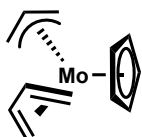


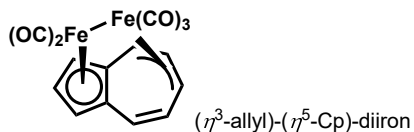
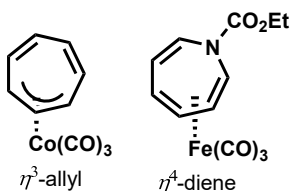
General**Defintion and general view:**How to define an η -coordination?

coordination via uninterrupted and contiguous series of atoms

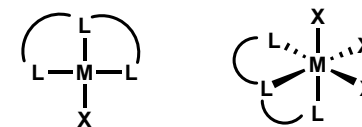
naming rules, see: F. A. Cotton* JACS, 1968, 6230

 $(\eta^3\text{-allyl})-(\eta^4\text{-butadiene})-(\eta^5\text{-cyclopentadienyl})\text{-Mo(II)}$

18 e- rule helps for rationalize

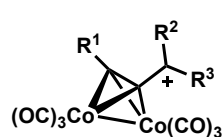
**choice of ligands**common π acid: CO, NO⁺, RNC, NC-
common σ donor:

multidentate ligands:

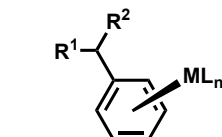


for square planar

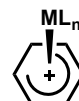
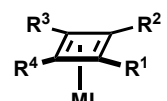
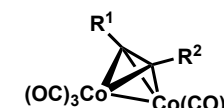
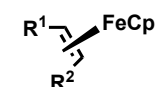
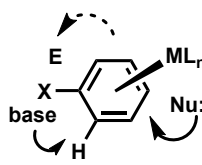
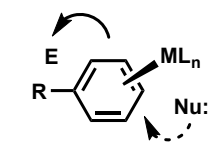
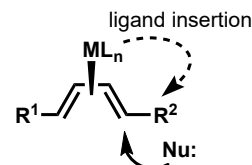
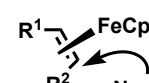
for octahedron

Classification**Stabilization:**

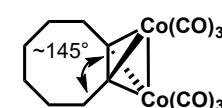
stabilized cation



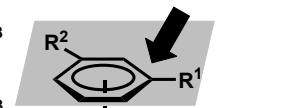
benzylic cation/anion/radical

 $\eta^5\text{-dienyl complex}$  $\eta^4\text{-dienyl complex}$ **Protection:**protecting group
for alkyneprotecting group
for alkene**Activation:** $\eta^6\text{-metal-arene complex}$  $\eta^2\text{-dihapto complex}$  $\eta^4\text{-metal-diene complex}$ 

Fp-alkene complex

Geometry:

distortion



blocked face

break the symmetry

Organization of this group meetingIncluded: η^2 -complex (Os, Re, W, Mo); η^4 -complex (Fe); η^5 -complex (Fe); η^6 -complex (Cr, Fe, Ru, Rh, Mo, Mn)

Not included: Activation of alkene/alkyne, allylic compounds, etc.

Part I

early transition metals

Part II

late transition metals

Part III

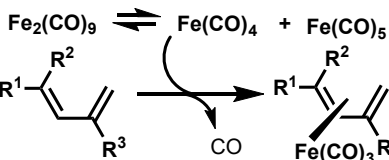
summary

References: Jiro Tsuji, *Transition Metal Reagents and Catalysts-Innovations in Organic Synthesis*, 2000, chapter 9.
Science of Synthesis, 2014/1, p1-192.E. P. Kundig, *Transition Metal Arene π -complexes in Organic Synthesis and Catalysis*, 2004, chapter 1-7.A. J. Pearson, *Iron Compounds in Organic Synthesis (Best Synthetic Methods)*, 1994W. D. Harman, *group 6 dihapto-coordinate dearomatization agents for organic synthesis*, *Chem. Rev.* 2017, 13721.

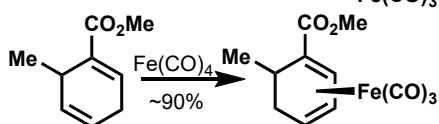
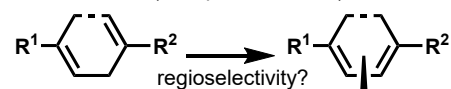
Realted context: metal-carbonyl complex; dearomatization.

η^4 and η^5 complex of iron: preparation and propertiesFormation of η^4 -Fe complex

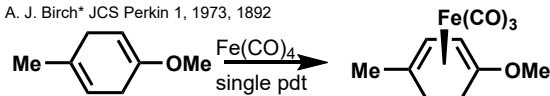
from 1,3-diene



from 1,4-diene (2 steps from arene)

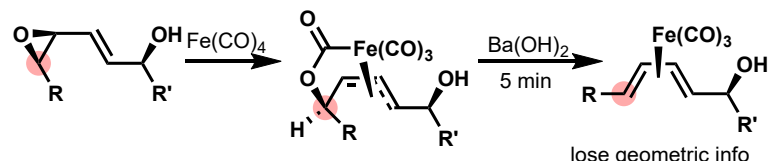


A. J. Birch* JCS Perkin 1, 1973, 1892



A. J. Birch* JCS A, 1968, 332

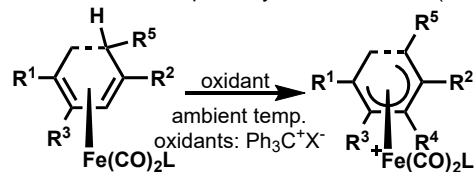
a carbonyl insertion/elimination process



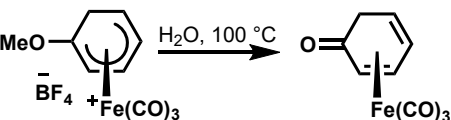
S. V. Ley* JCS Perkin 1, 1997, 1125

Formation of η^5 -Fe complex

from iron-diene complex - hydride abstraction (most used)



L = CO/PR3/P(OR)3, etc.

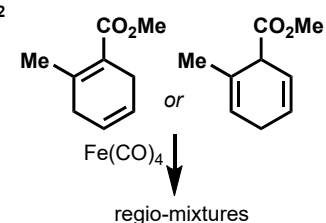
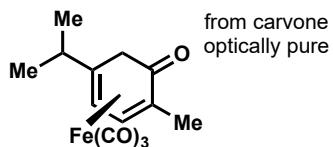
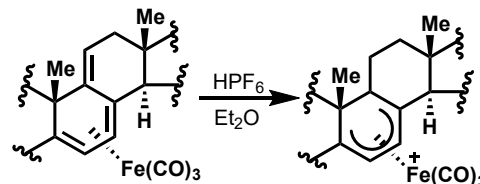


A. J. Birch* JCS A, 1968, 332

other iron sources:

Fe(CO)5; hv; Fe3(CO)12

Fe(CO)4(NR3); Fe(CO)3(enone)

Formation of η^5 -Fe complex

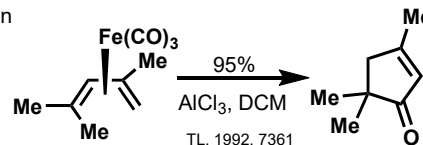
JOMC, 1992, 357

Decomplexation

oxidative decomposition: Cu^{II}/CAN/DDQ/N-oxide/I₂/MnO₂ etc.

photolysis in existence of other ligands.

