MAX-PLANCK-INSTITUT
FÜR KOLLOID- UND
GRENZFLÄCHENFORSCHUNG

ALLYLIC SUBSTITUTION

[HARTIWG CH. 20]

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Biomolecular Systems
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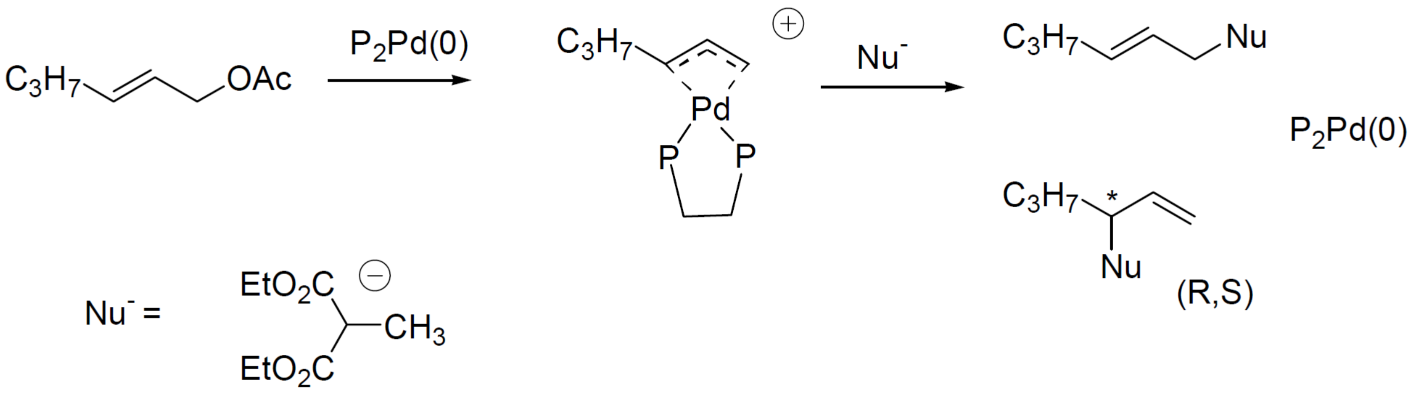
8.1 ALLYLIC SUBSTITUTION

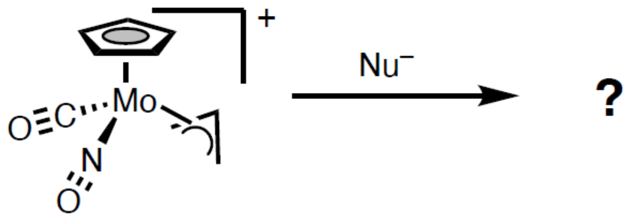


Formal S_N2

Formal S_N2'

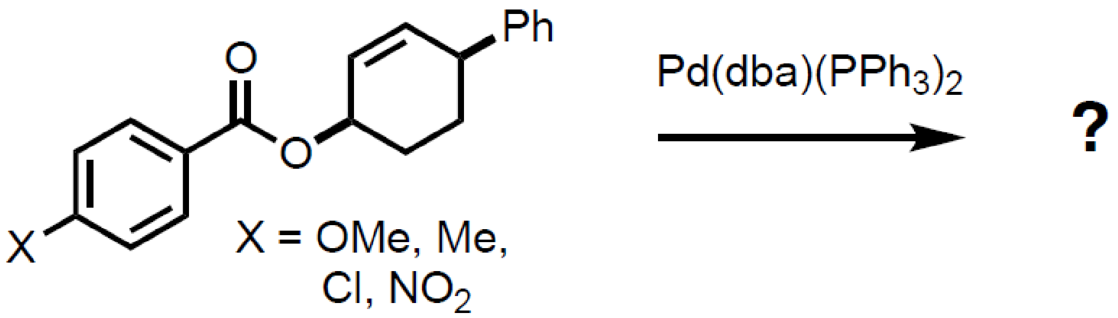
POD #2

Consider the following molybdenum complex. Based on the Davies–Green–Mingos rules and *trans* effect/influence trends, **predict the site of attack for a generic stabilized nucleophile (Nu–).**

