

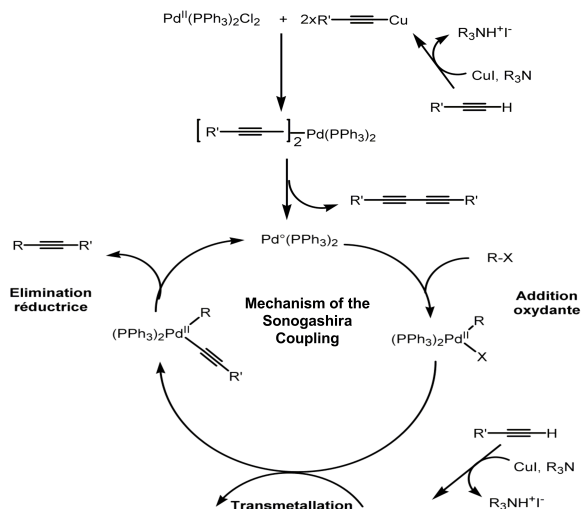
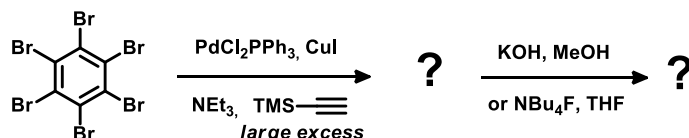
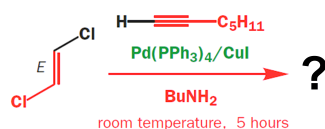
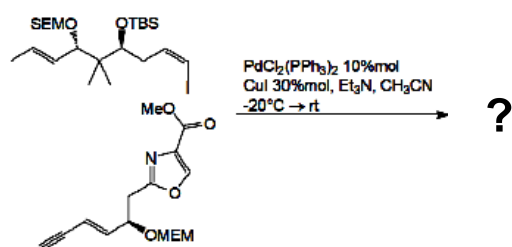
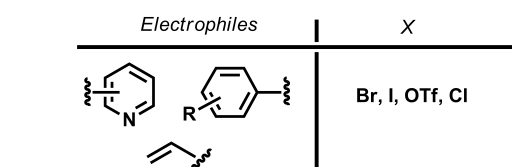
TD 5 « Les réactions modernes de chimie organométallique dans les industries » : Applications en synthèse – La Chimie du Pd (#3)

Couplage Sonogashira, Heck, π -Allylation de Tsuji-Trost

1) Couplage de Sonogashira

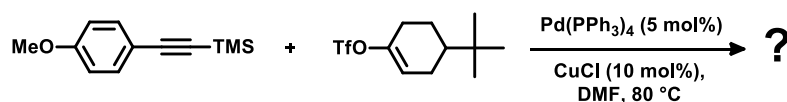
This coupling of terminal alkynes with aryl or vinyl halides is performed with a palladium catalyst, a copper(I) cocatalyst, and an amine base. Typically, the reaction requires anaerobic conditions. Newer procedures have been developed in presence of H_2O and acidic protons (O-H, N-H, S-H).

Convenient electrophiles for the Sonogashira coupling:

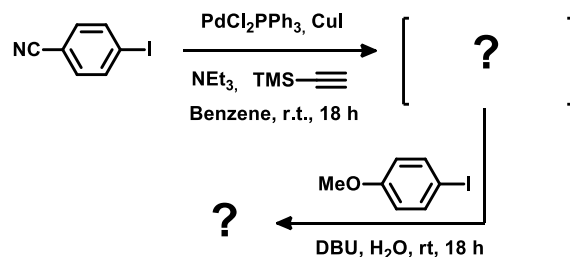


Réaction de sila-Sonogashira

Pourquoi dans ce cas-ci est-il possible d'utiliser un alcyne qui n'est pas nécessairement vrai? Justifier au travers d'un mécanisme.



One-Pot Sonogashira/sila-Sonogashira couplings



2) Réaction de Heck

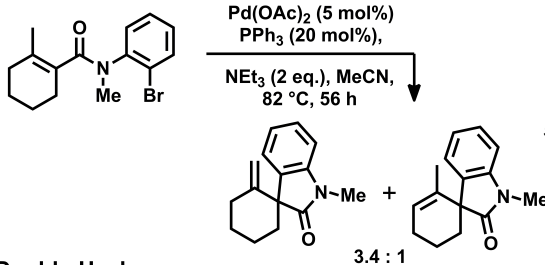
The palladium-catalyzed C-C coupling between aryl halides or vinyl halides and activated alkenes in the presence of a base is referred as the "Heck Reaction". Recent developments in the catalysts and reaction conditions have resulted in a much broader range of donors and acceptors being amenable to the Heck Reaction.