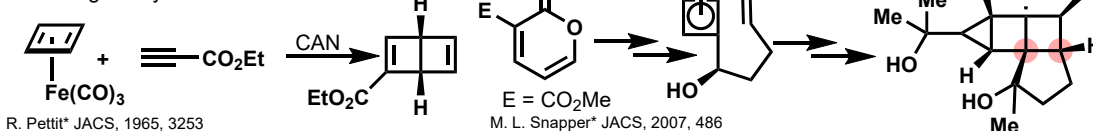
carbonyl insertion



TL, 1992, 7361

Reactions of η^4 -Fe complex

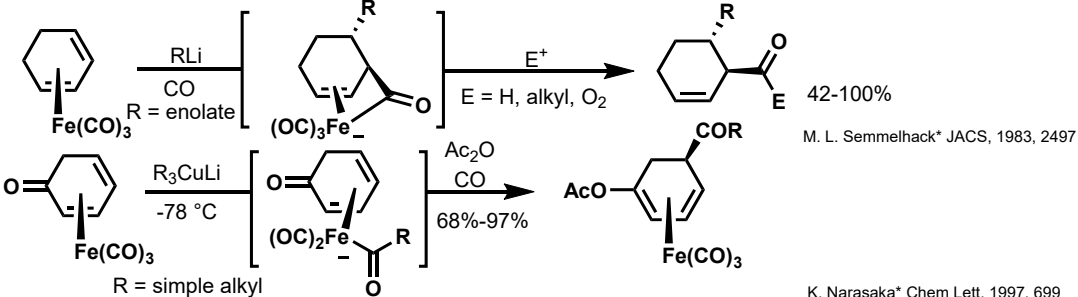
stabilizing the cyclobutadiene



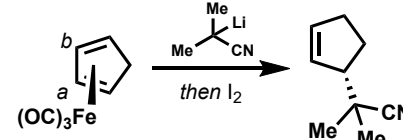
R. Pettit* JACS, 1965, 3253

M. L. Snapper* JACS, 2007, 486

CO on iron involved nucleophilic attack



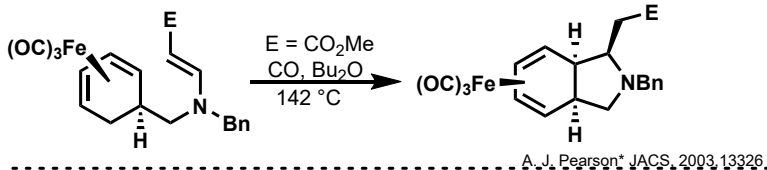
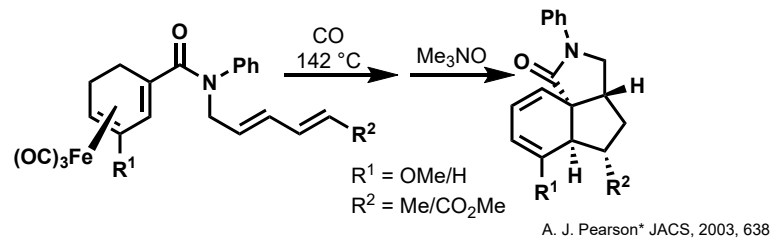
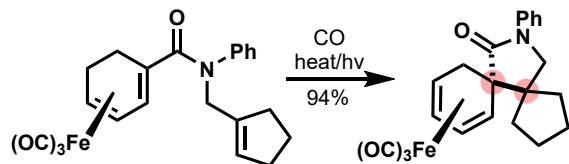
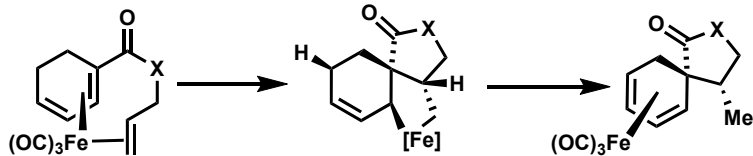
direct nucleophilic attack limited to active carbanions



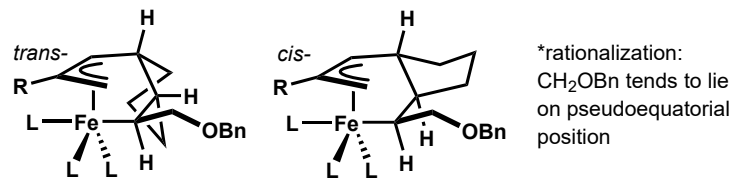
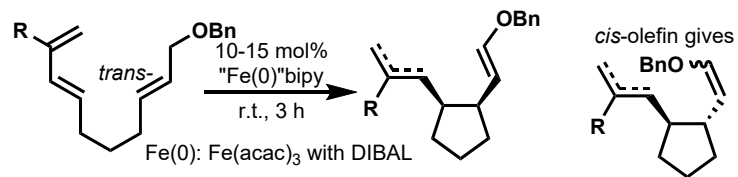
K. Narasaka* Chem Lett, 1997, 699

η^4 and η^5 complex of iron: preparation and propertiesReactions of η^4 -Fe complex

reaction with alkene - limited to intramolecular system



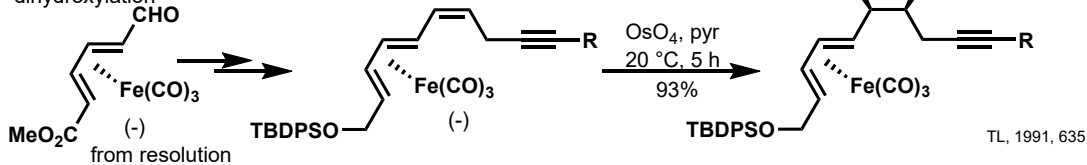
catalytic ene reaction



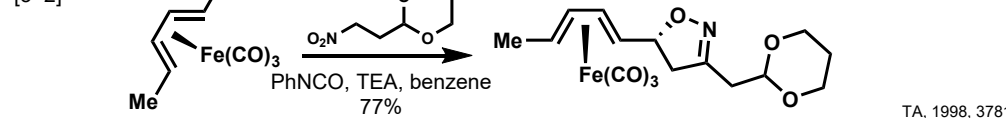
JACS, 1987, 2200

diene-complex for stereocontrol - limited to concerted reaction

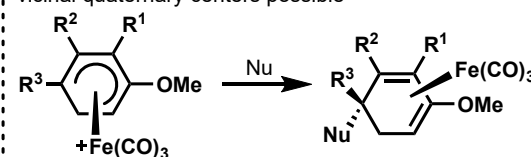
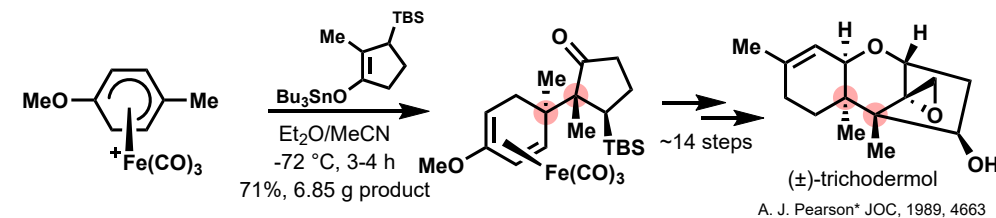
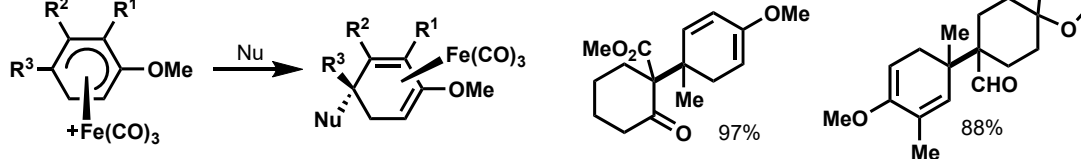
dihydroxylation