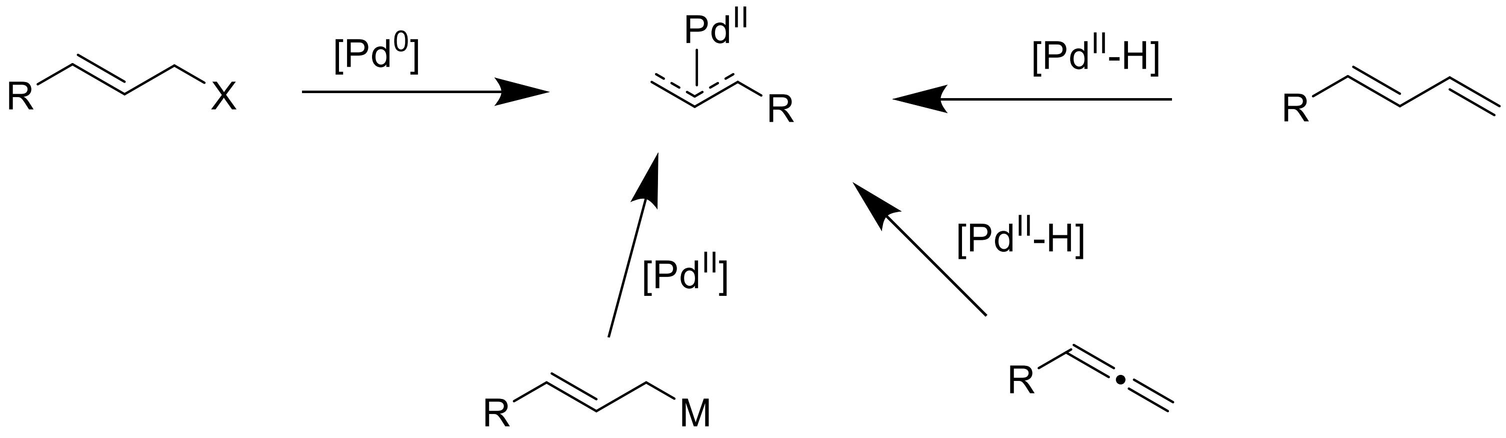


POD #3

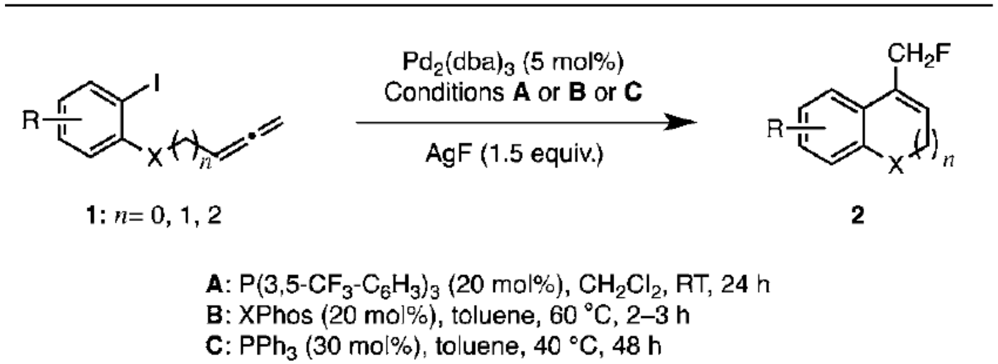
Consider the series of reactions depicted below. **Draw the product(s) and order the four substrate in terms of predicted reaction rate.**



