

Propargyl Cation-Dicobalt Hexacarbonyl Complexes

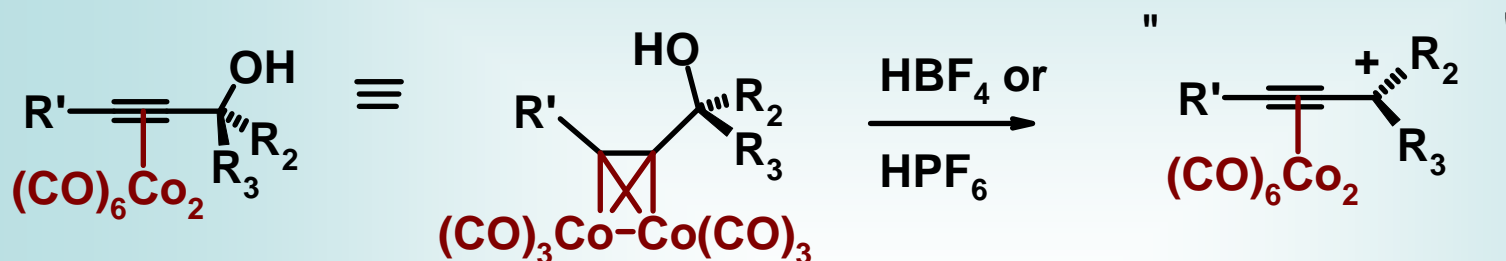
R Green, J. R. *Curr. Org. Chem.* **2001**, 5, 809.

R Teobald, B. J. *Tetrahedron* **2002**, 58, 4133.

R Caffyn, A.J.M.; Nicholas, K. M. in *Comprehensive Organometallic Chemistry II*, 1995, V.12, Ch. 7.1

R Nicholas, K. M. *Acc. Chem. Res.* **1987**, 20, 208.

(Di)Cobalt alkyne complexes form cations at the propargylic site very easily

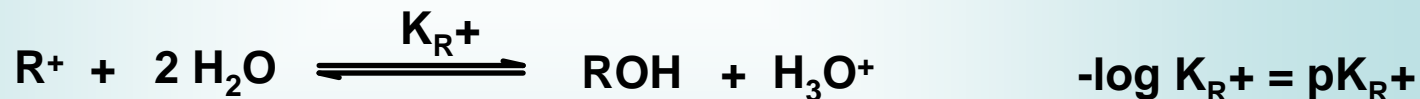


thermally stable, dark red/beet/brown solids

structure is a lie

-as cations go, these are very stable

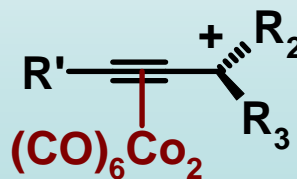
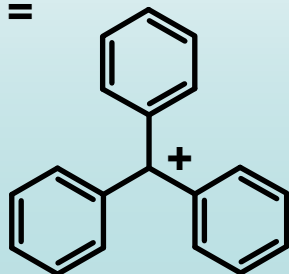
Consider



i.e., the less negative (more positive) the number, the more stable

Consider Ph_3C^+ =

$\text{p}K_{\text{R}^+} = -6.6$



$\text{p}K_{\text{R}^+} = -6.8 - -7.4$

or -5.5

depending on reference

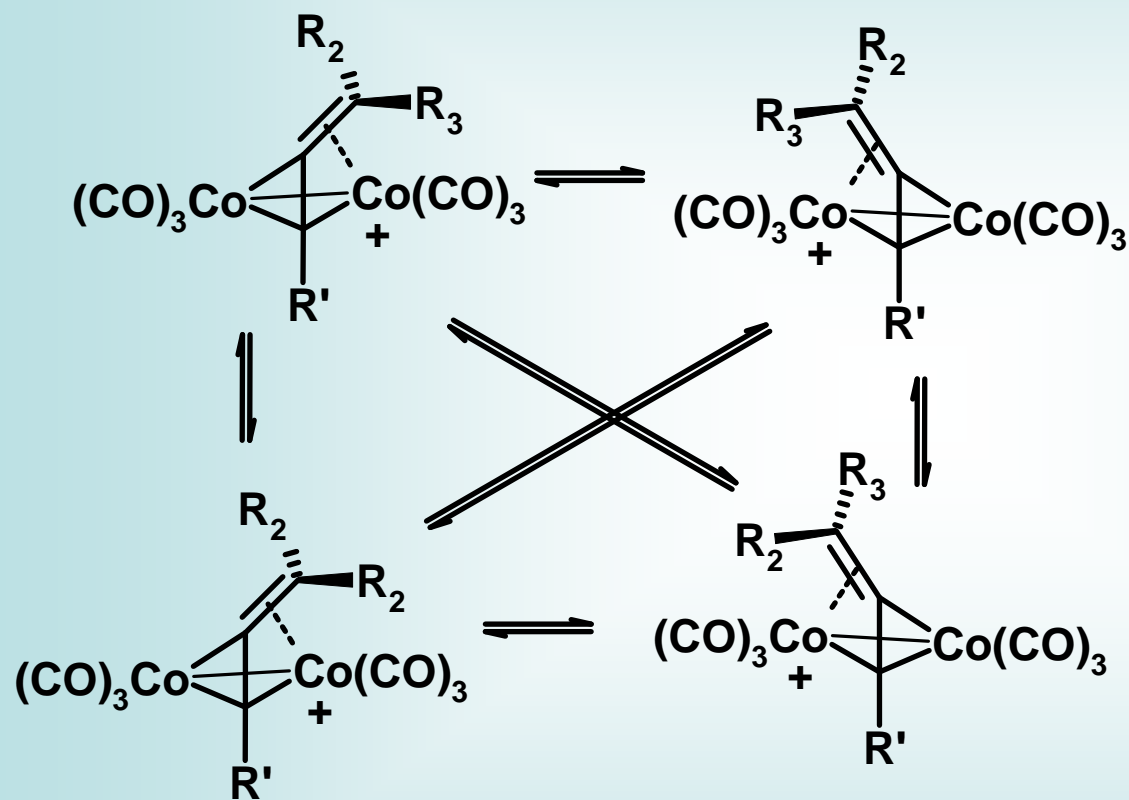
meaning, about the same⁸¹

-best estimation of structure

-X-Ray of cation

Schreiber, S. L.; et al *J. Am. Chem. Soc.* 1987, 109, 5749.

Melikyan, G. G. et al *Angew. Chem. Int. Ed. Engl.* 1998, 37, 161.



-both antarafacial and supra-facial migrations going on, along with epimerization

-actually pretty complicated

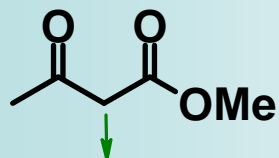
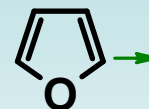
-these are much more electrophilic than allylpalladiums, so they are electrophilic enough to react with several types of nucleophiles



