

ORGANIC CHEMISTRY 2 LECTURE GUIDE 2019

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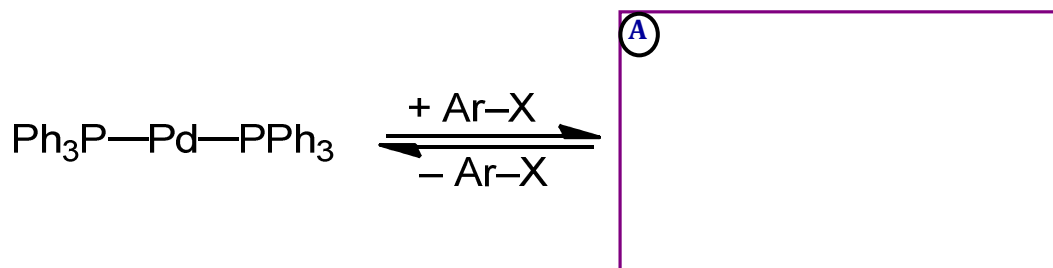
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Lesson V.4. Palladium-Catalyzed C-C Bond-Forming Reactions*Palladium complexes undergo reversible oxidative addition*

Organopalladium compounds can undergo reversible oxidative addition with various organic compounds, such as aryl halides:



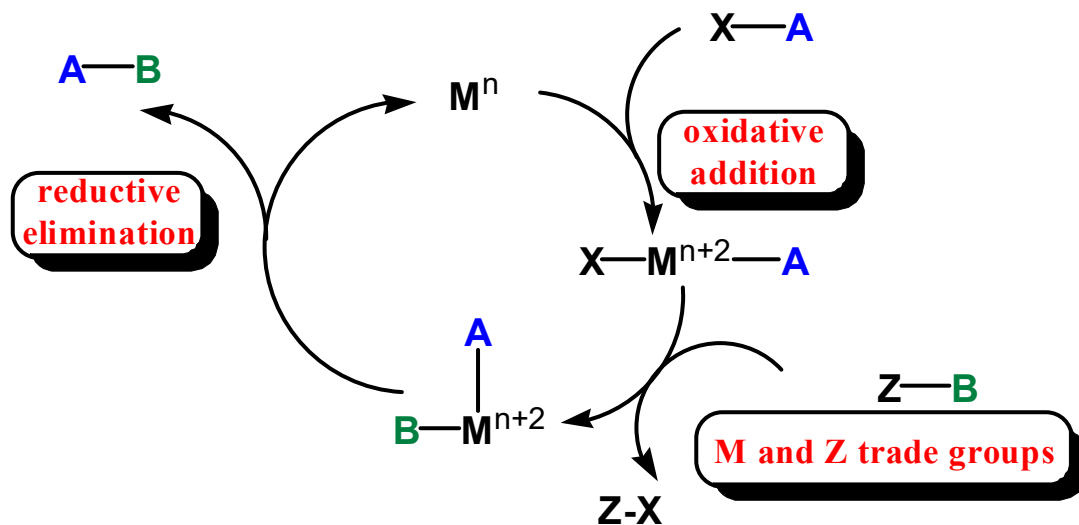
The reversible nature of this process makes it a good candidate for catalytic CC bond-forming reaction. As we will see, many such reactions have been discovered and they have become so useful that the pioneers of the field won the Nobel Prize in Chemistry for this work.

Notes

Lesson V.4. Palladium-Catalyzed C-C Bond-Forming Reactions

Catalytic cycle

A generalized Pd-catalyzed C-C bond forming reaction is given here:



Notes

Lesson V.4. Palladium-Catalyzed C-C Bond-Forming Reactions

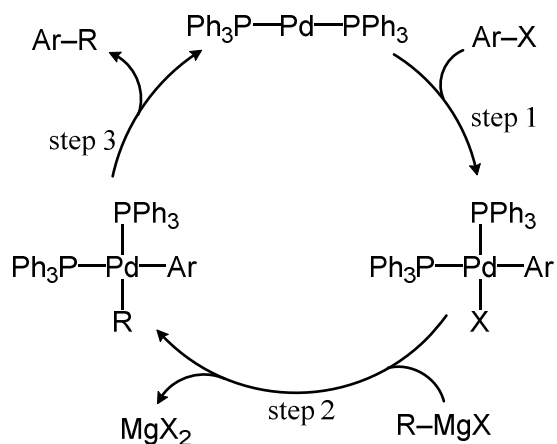
Kumada reaction

The **Kumada Reaction** couples:

A

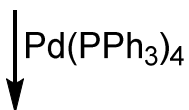
R = aryl, benzyl or vinyl; X = OTf, Cl, Br, or I

A simplified catalytic cycle:



An example:

PhMgCl + 4-iodotoluene



B

Notes

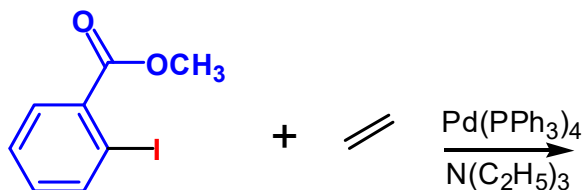
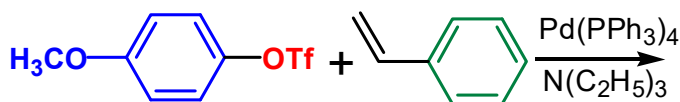
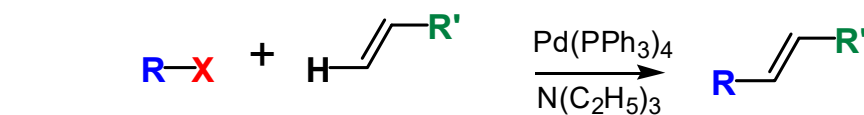
Lesson V.4. Palladium-Catalyzed C-C Bond-Forming Reactions

Heck reaction

The **Heck Reaction** couples:

(A)

R = aryl, benzyl or vinyl; X = OTf, Cl, Br, or I



(B)

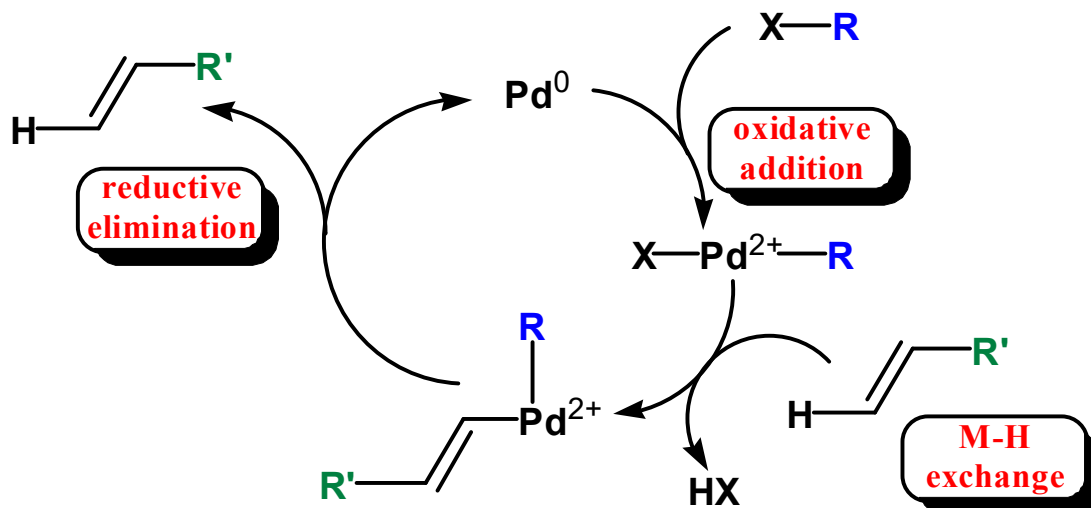
(C)

Notes

Lesson V.4. Palladium-Catalyzed C-C Bond-Forming Reactions

Heck reaction

A simplified mechanism for the Heck Reaction:



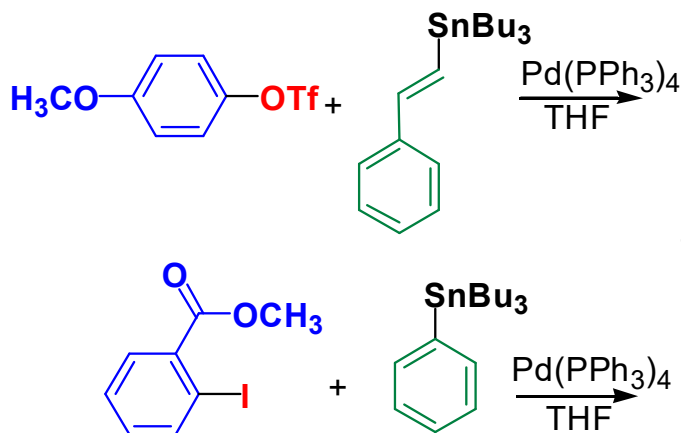
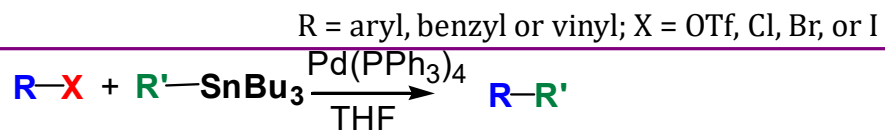
Notes