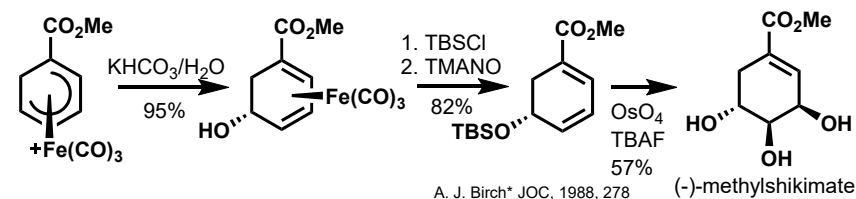
[3+2]

Reactions of η^5 -Fe complex - nucleophilic addition

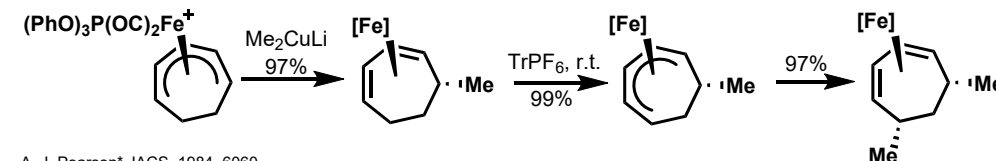
vicinal quaternary centers possible

Nu scope: enolate, ArLi, RCu, R_2CuLi , RNH_2 ,
alkyne-Li, e-rich Ar...

facile hydration

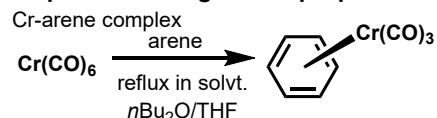


difunctionalization

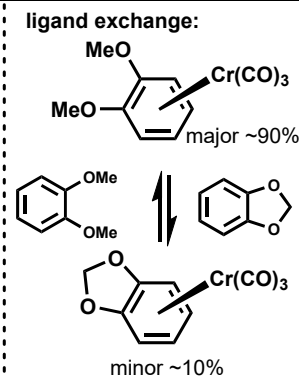
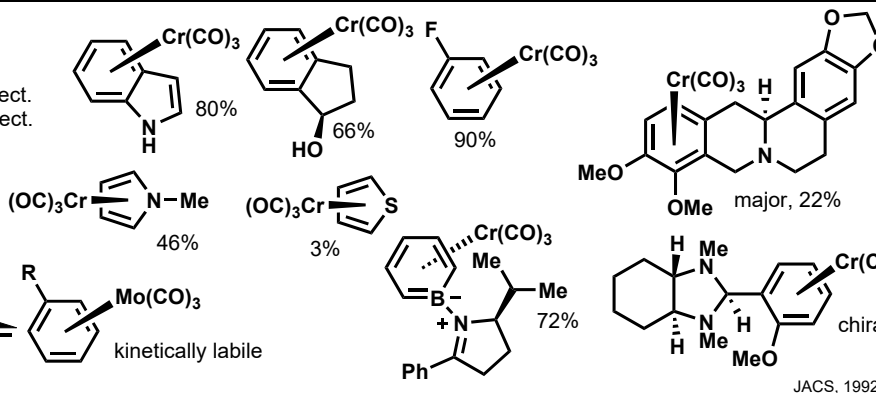


η^5 metal-arene complex (Cr/Mo/Fe/Ru/Rh)

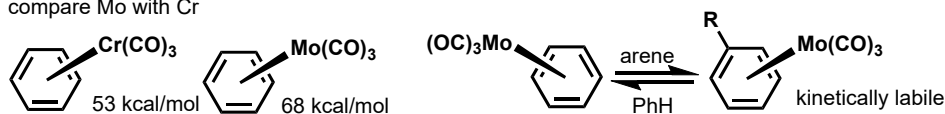
Preparation and general properties



- Rules for coordination:
1. sensitive to steric effect.
 2. possess directing effect.
 3. prefer e-rich arene.

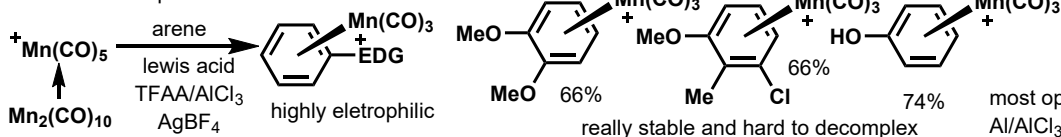


other ways: photolysis
other Cr source: $\text{Cr(CO)}_3\text{L}_3$, L could be $\text{NH}_3/\text{MeCN}/\text{pyr}/\text{cod}/\text{PR}_3$, etc.
compare Mo with Cr



JOMC, 1985, 201 lower yield for Mo complex

Mn-arene complex



Fe-arene complex - hard to prepare but stable

Ru-arene complex - easier to prepare

Decomplexation

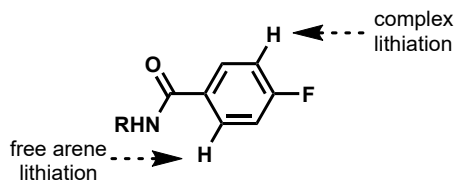
for Cr: I_2 enough for decomplexation, Ph_3C^+ not

for Mn: hard, using DDQ/CAN/Jones, I_2 doesn't work

for Ru: hv/sunshine in MeCN

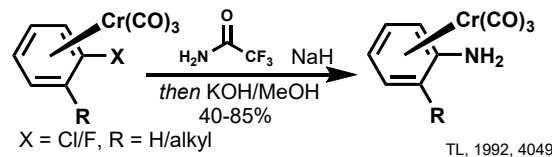
Reaction of metal-arene complex

direct lithiation

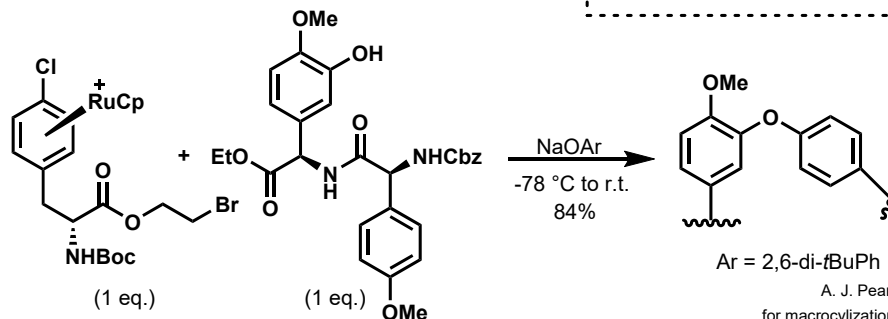


classical directing effect: $\text{CONR}_2 > \text{SO}_2\text{NR}_2 > \text{NHCOR} > \text{CH}_2\text{NR}_2 > \text{OMe} > \text{NMe}_2 \sim \text{F}$
after coordination: $\text{F} > \text{CONR}_2 > \text{NHCOR} > \text{CH}_2\text{NR}_2 \sim \text{OMe} \gg \text{CH}_2\text{OR} > \text{NMe}_2$