8.1.1 SYNTHESIS OF PI-ALLYL

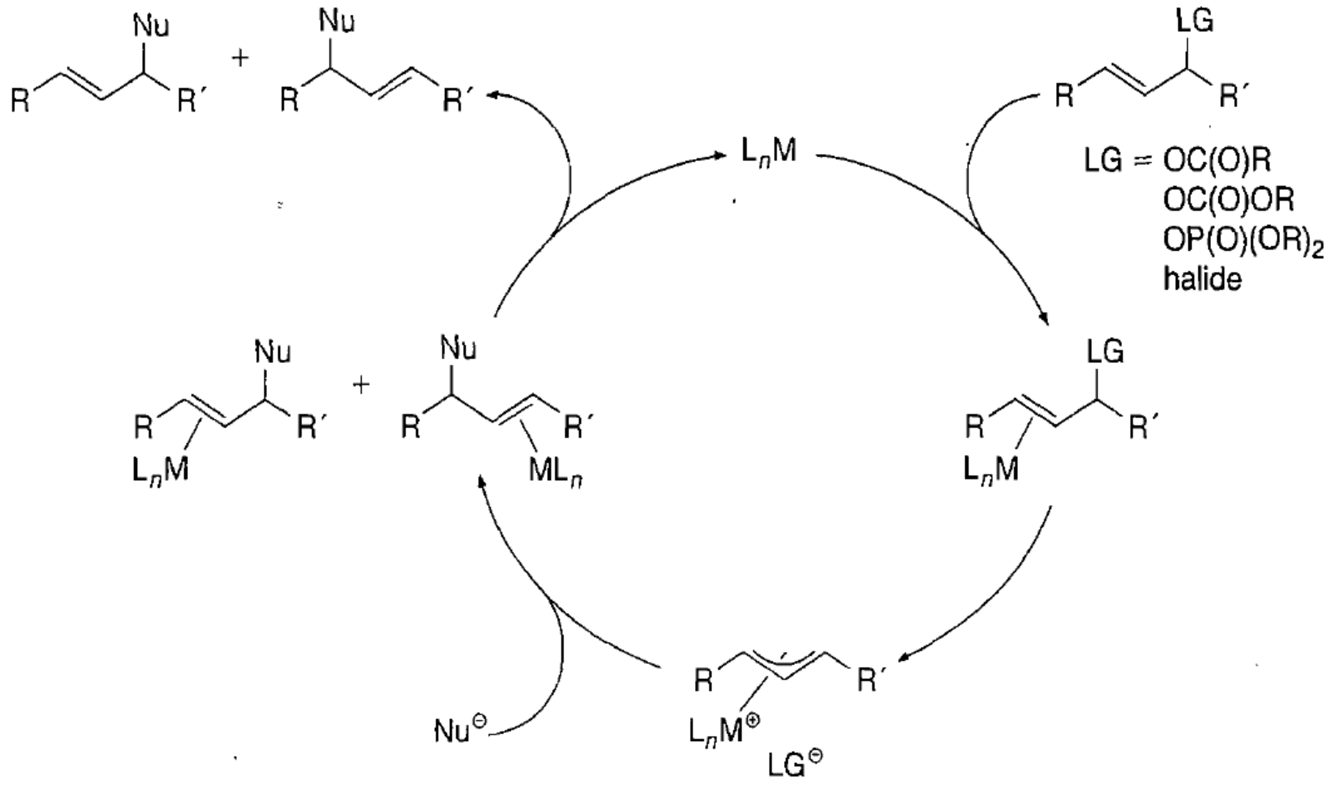


8.1.1 SYNTHESIS OF PI-ALLYL - EXAMPLE



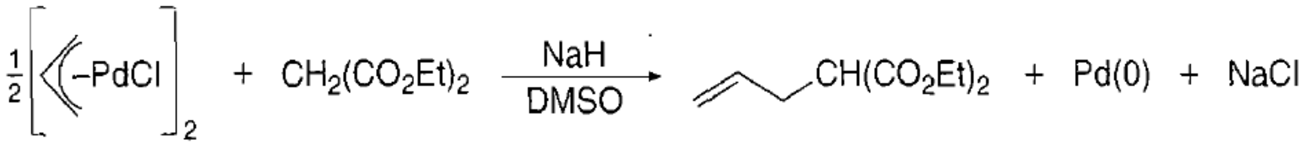
Doyle *Chem Sci* **2013** 4 1216. DOI: 10.1039/C2SC22198E