=> One of the benefits of the Heck Reaction is its outstanding *trans* selectivity.

Olefins must be monosubstituted or 1,1-disubstituted

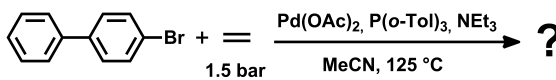
Heck Intramoléculaire

Rationnaliser le résultat observé au travers d'un mécanisme ?



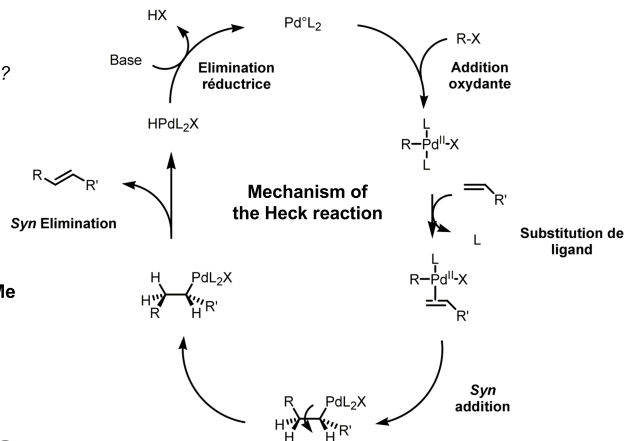
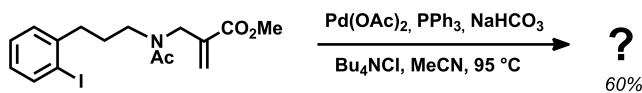
Double-Heck

Quelle est la géométrie du produit observé ?

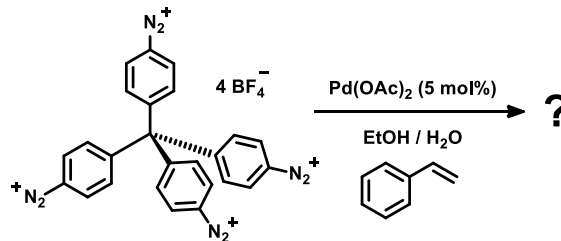


Macrocyclisation

N.B.: La réaction de Heck est une excellente méthodologie pour former des composés polycycliques très tendus.

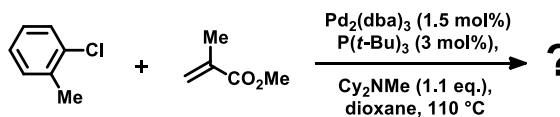
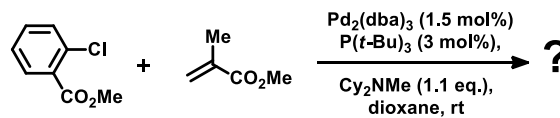


Diazonium salts



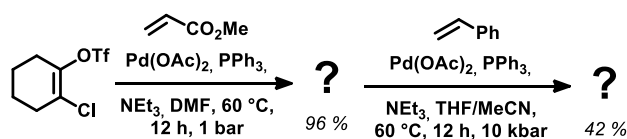
Activation

Quelles sont les différences entre ces réactions ?
Que peut-on en conclure ?



Chimiosélectivité

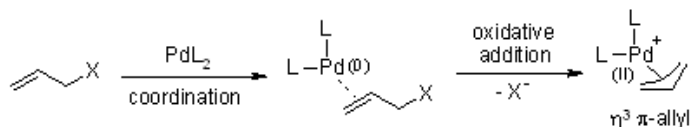
Comment pourrait-étre synthétiser le produit de départ ? Sur quoi se base-t-on pour rendre ce procédé chimiosélectif ?