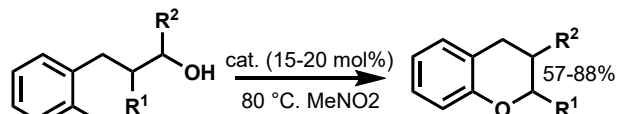
$\text{S}_{\text{N}}\text{Ar}$ reaction - facile way to form $\text{C(sp}^2\text{)-X}$ bond



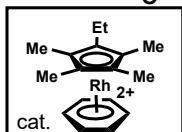
facile synthesis of aryl-aryl ether



catalytic $\text{S}_{\text{N}}\text{Ar}$ with RhCp complex - the only one example

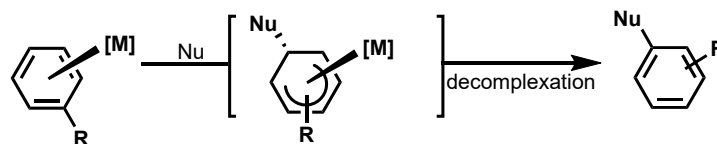


$\text{R}_1 = \text{H/Me}$
 $\text{R}_2 = \text{H/CH}_2\text{OH/benzyl}$

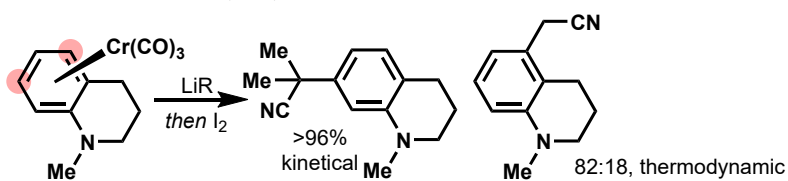
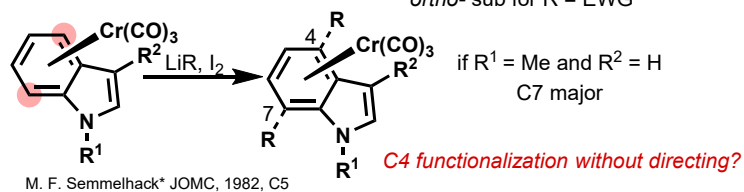
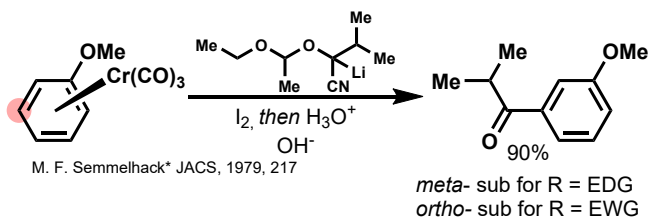


*highly limited:
EWG on ring: no rxn
EDG: slow down

Reaction of metal-arene complex
addition/oxidation - methods for substituted arene

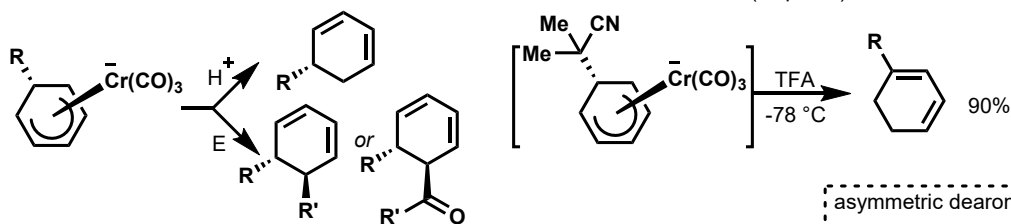


regioselectivity (arene and heterocycle)

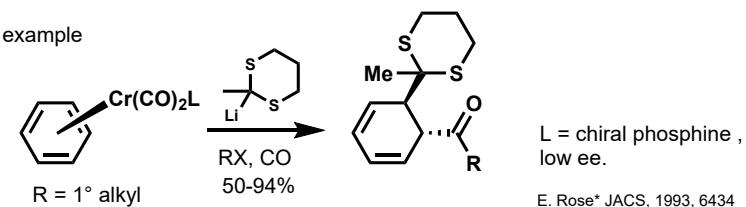


dearomatization

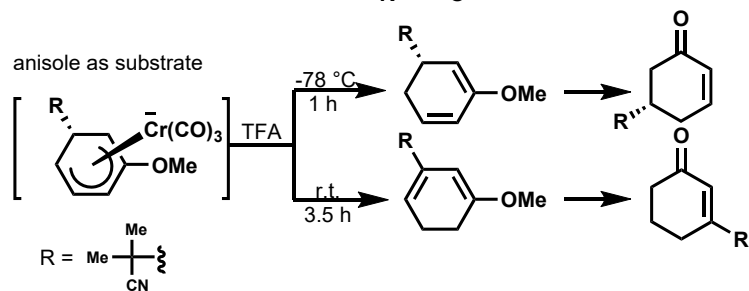
side reaction - 1,5-H-shift (stepwise):



example

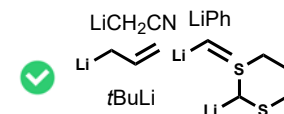
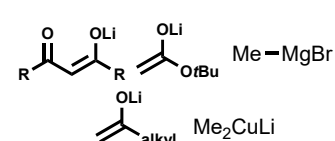


anisole as substrate



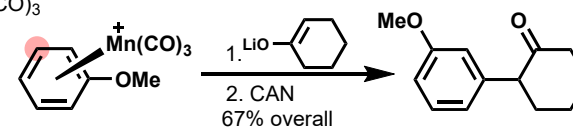
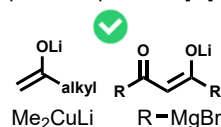
nucleophile scope when [M] = Cr(CO)₃

no rxn:



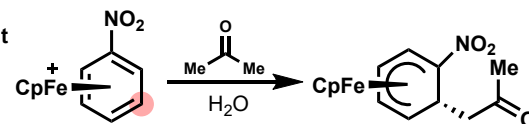
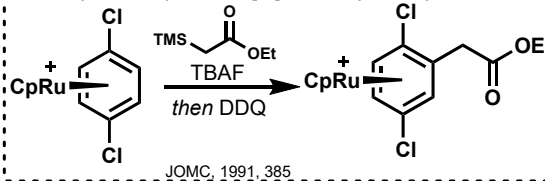
only active lithium reagents work