8.1.2 MECHANISM

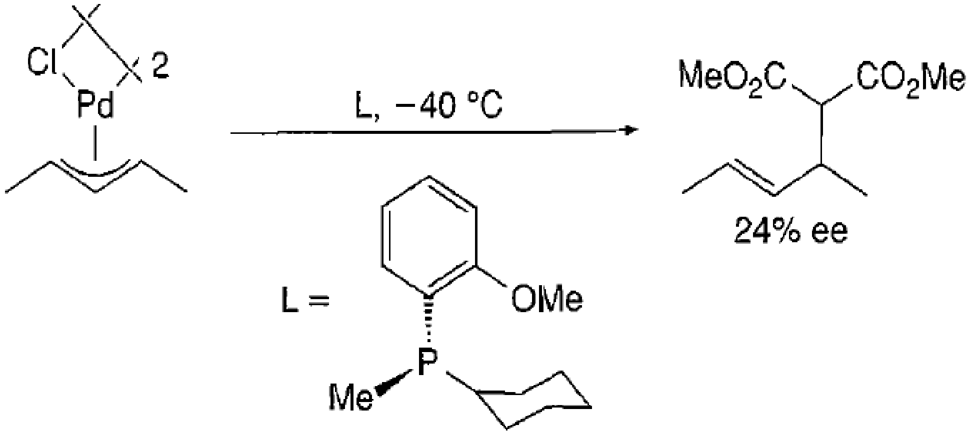


8.1.3 HISTORY – TSUIJ-TROST

Tsuij



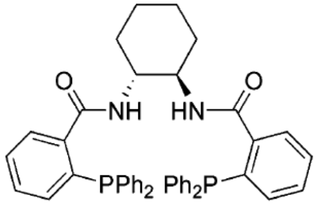
Trost



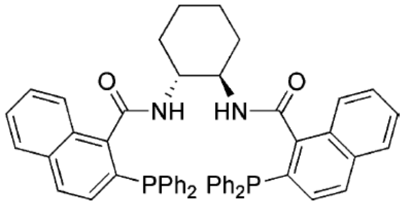
Tsuij *Tet Lett* **1965** 6, 4387. DOI: czphwv
Trost *JACS* **1973** 95, 292. DOI: 10.1021/ja00782a080

8.1.3 TROST LIGANDS

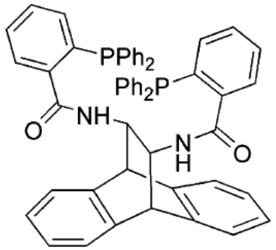
Palladium-catalyzed asymmetric allylic alkylation (Pd AAA)