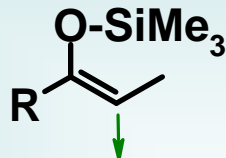
electron rich
aromatics

-arene needs one or more activating groups, i.e.,

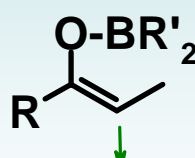
-OCH₃, -OH, -NMe₂



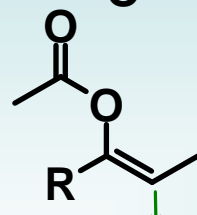
β -dicarbonyls



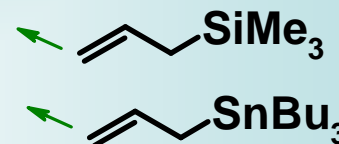
silyl enol ethers
silyl ketene acetals



enol borinates



enol
acetates



allylsilanes or
allyltins

NaBH_4

or

$\text{Et}_3\text{SiH} + \text{CF}_3\text{COOH}$

reduction

R_2NH

amines

Et_2AlCN

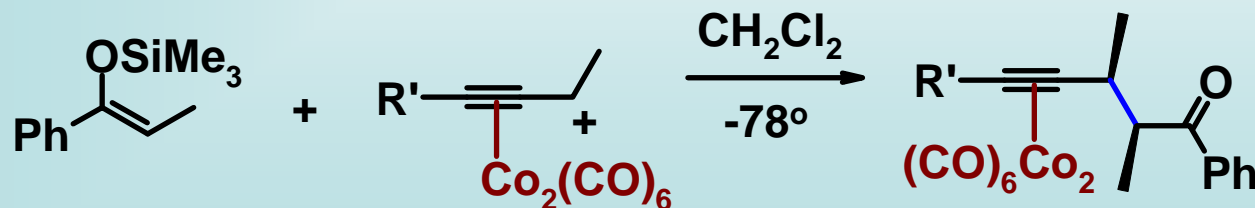
cyanation

R_3Al

alkylation

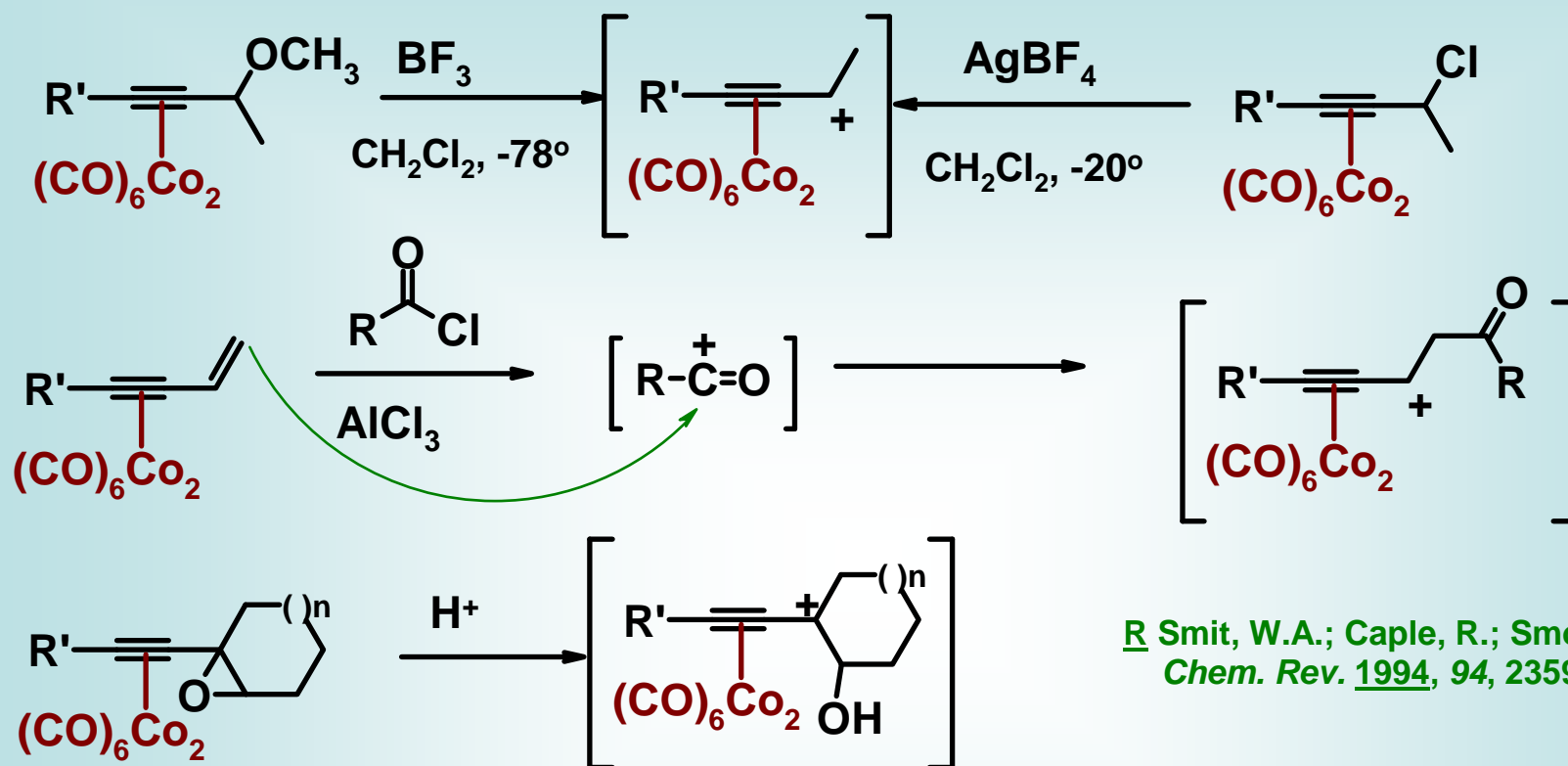
$\text{R}_2\text{Cu}(\text{CN})\text{ZnI} ???$

A couple of examples



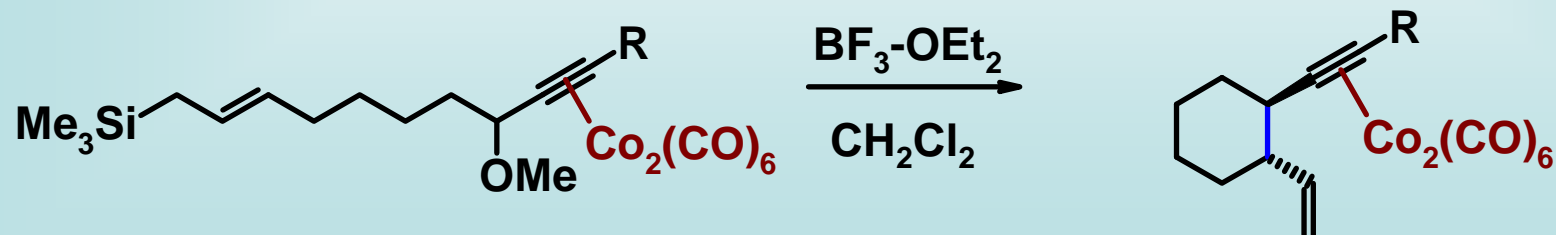
pretty high *syn*
stereoselection

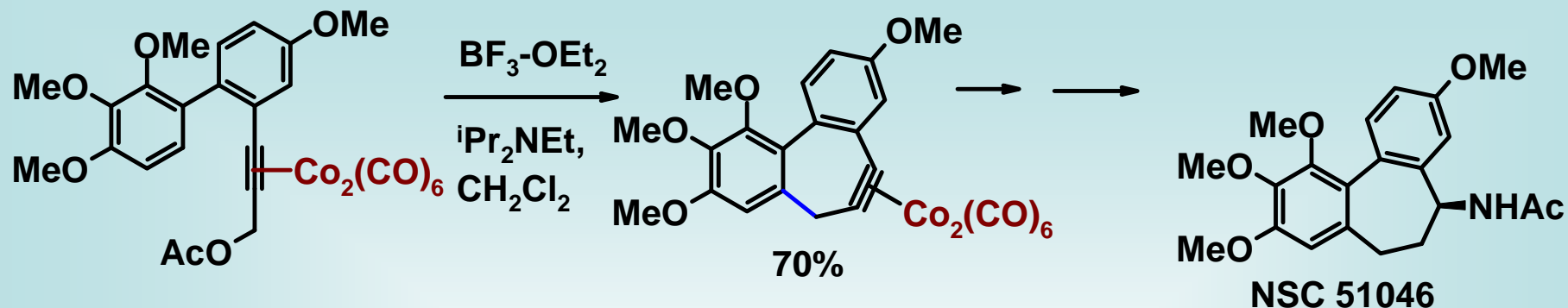
-the cations can be generated in several related ways, such as from ethers or acetates, halides, alkenes, epoxides, etc.



R Smit, W.A.; Caple, R.; Smoliakova, I.P.
Chem. Rev. 1994, *94*, 2359.

-intramolecular variants of this reaction are certainly viable

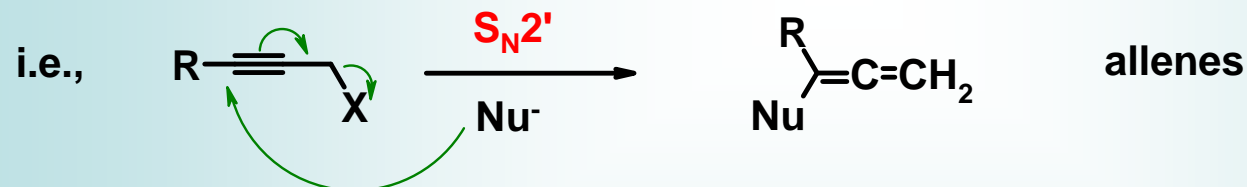




-notice stabilization of 7 membered ring alkyne

in general, the cobalt carbonyl unit can be removed as before (Ce^{+4} , Fe^{+3} , $\text{Me}_3\text{N}^+\text{-O}^-$)

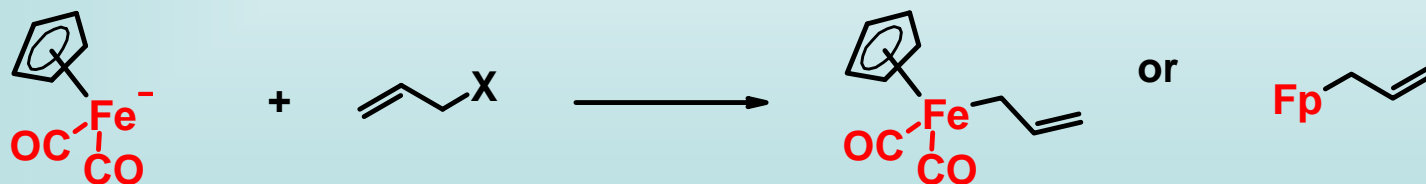
Importance - in traditional organic chemistry, $\text{S}_{\text{N}}2'$ reactions are a major competitive problem in substitutions of propargyl-X