Lesson V.4. Palladium-Catalyzed C-C Bond-Forming Reactions

Stille Reaction

The **Stille Reaction** couples:

(A)



(B)

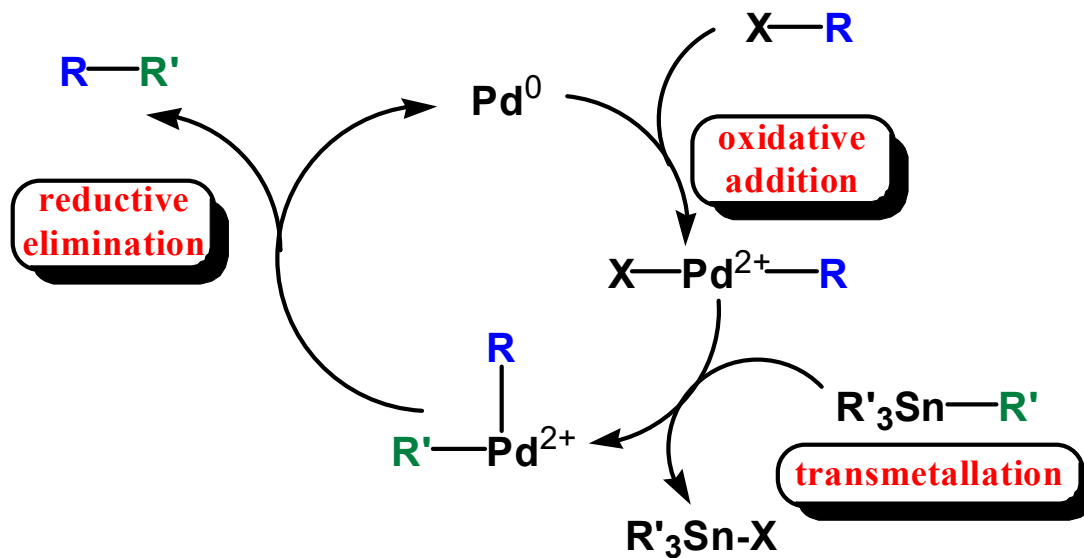
(C)

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Lesson V.4. Palladium-Catalyzed C-C Bond-Forming Reactions

Stille Reaction

A simplified mechanism for the Stille reaction is:



Notes

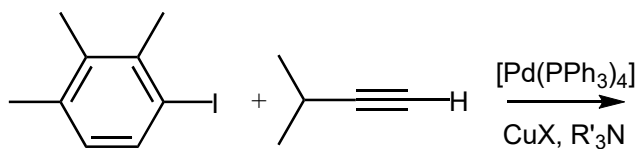
Lesson V.4. Palladium-Catalyzed C-C Bond-Forming Reactions

Sonogashira reaction

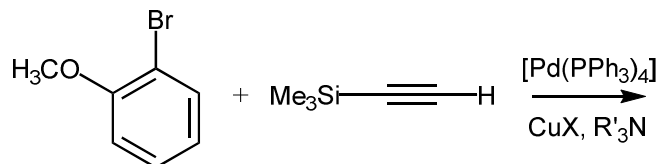
The **Sonogashira Reaction** couples:

A

R = aryl, benzyl or vinyl; X = OTf, Cl, Br, or I



B



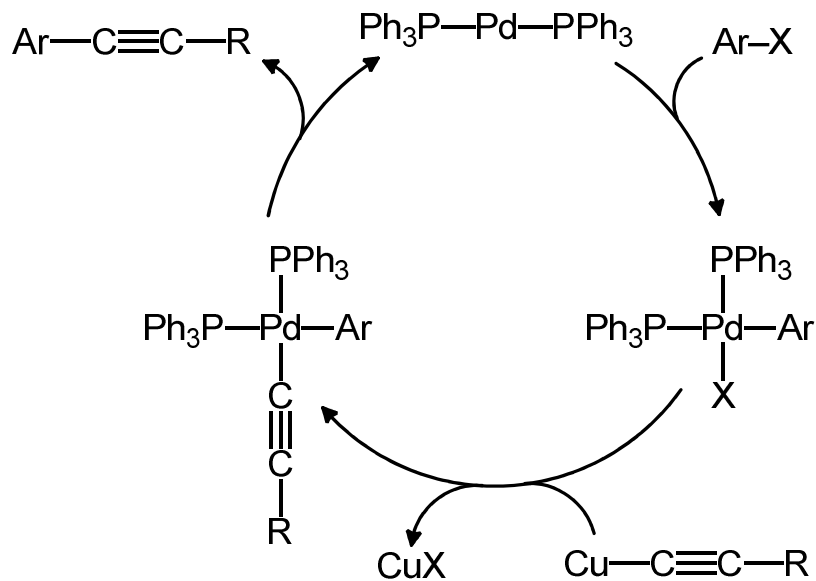
C

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Lesson V.4. Palladium-Catalyzed C-C Bond-Forming Reactions

Sonogashira reaction

A simplified mechanism for the Sonogashira reaction is:



Notes

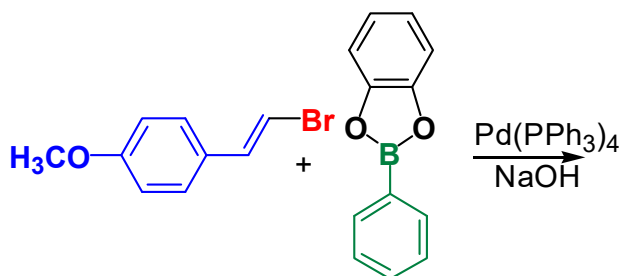
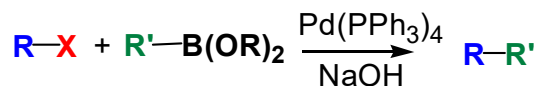
Lesson V.4. Palladium-Catalyzed C-C Bond-Forming Reactions

Suzuki reaction

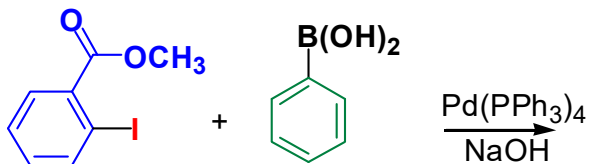
The **Suzuki Reaction** couples:

(A)

R = aryl, benzyl or vinyl; X = Cl, Br, or I



(B)



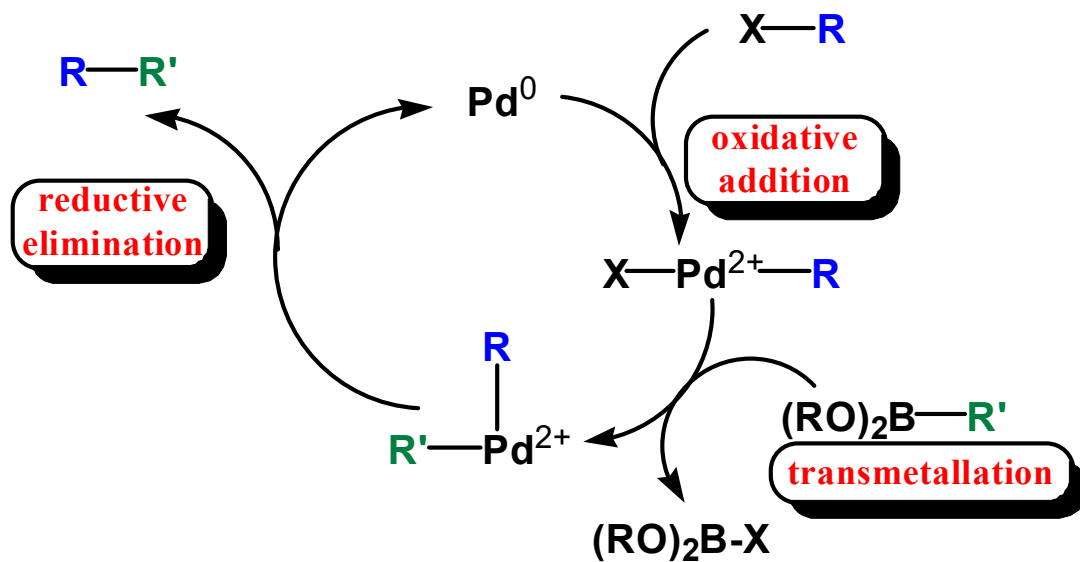
(C)

Notes

Lesson V.4. Palladium-Catalyzed C-C Bond-Forming Reactions

Suzuki reaction

A simplified mechanism for the Suzuki reaction is:



Notes