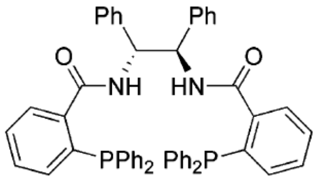
(*R*,*R*)-standard



(*R*,*R*)-naphthyl

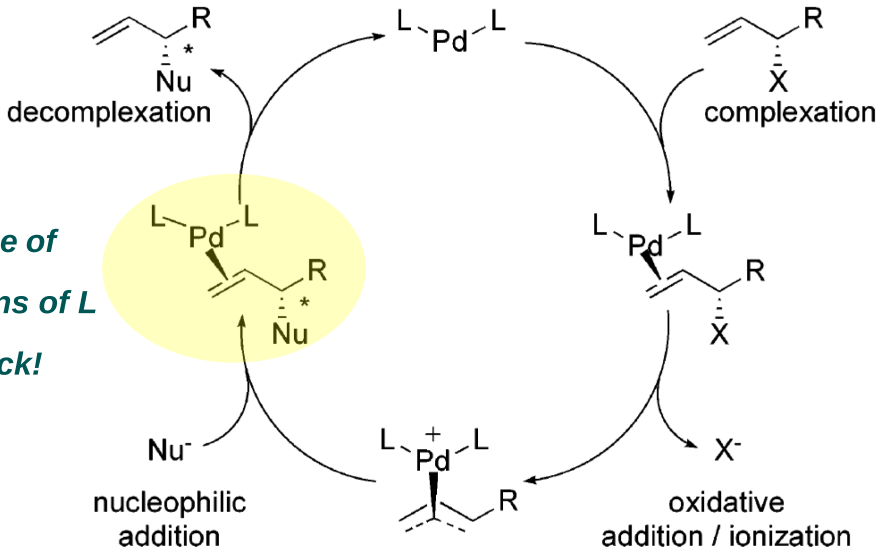


(*R*,*R*)-anthracenyl



(*R*,*R*)-stillbene

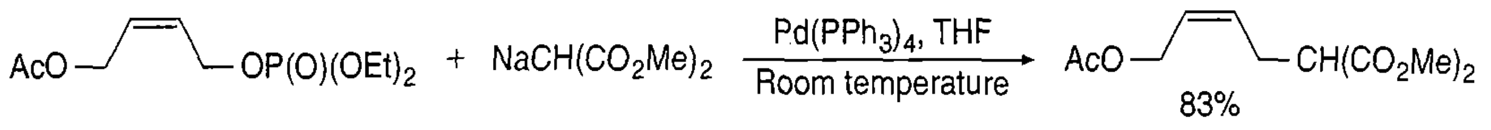
Hard because of relative positions of L and Nu attack!



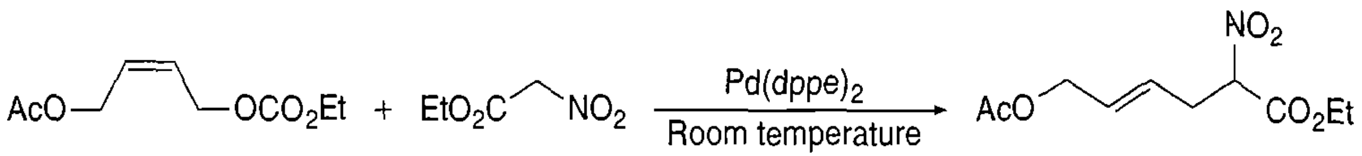
Trost Acc Chem Res 2006 39, 747. DOI: [10.1021/ar040063c](https://doi.org/10.1021/ar040063c)

8.1.4 ELECTROPHILES SCOPE

Most common: acetates, phospates, carbonates (increasing reactivity)