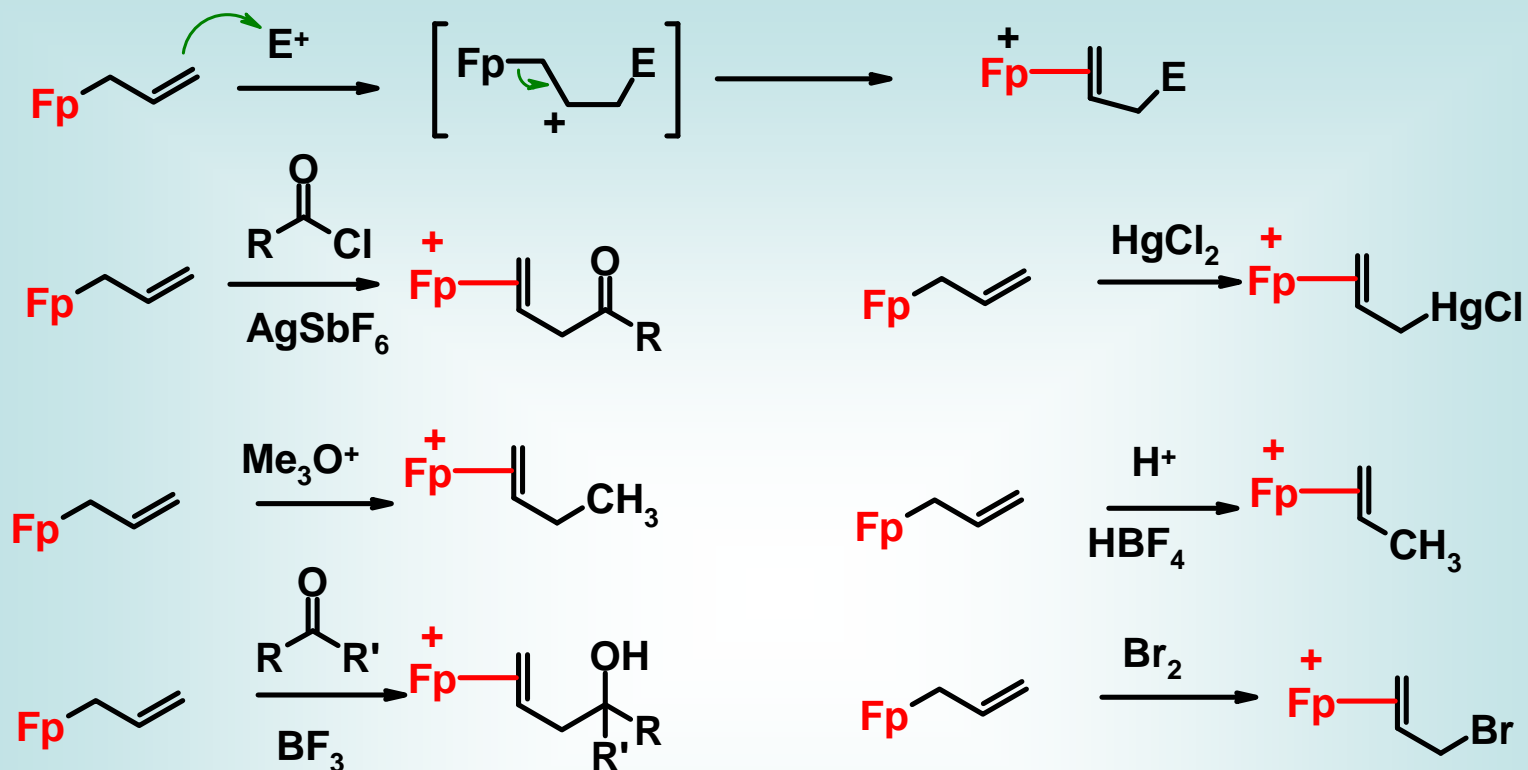
-this never, ever, ever happens with Co propargyl cations (Nicholas reactions)

Other Nucleophilic Allys

- η^1 -allyl Fp $[\text{CpFe}(\text{CO})_2]$ complexes

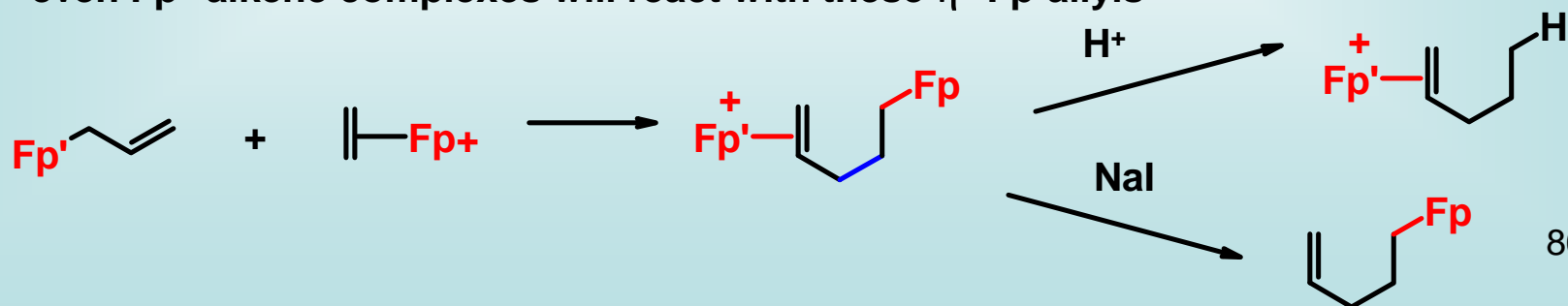


-behave as modestly reactive nucleophiles to a pretty wide range of E^+



R Rosenblum, M. *J. Organomet. Chem.* 1986, 300, 191.

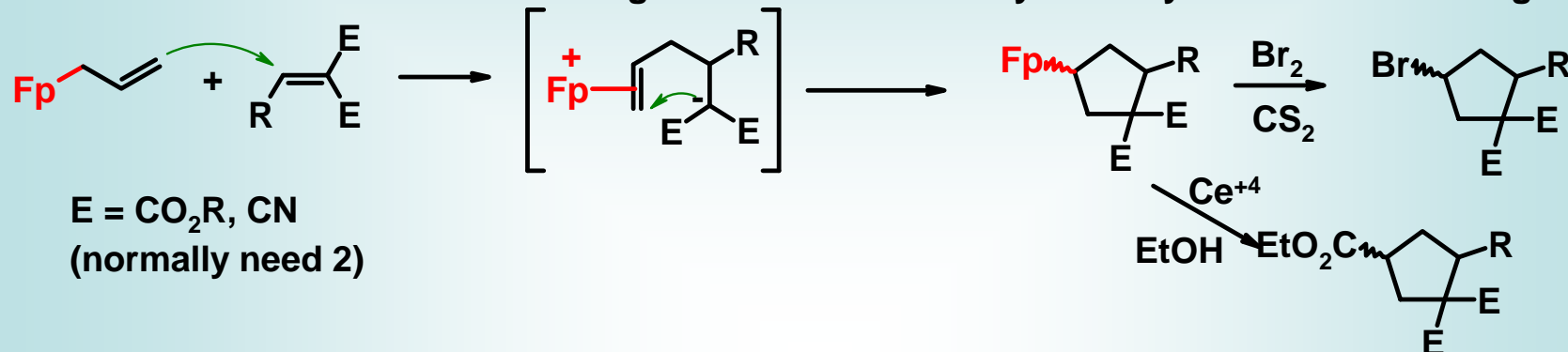
-even Fp^+ -alkene complexes will react with these η^1 -Fp-allyls



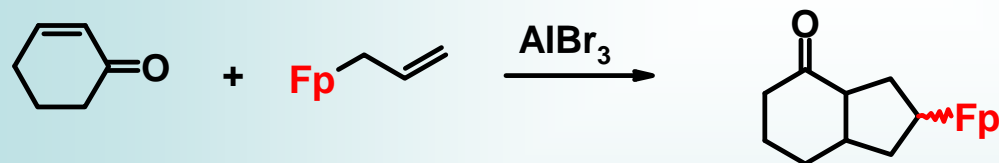
η^1 -propargyls do analogous chemistry



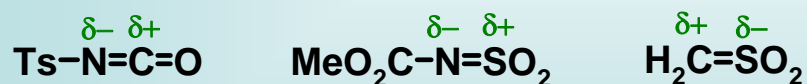
η^1 -allyls react with electron poor alkenes by initial nucleophilic attack, followed by electrophilic attack back onto the iron containing unit - this is ultimately a 3+2 cycloaddition resulting



