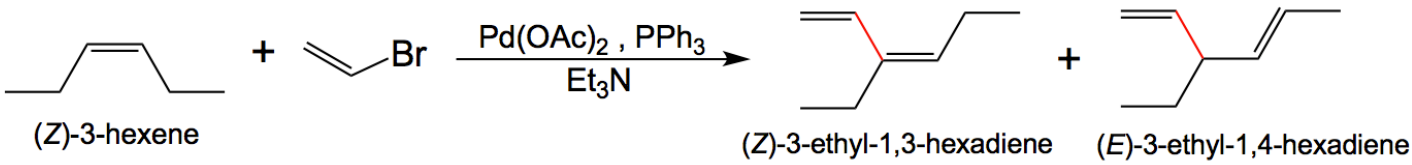
3a) **Reductive Elimination 1**: New complex undergoes a C–C bond rotation followed by <u>syn</u> elimination to give the alkene.



3b) **Reductive Elimination 2:** The base (_____ or_____) removes HX to regenerate the palladium catalyst.



EXAMPLE: A Heck reaction between (Z)-3-hexene and bromoethene creates both (Z)-3-ethyl-1,3-hexadiene and (E)-3-ethyl-1,4-hexadiene. Illustrate how both products can be formed.



(Z)-3-hexene

(Z)-3-ethyl-1,3-hexadiene

(E)-3-ethyl-1,4-hexadiene