nucleophile scope when [M] = ⁺Mn(CO)₃



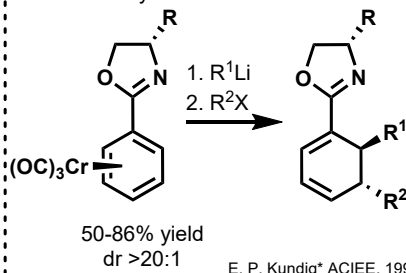
A. J. Pearson* JOMC, 1983, C41

nucleophile scope when [M] = ⁺RuCp/⁺FeCp

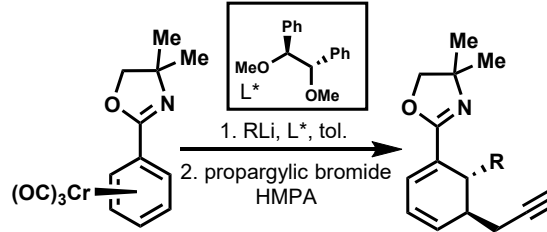


asymmetric dearomatization

chiral auxiliary



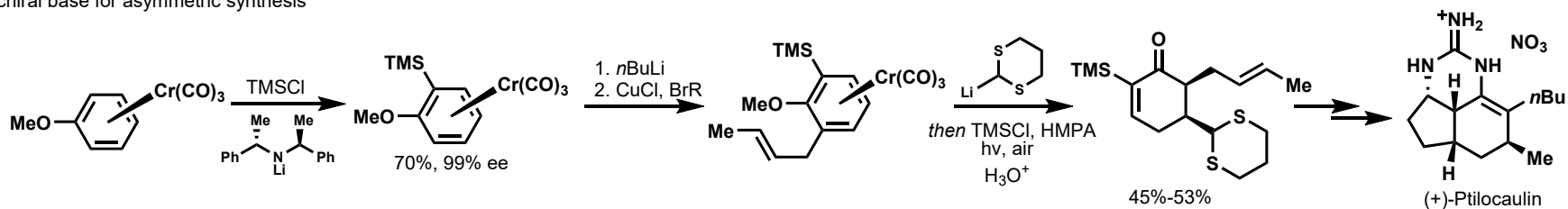
chiral base



Reaction of metal-arene complex

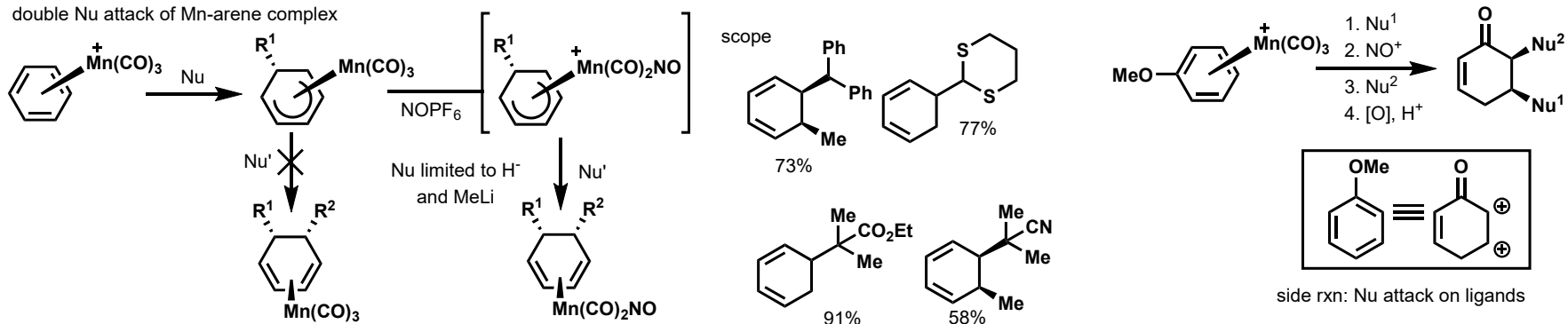
asymmetric dearomatization

chiral base for asymmetric synthesis



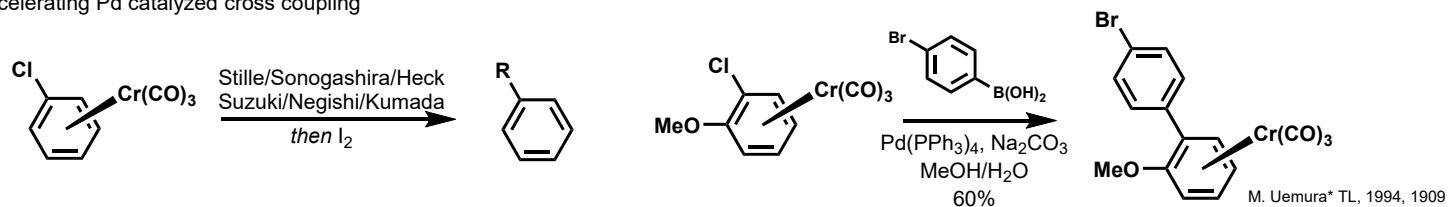
CEJ 1998, 57

double Nu attack of Mn-arene complex

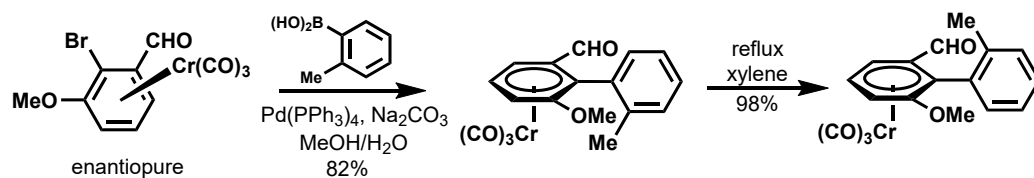


E. P. Kundig* JOC, 1996, 2258

accelerating Pd catalyzed cross coupling



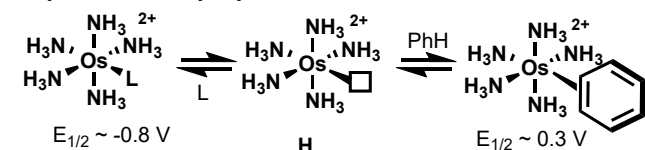
atropisomers for aryl-aryl coupling



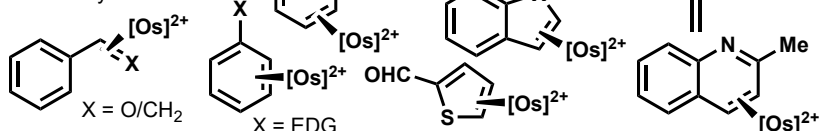
SynLett, 1995, 1040

η^2 (dihapto)-complex (Os(II)/Re(I)/W(0))

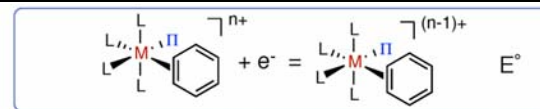
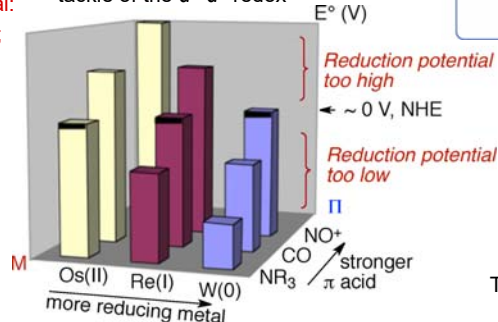
Preparation and properties