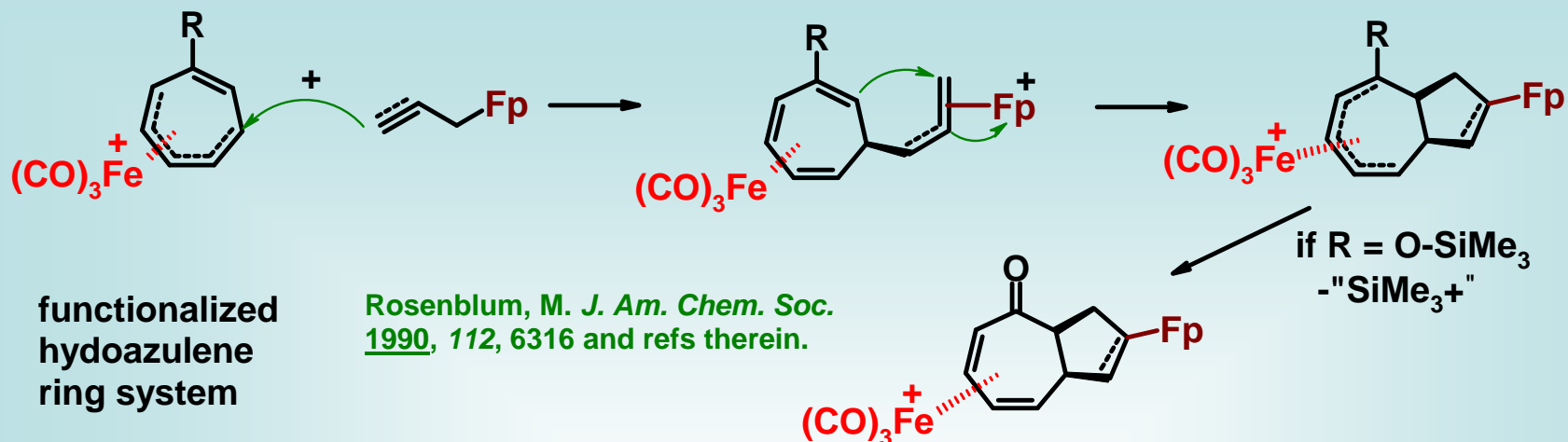
-to be sufficiently reactive, the alkene usually needs two electron withdrawing groups, although some cyclic alkenones work with a Lewis acid added (AlBr_3)



-several more obscure electron deficient $\text{X}=\text{X}$ systems do this [3+2] cycloaddition, but they aren't as important so we'll just list them

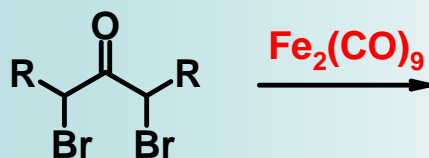


-one further [3+2] cycloaddition partner that is interesting enough to show is specialized; cycloheptadienyl iron cation with an included alkene



R Ruck-Braun, K.; Mikulas, M.; Amrhein, P. *Synthesis* 1999, 727.

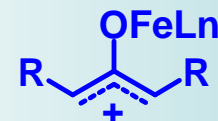
η^3 (?), η^4 (?) Complexes - The Iron Oxyallys



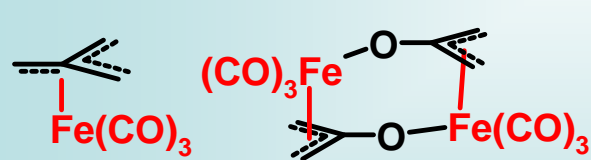
some magical species which has never been isolated

R Noyori, R. *Acc. Chem. Res.* 1979, **12**, 61.
R Noyori, R. *Org. React.* 1983, **29**, 163.
R Mann, J. *Tetrahedron* 1986, **42**, 4611.

Noyori proposed



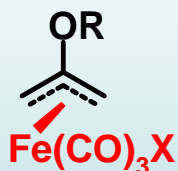
But....the following have been isolated at various times



see later

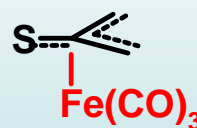
Frey, M.; Jenny

Organometallics 1990, **9**, 1806.



X = Br, Cl
 R = H, TMS

J. Organomet. Chem. 1991, **421**, 257.



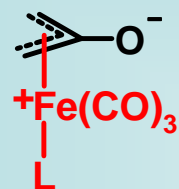
Ando, W.
J. Am. Chem. Soc. 1990, **112**, 4574.



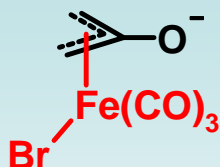
M = Pd, Pt

Albright, T.A. *Organometallics* 1989, **8**, 199.
 Emerson, G.I. *J. Am. Chem. Soc.* 1966, **88**, 3172.

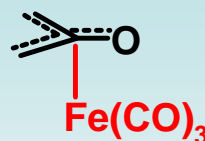
-therefore, the most likely structures for these iron oxyallyls are....



or



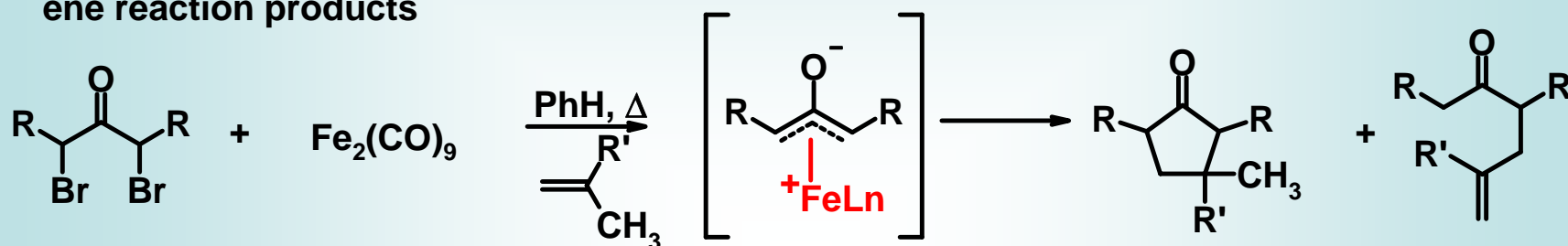
or



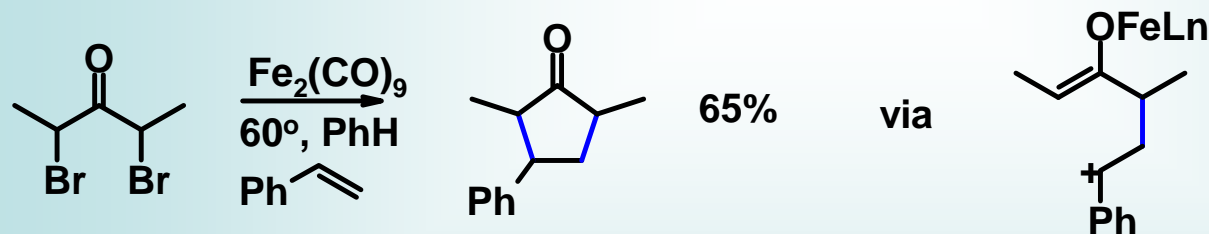
or perhaps a dimer

called oxyallyl cations

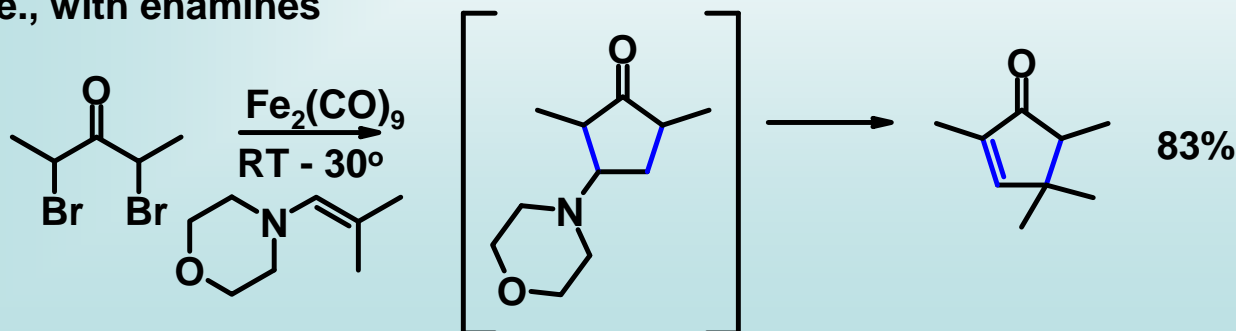
-the iron oxyallyls react with simple alkenes to give either [3+2] cycloaddition products or ene reaction products