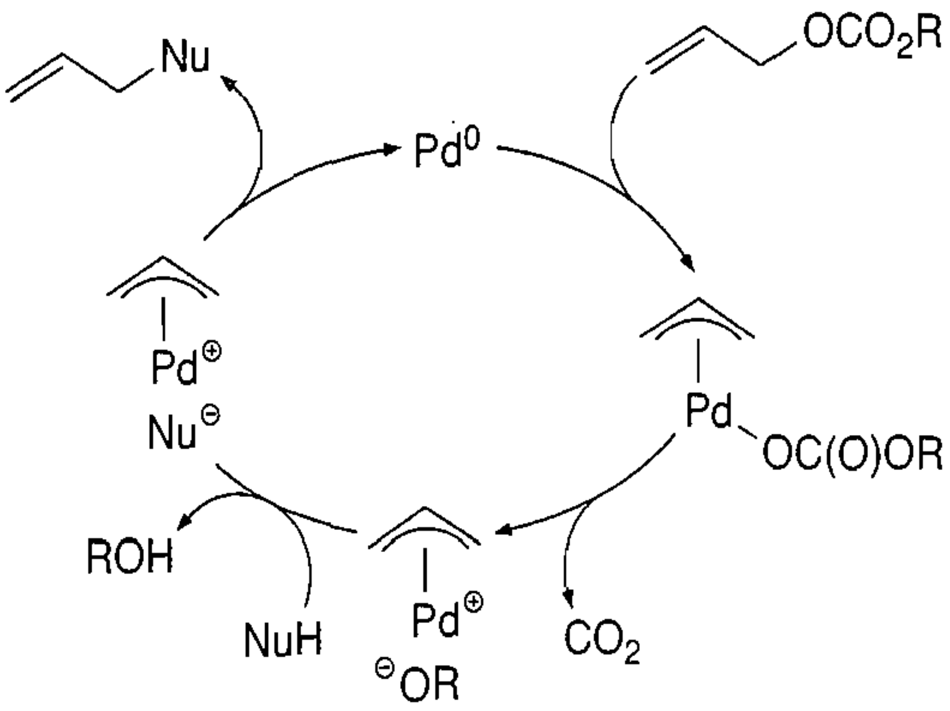
(20.5)



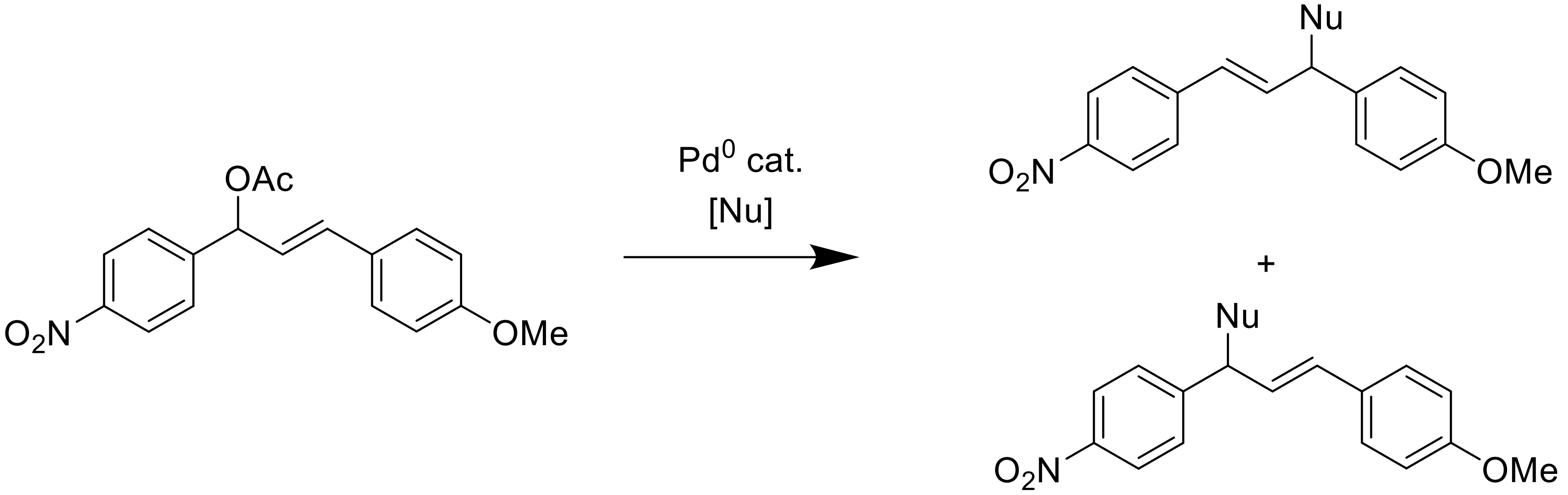
(20.6)