L = σ -donor (H₂O/pyr/Cl)
selectivity

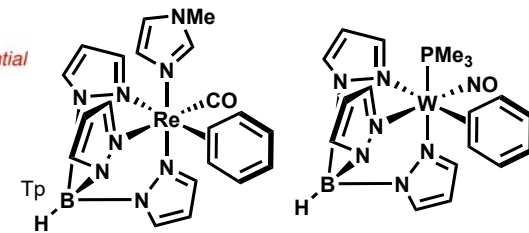


demand for central metal:
 d^6 configuration; π -base;
octahedral

tackle of the d^5 - d^6 redox

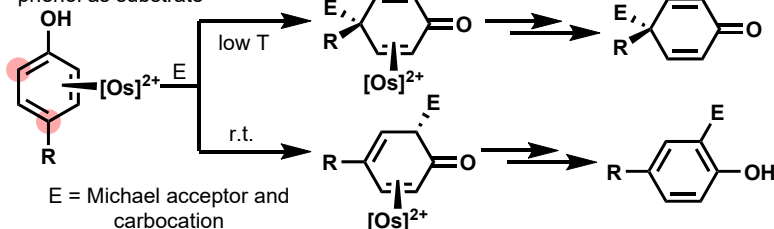
Chem. Rev. 2017, 13721

successfully developed dihapto complex

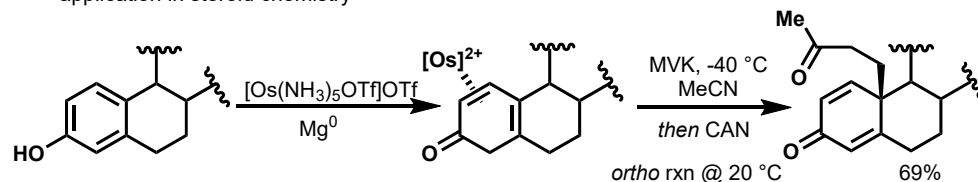


Reactions of Os(II)-arene complex - based on effect of aromatic substrate

phenol as substrate

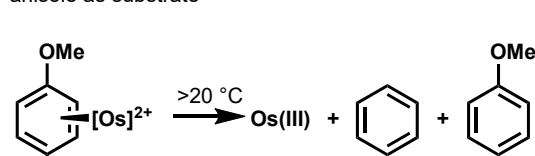


application in steroid chemistry



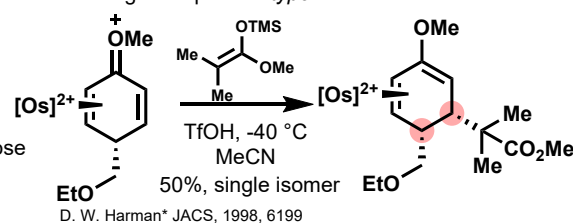
W. D. Harman* JACS, 1993, 5322

anisole as substrate

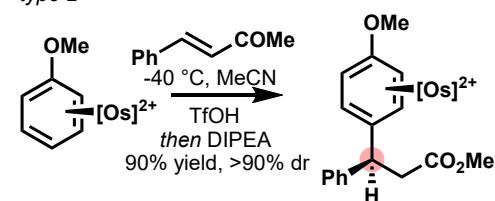
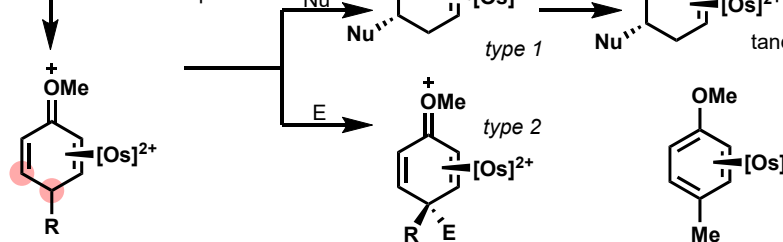


lead to decompose

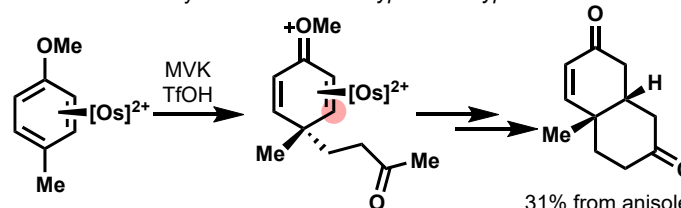
interesting examples for type 1



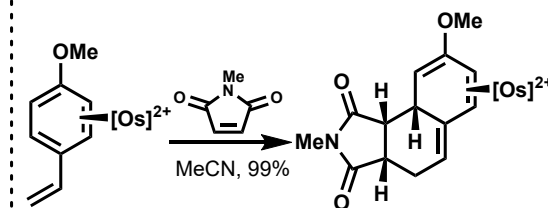
type 2

Lewis/Bronsted acid
low temp.

tandem cyclization based on type 1 and type 2



[4+2]



from benzylic alcohol

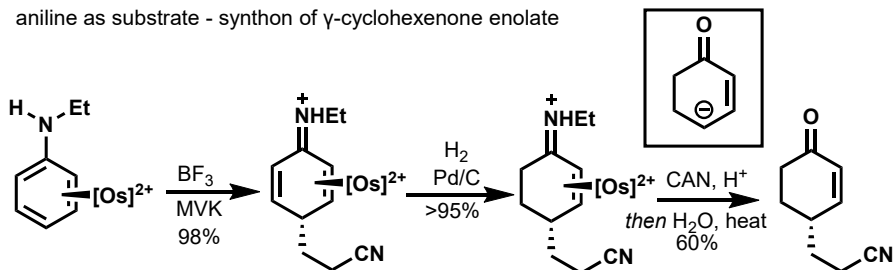
D. W. Harman* Chem. Rev., 1997, 1953

D. W. Harman* JACS, 1998, 6199

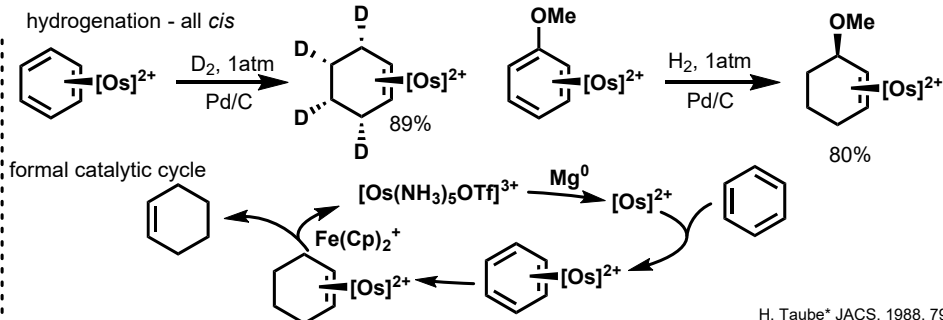
D. W. Harman* JACS, 1998, 6199

Reactions of Os(II)-arene complex - based on effect of aromatic substrate

aniline as substrate - synthon of γ -cyclohexenone enolate

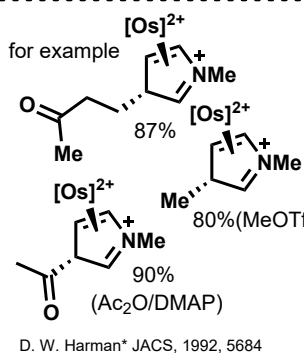
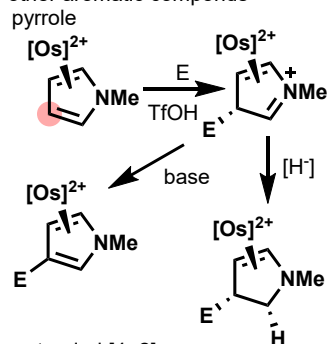