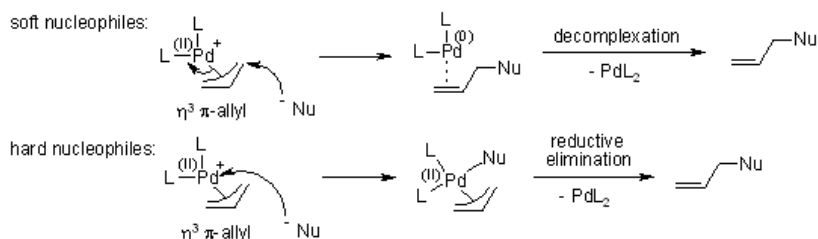
3) Tsuji-Trost π -Allylation

The Tsuji-Trost Reaction is the palladium-catalyzed allylation of nucleophiles such as active methylenes, enolates, amines and phenols with allylic compounds such as allyl acetates and allyl bromides.

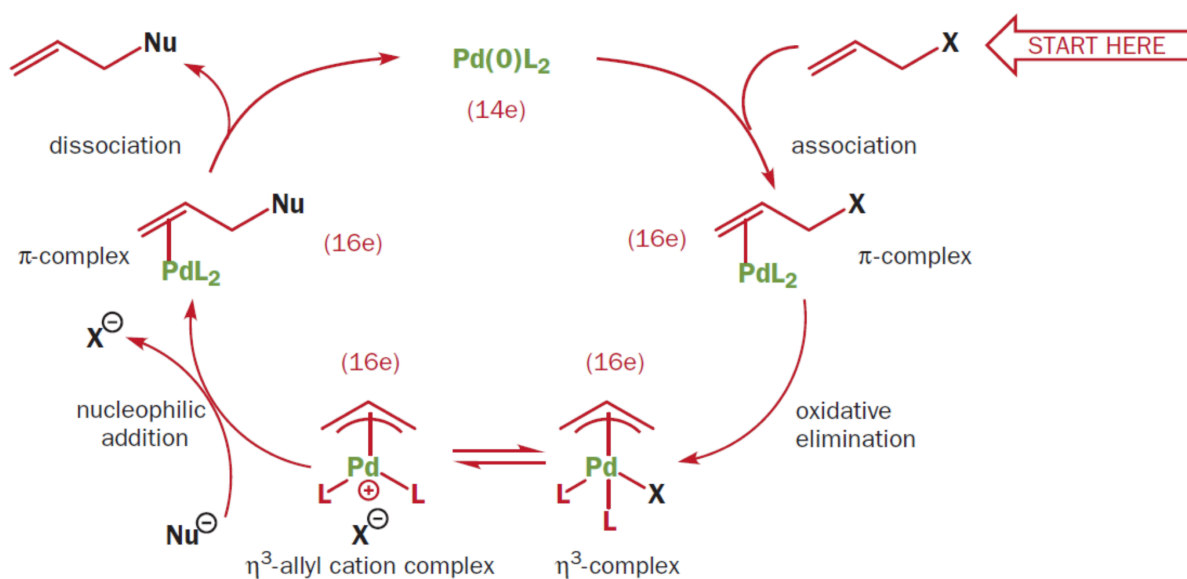
The coordination of the Pd(0)-catalyst to the double bond forms an η^2 π -allyl complex. An oxidative addition, during which the leaving group is expelled, gives an η^3 π -allyl complex. This step is also called ionization:



Depending on the strength of the nucleophile, the reaction can take two different pathways. Soft nucleophiles, such as those derived from conjugate acids with a $pK_a < 25$, normally add directly to the allyl moiety, whereas hard nucleophiles first attack the metal center, followed by reductive elimination to give the allylation product:

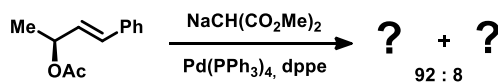
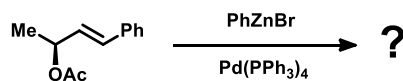
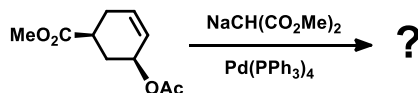


Tsuji-Trost Catalytic Cycle

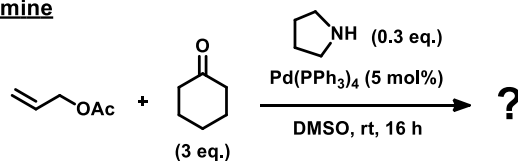


Inversion vs. rétention de configuration

Dans quel cas a-t-on rétention de configuration ?
Quel est le produit majoritaire dans le 3ème cas ?



Enamine



Cyclisation intramoléculaire

Expliquez par le biais de mécanismes la formation ainsi que le ratio des produits observés ?