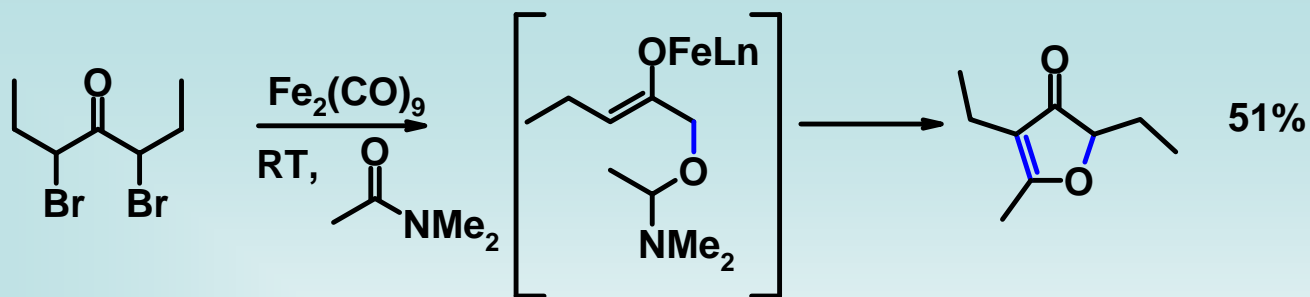


-the [3+2] cycloadditions work best when the alkene has some carbocation stabilizing groups



-i.e., with enamines



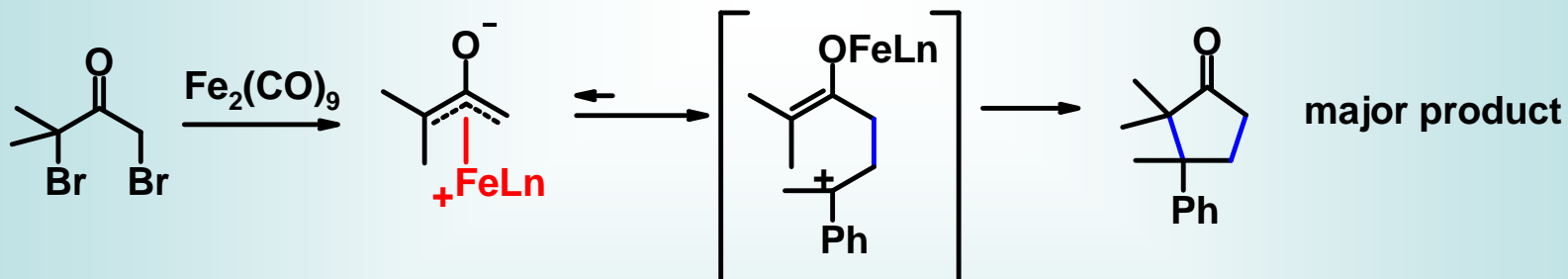


-nitriles also react in a few cases

Regiochemistry

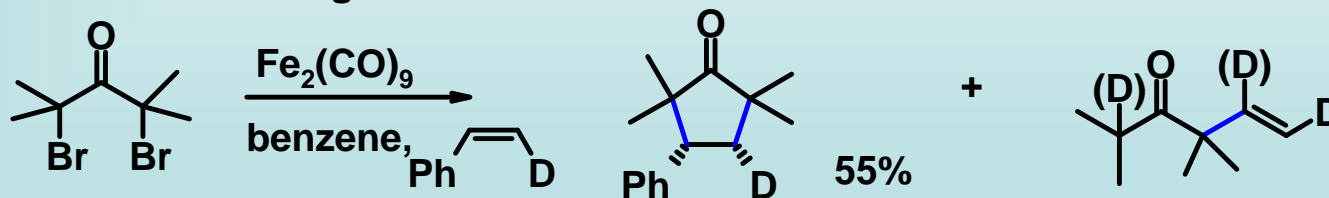
-on the oxyallyl - the major product results from initial reaction at the least substituted end of the allyl (to give the most substituted Fe enolate)

-on the alkene - the major product is the one that goes through the most stable carbocationic intermediate

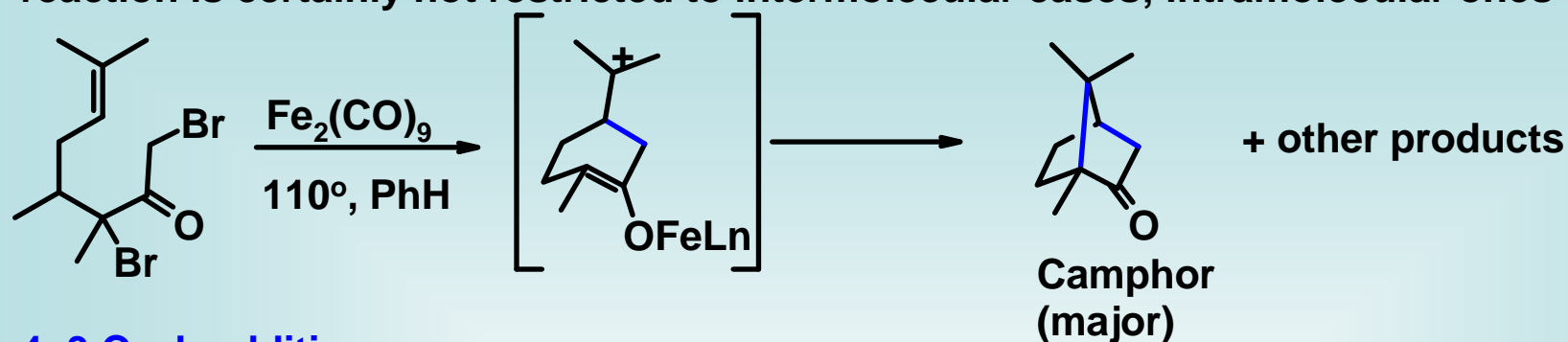


Stereochemistry - normally, one gets retention of stereochemistry about the alkene

-does not mean concertedness; apparently, the intermediate cation is (very) short-lived
-not enough time for bond rotation

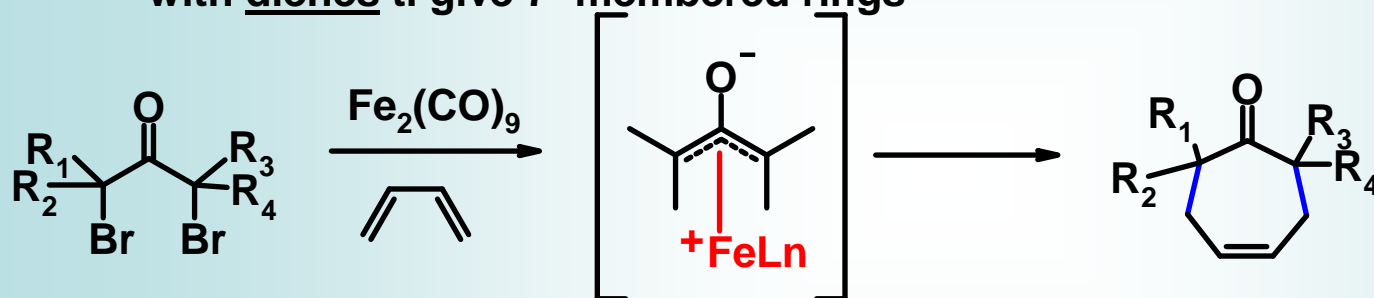


-reaction is certainly not restricted to intermolecular cases; intramolecular ones work as well

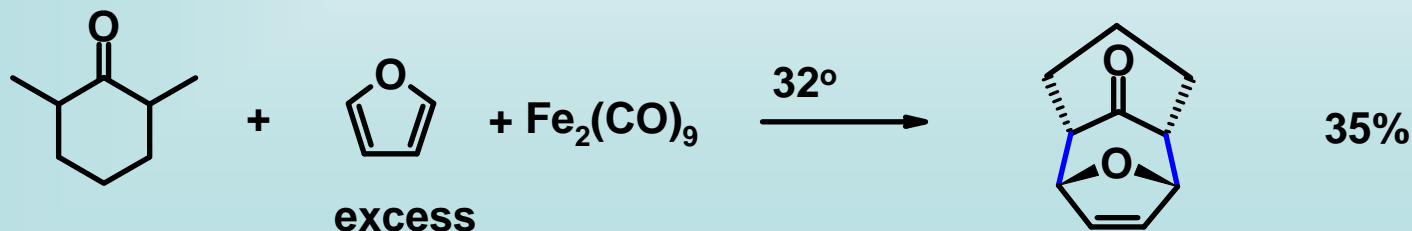
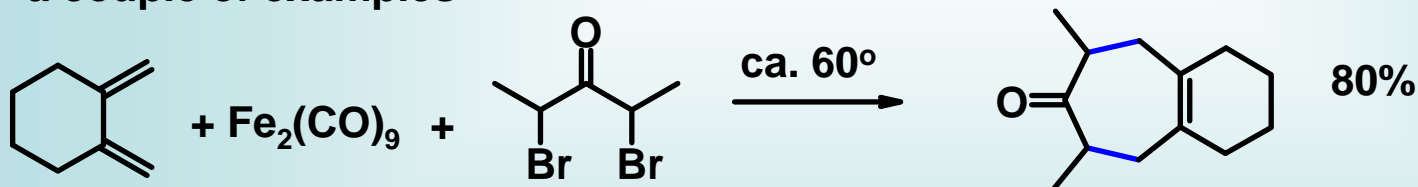