W. D. Harman* OM, 1996, 245



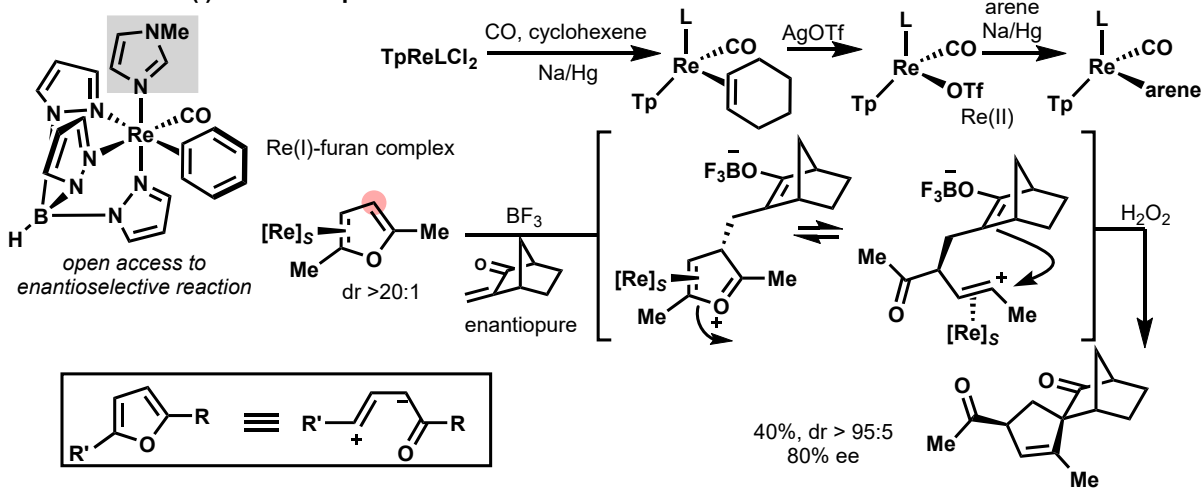
H. Taube* JACS, 1988, 7906

other aromatic compounds



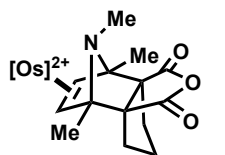
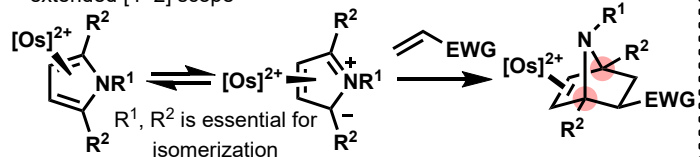
D. W. Harman* JACS, 1992, 5684

Reactions of Re(I)-arene complex - more electron rich



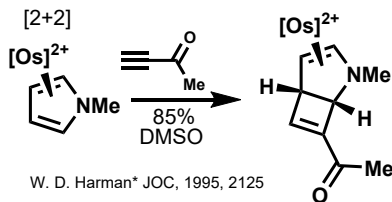
W. D. Harman* JACS, 2003, 14980

extended [4+2] scope



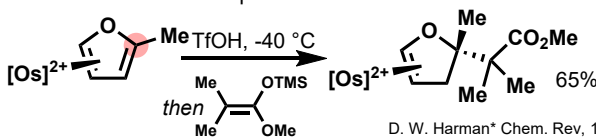
84% *exo:endo* = 10:1

W. D. Harman* JACS, 1995, 3405



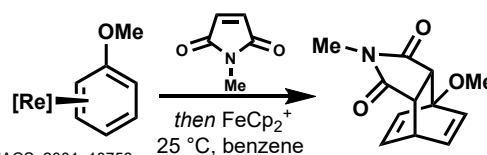
W. D. Harman* JOC, 1995, 2125

furan - react with nucleophile



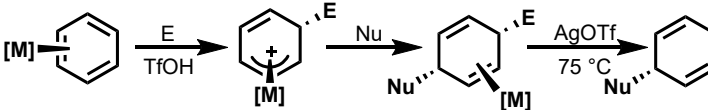
D. W. Harman* Chem. Rev, 1997, 1953

[4+2]



W. D. Harman* JACS, 2001, 10756

comparison of Re(I) and Os(II) in direct dearomatization

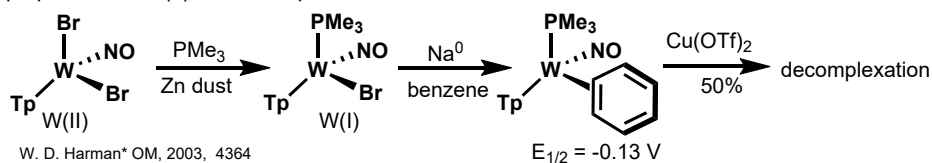


W. D. Harman* JACS, 2004, 13752

E	Nu	Os(II)	Re(I)
		0%	76%
		16%	71%
		23%	46%
		0%	56%

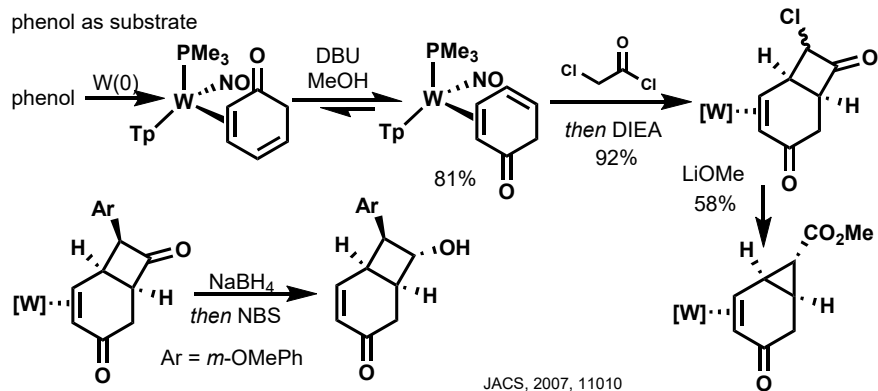
Reactions of W(0)-arene complex

preparation of W(0)-arene complex

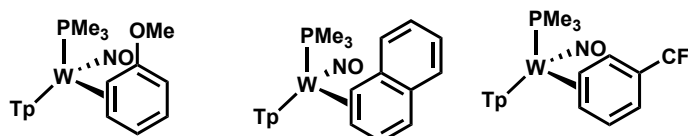


W. D. Harman* OM, 2003, 4364

phenol as substrate



known complexes



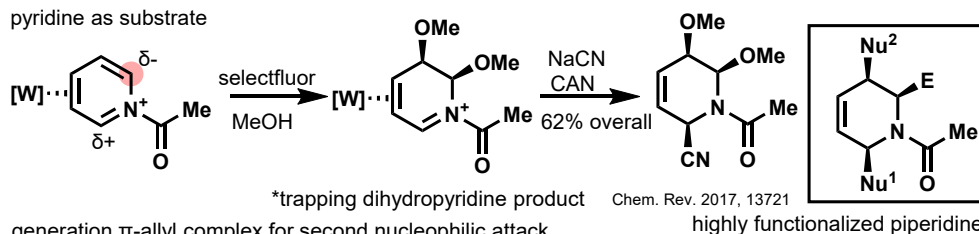
OM, 2007, 2791

all mixtures are:

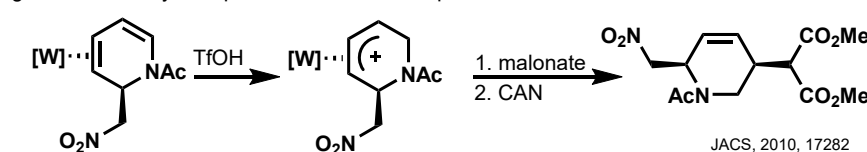
air stable and mixture of diastereoisomer

similar selectivity to Os(II): EWG: C3-C4/EDG: C2-C3

pyridine as substrate

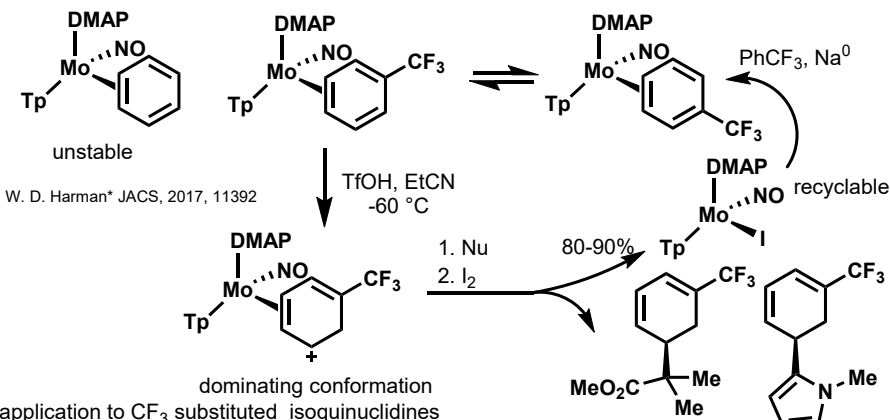


generation π -allyl complex for second nucleophilic attack



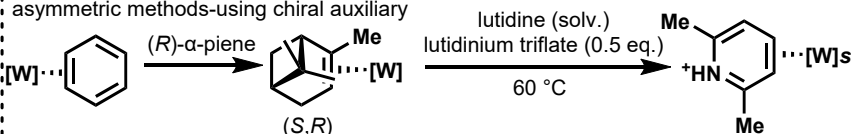
Reactions of Mo(0)-arene complex

Mo(0) possesses a weaker metal-arene bond

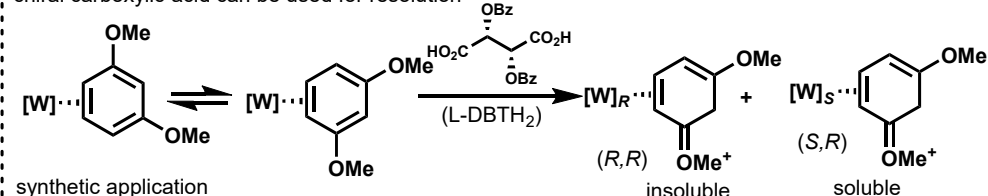


W. D. Harman* JACS, 2019, 18890

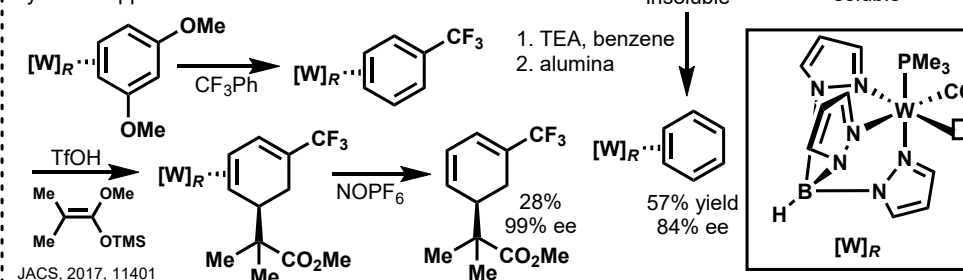
asymmetric methods-using chiral auxiliary



chiral carboxylic acid can be used for resolution

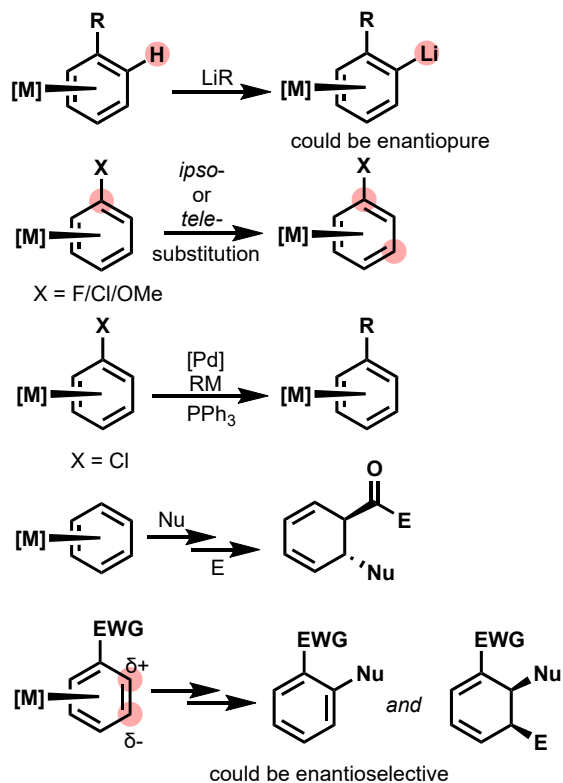


synthetic application

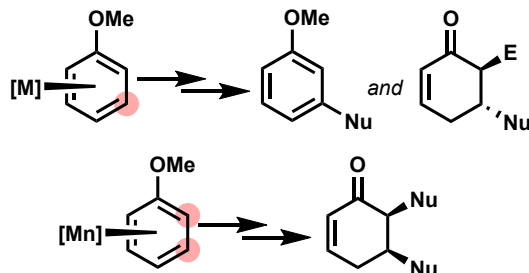
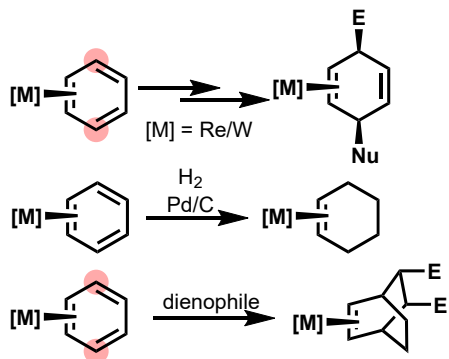


Summary

Characters of Cr(0)/Mn(I)/Fe(II)/Ru/Rh arene complexes



Characters of Os(II)/Re(I)/W(0)/Mo(0) dihapto complexes



stronger π acid \rightarrow

VI	VII	VIII	IX
Cr d^5s^1	Mn d^5s^2	Fe d^6s^2	Co d^7s^2
Mo d^5s^1	Tc d^5s^2	Ru d^7s^1	Rh d^8s^1
W d^4s^2	Re d^5s^2	Os d^6s^2	Ir d^7s^2

\leftarrow stronger π base

Characters of Fe-diene/dienyl complexes