8.1.4 WHY CARBONATES ARE SO EFFECTIVE

No need for external base to deprotonate acidic pronucleophiles (generated *in situ* after decarboxylation)



8.1.5 ELECTROPHILE ELECTRONICS



97

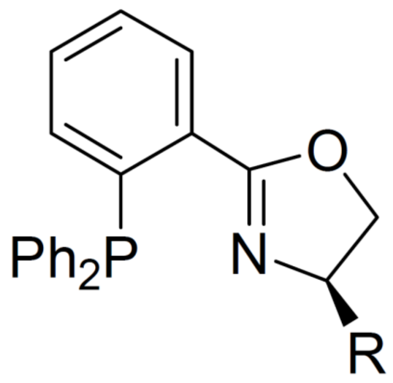
:

3

Tet **1992** 48, 1695. DOI: fvndf7

8.1.6 LIGAND EFFECT

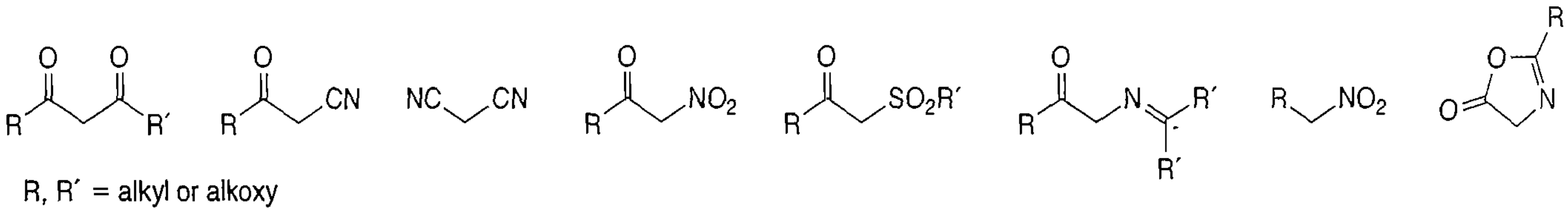
Trans influence, exploited e.g. in PHOX ligands -> *attack trans to P*