4+3 Cycloadditions

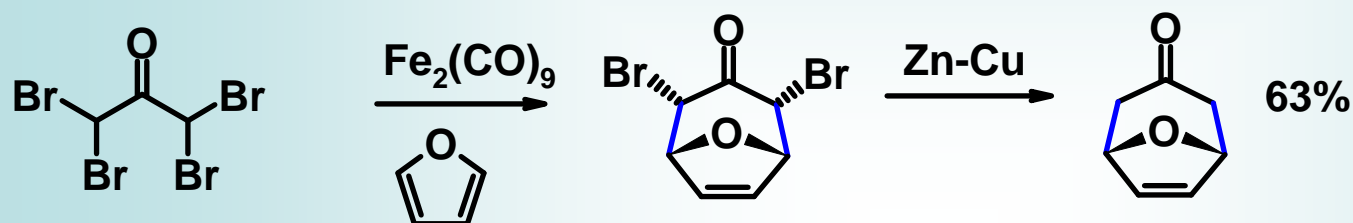
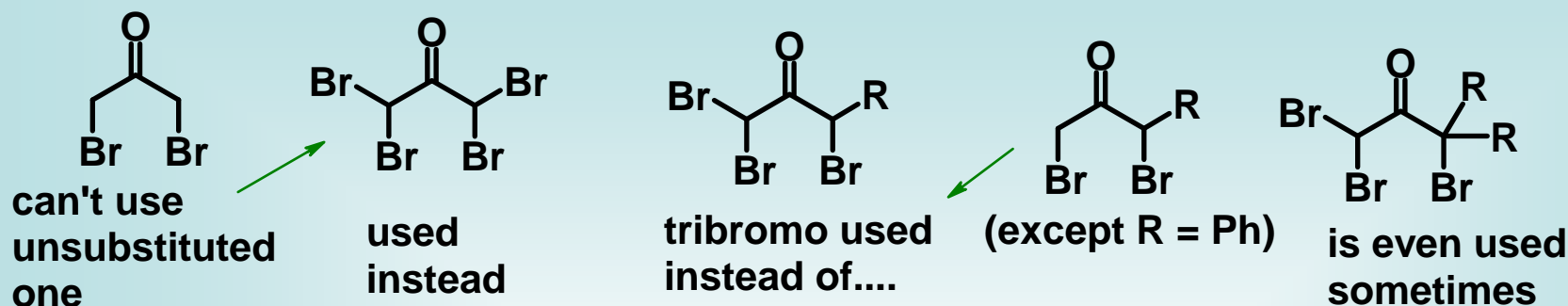
-probably more importantly than the [3+2] cycloadditions, these oxyallyl cations react with dienes to give 7-membered rings



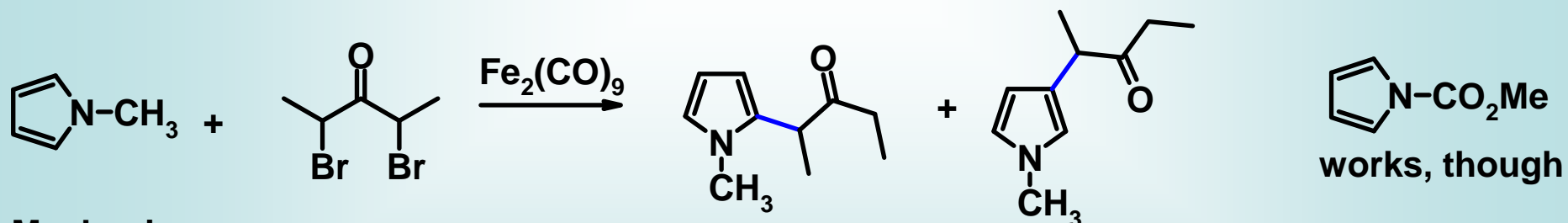
-a couple of examples



Limitations on Reagents in [4+3] - on the dibromoalkene



-in cases with pyrroles, N-alkyl cases give electrophilic aromatic substitution
N-acyl cases usually give the [4+3]



Mechanism

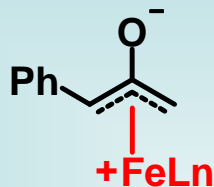
- allyl cation is a 3C, 2π electron system; diene is a 4π electron system
- could this be a concerted $[4\pi + 2\pi]$ cycloaddition?
- Noyori thinks yes
- Hoffmann thinks only sometimes, but mostly no

(Angew. Chem Int. Ed. Engl. 1984, 23, 1)

Regiochemistry

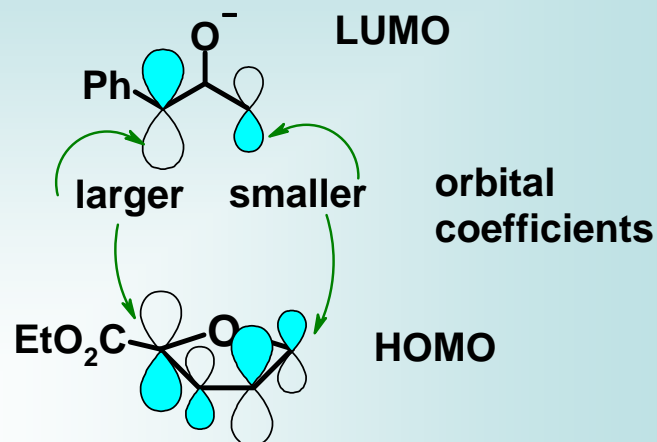
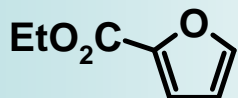
- behaves as if it is a concerted reaction
- therefore, it is controlled by HOMO-LUMO interactions

Consider



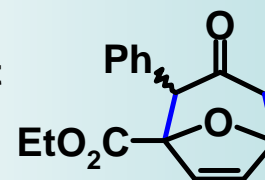
if we leave out the iron

and

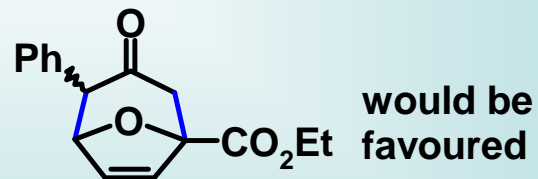
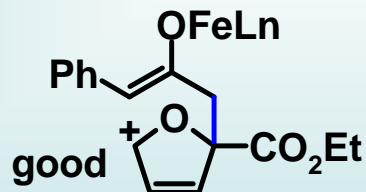
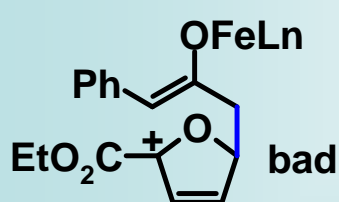


-frontier molecular orbital arguments require that atoms with larger orbital coefficients, and smaller with smaller

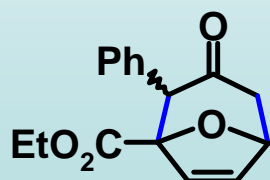
-therefore, frontier molecular orbital (FMO) arguments would predict



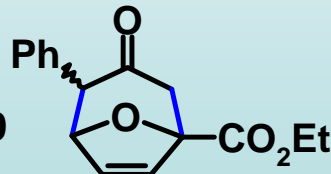
-but if stepwise, one would predict....



-the actual result is....

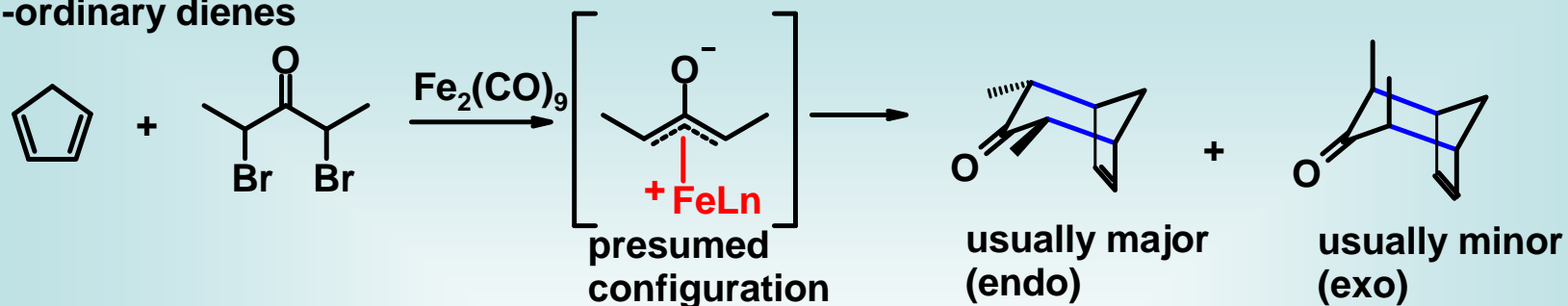


90 : 10

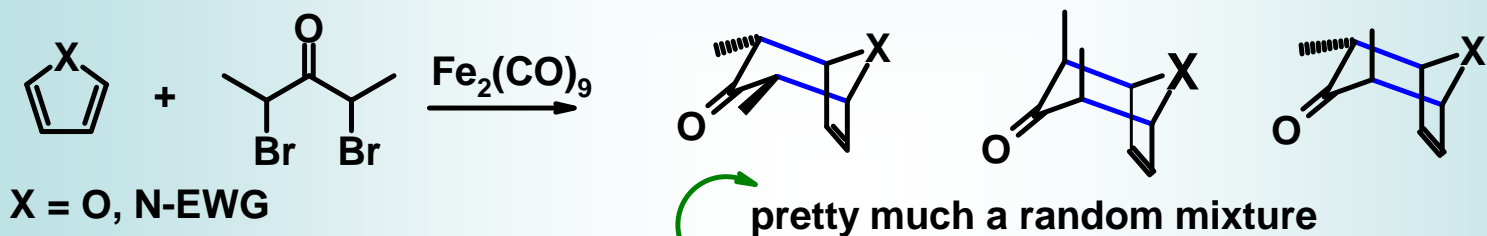


Stereochemical consequences

-ordinary dienes

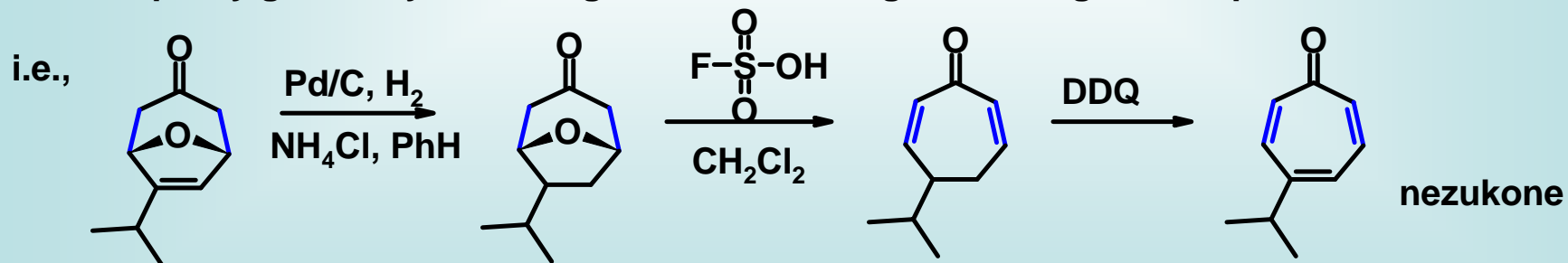


-aromatic dienes

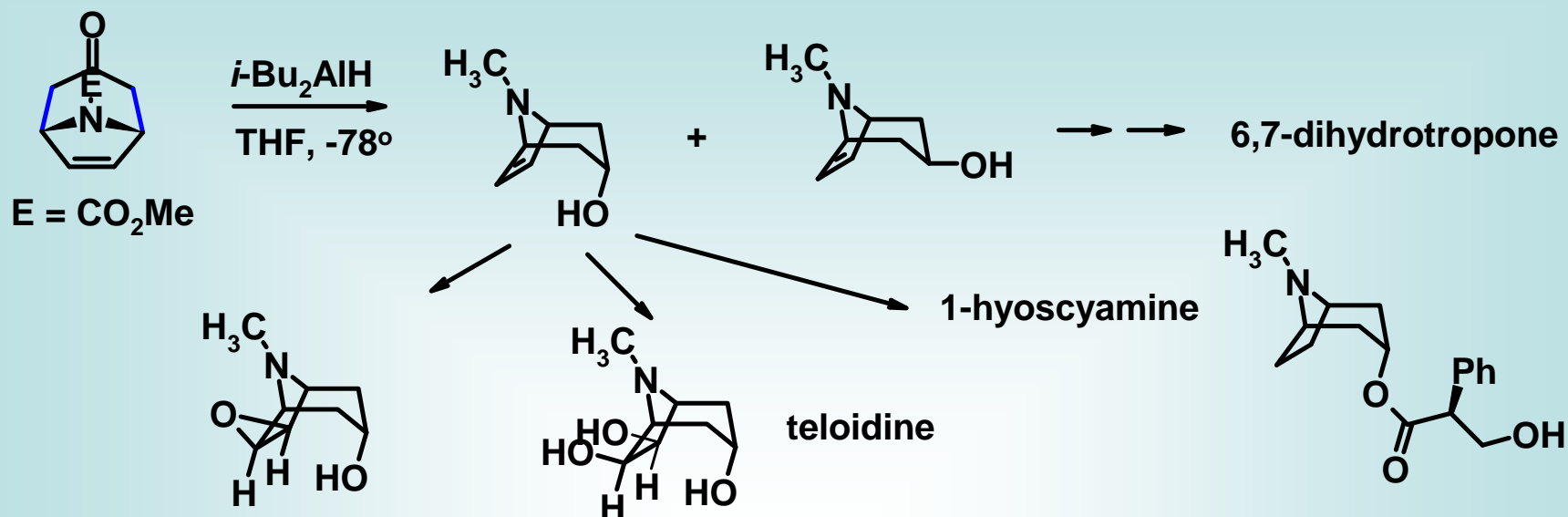


-it is the presence of these types of products that makes Hoffmann think that the reaction is not concerted

-use - pretty good way of making 7-membered ring containing natural products



-also, in tropane alkaloid synthesis...



many other natural product syntheses

for reviews, see

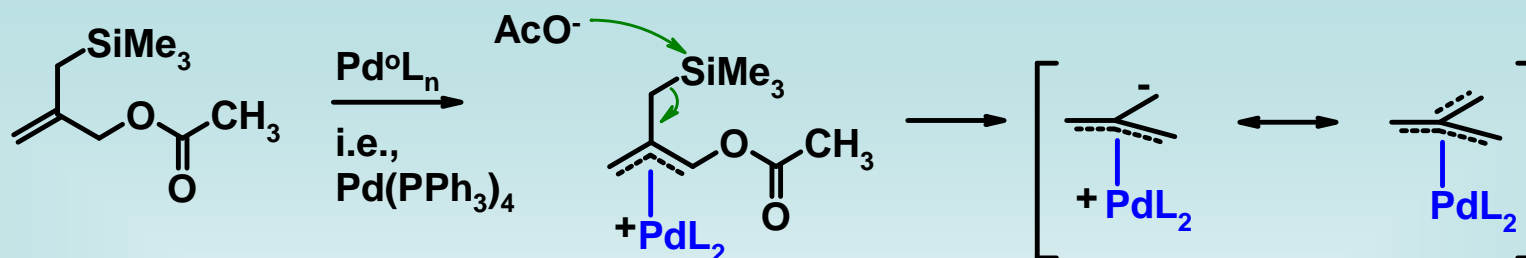
- [R Noyori, R. Acc. Chem. Res. 1979, 12, 61.](#)
- [R Noyori, R. Org. React. 1983, 29, 162.](#)
- [R Mann, J. Tetrahedron 1986, 42, 4611.](#)
- part of [R Rigby, J. H. Pigge, F. C. Org. React. 1997, 51, 351](#)
- [R Harmata, M. Tetrahedron 1997, 53, 6235](#)

η^4 - Complexes

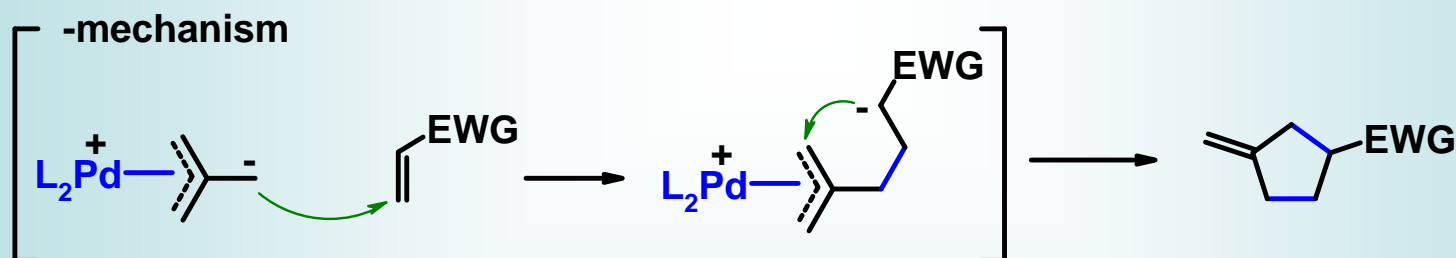
η^4 -Trimethylenemethane Complexes

- predominantly used with palladium, due to use of metal in catalytic amounts
- iron also known and used some, but it is stoichiometric