PHOX

8.1.7 NUCLEOPHILE SCOPE

Soft, stabilized C-nucleophiles are the most common

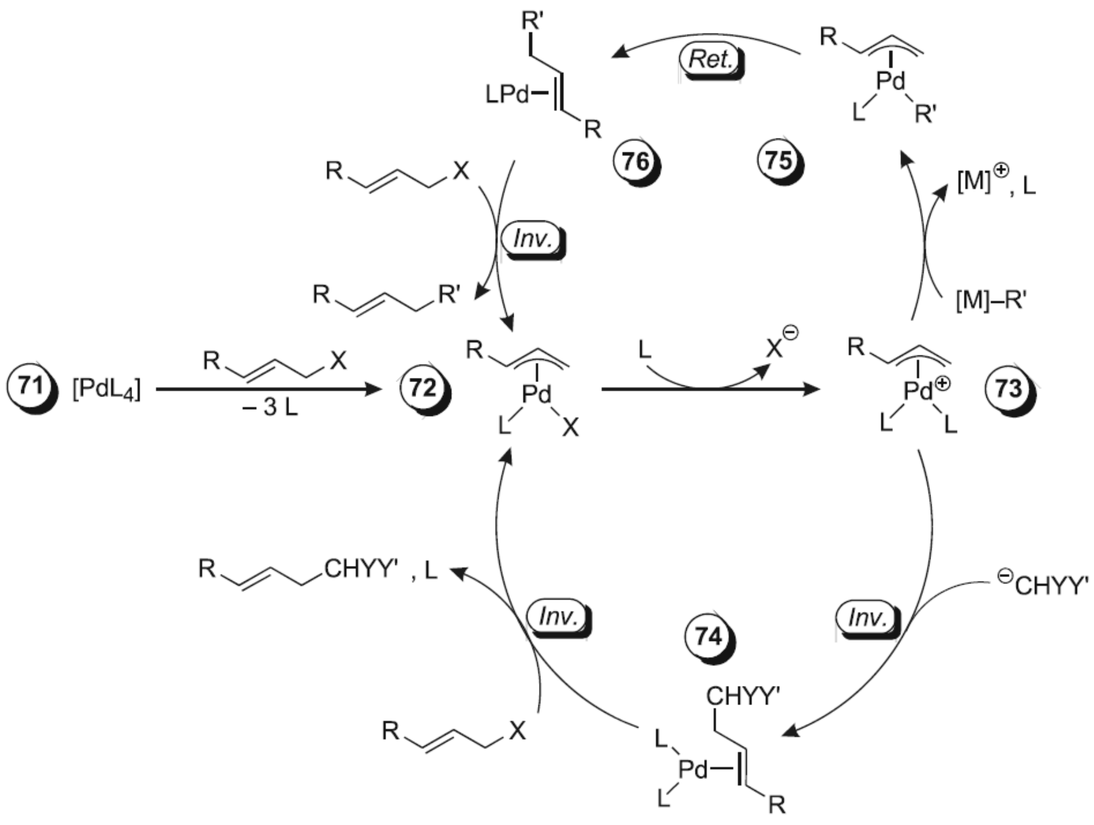


8.1.7 STEREOCHEMICAL OUTCOME AND NUCLEOPHILE TYPE

Soft nucleophiles (e.g. malonates): overall retention (double inversion)
Pd π-allyl complex attached anti by external, outersphere, nucelophile

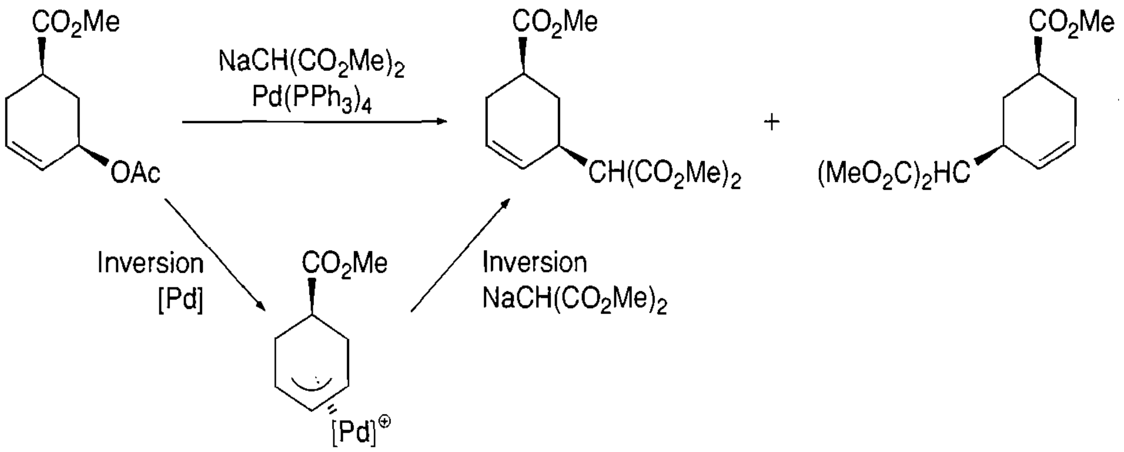
Hard nucleophiles (e.g. Griganrds): overall inversion (inversion + retention)
First nucleophile reacts at Pd (e.g. rapid transmetallation of Grigard) η^1 then reductive elimination

8.1.7 STEREOCHEMICAL OUTCOME AND NUCLEOPHILE TYPE



8.1.7 STEREOCHEMICAL OUTCOME AND NUCLEOPHILE TYPE

Soft nucleophiles



Hard nucleophiles