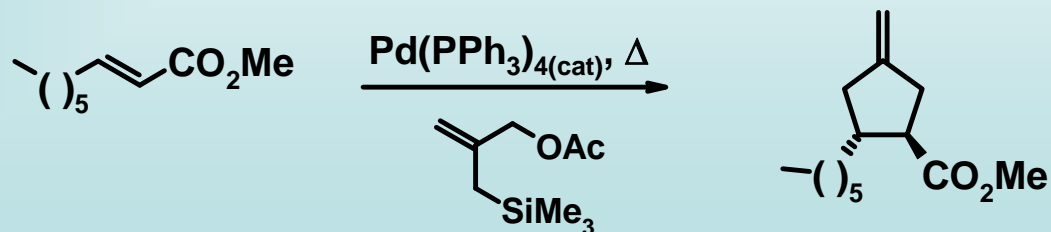
-consider the following substrate that looks like a precursor to an η^3 -allylpalladium

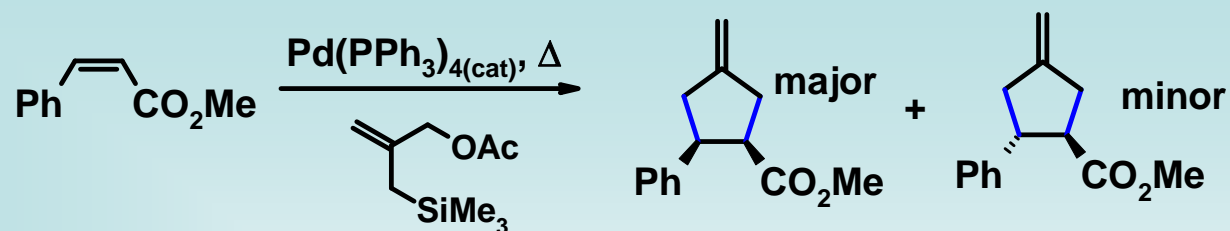


- in these cases, the Pd is coordinated to all 4 carbon atoms
- this is a trimethylenemethane complex
- excellent reagent for 3+2 cycloaddition reactions

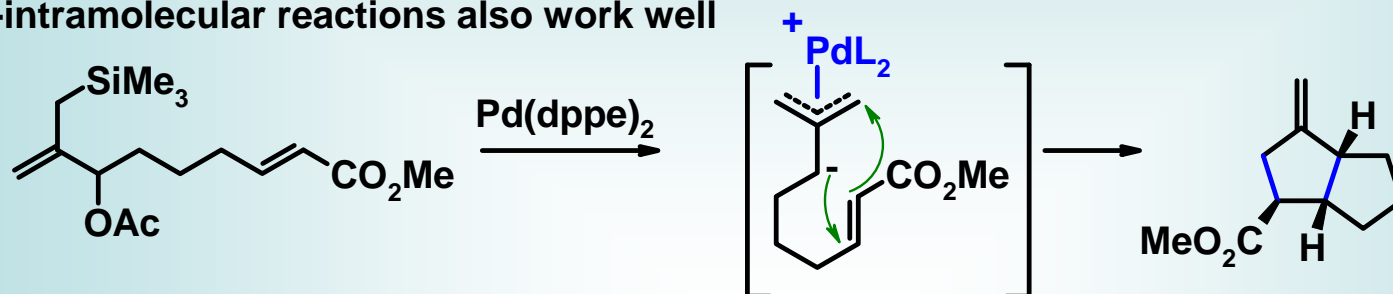


- stereochemical considerations
- about alkene - get mostly retention of configuration, but not perfectly so



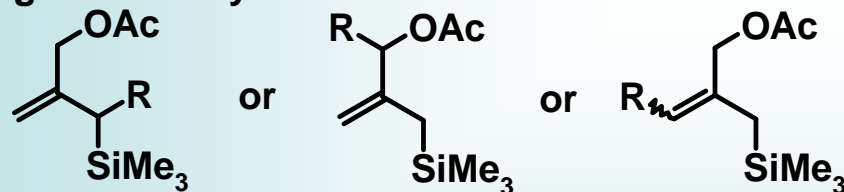


-intramolecular reactions also work well



-other aspects of the stereochemistry (i.e., diastereoselectivity) have been well established, but are beyond the course's scope

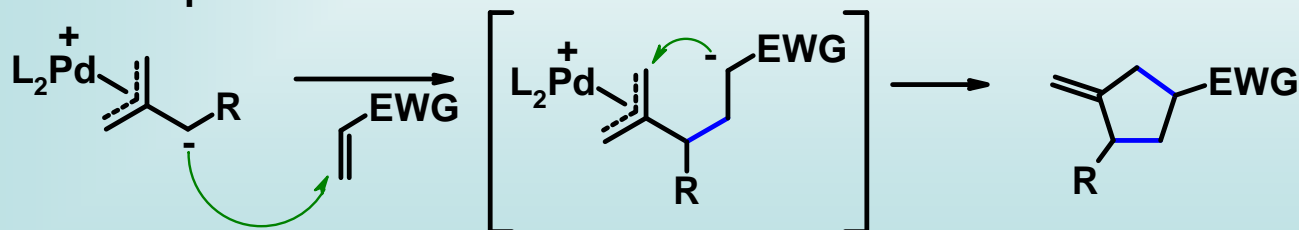
Regiochemistry



R = alkyl
 electron withdrawing
 electron donating

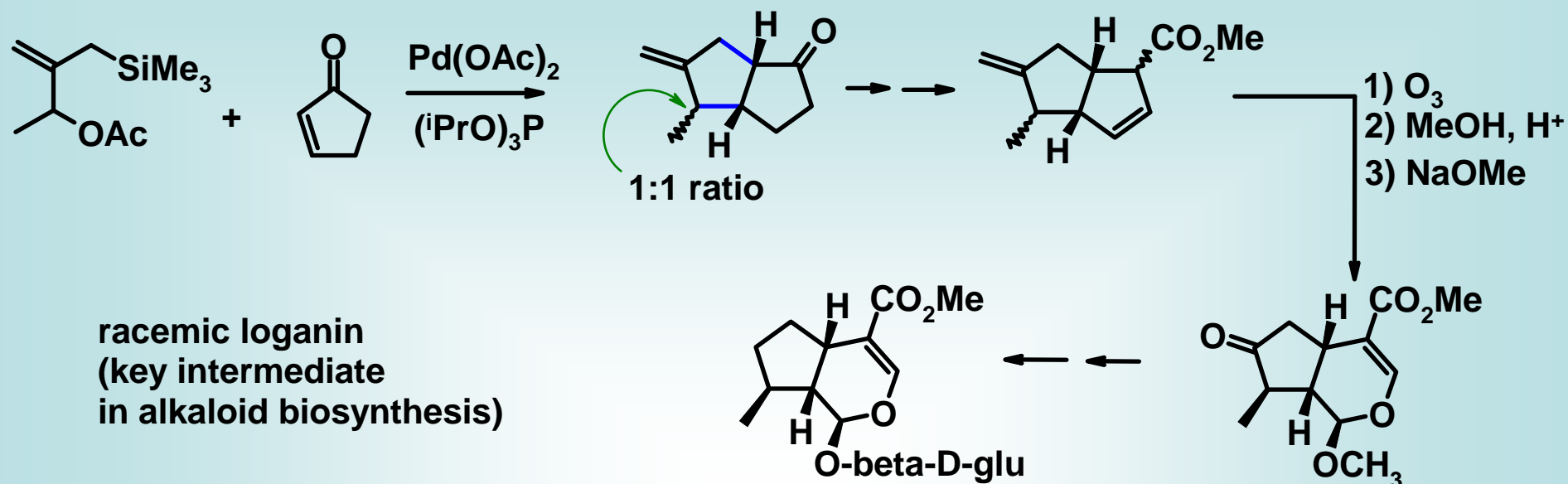
-regardless, it doesn't matter (much),

-the product is as if.....



-no *real* mechanistic explanation for this result

-example of use in synthesis - loganin



-there is *some* work on reacting TMM-Pd complexes with C=O and C=N-EWG in the presence of R₃Sn-X co-catalysts

-see Trost, B. M. et al J. Am. Chem. Soc. 1990, 112, 408.
Trost, B. M. et al J. Am. Chem. Soc. 1993, 115, 6636.

For reviews in the area see:

Trost R Angew. Chem. Int. Ed. Engl. 1986, 25, 1.
R Pure Appl. Chem. 1988, 60, 1615.
R 'Comprehensive Organic Synthesis' V. 5, p. 271 (1991)
R Org. React. 2002, 61, 1.

Iron tricarbonyl - trimethylenemethane complexes also known

see Donaldson, W.A. J. Org. Chem. 1995, 60, 1611.
Frank-Neumann, M. Tetrahedron: Asymm. 1996, 7, 3193.
R Green, J. R.; Donaldson, W.A. 'Encyclopedia of Inorganic Chemistry, Vol. 4, 1994

