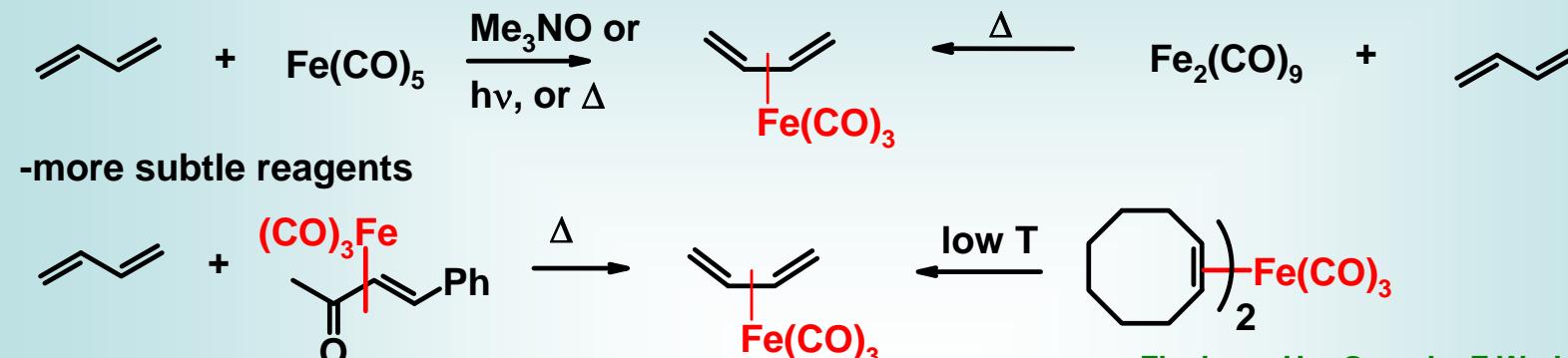


## $\eta^4$ -Diene Complexes

-absolutely dominated by iron tricarbonyl complexes



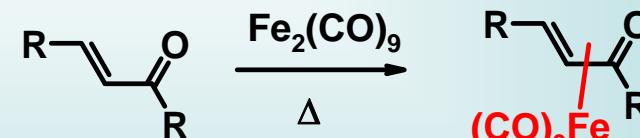
### Preparation



Fleckner, H.; Grevels, F.W.; Hess, D.  
*J. Am. Chem. Soc.* **1984**, *106*, 2027.

$\text{Me}_3\text{NO}$  mediated transfer Shvo, Y.; Hazum, E. *J. Chem. Soc. Chem. Commun.* **1975**, 829

-the  $\text{Fe}(\text{CO})_3$  unit is unusually stable; even in cases where it could lose more CO ligands, it normally does not



Note: esters, amides only form  $\eta^2$ - $\text{Fe}(\text{CO})_4$  complexes

### Reviews

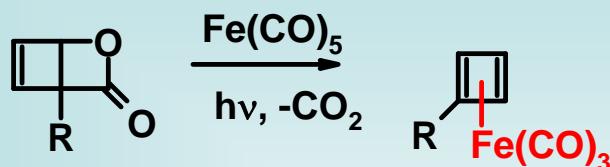
R Pearson, A.J. 'Iron Compounds in Organic Synthesis', Ch. 4, 1994.

R Green., J. R.; Donaldson, W. A. 'Encyclopedia of Inorganic Chemistry', 1994, Vol. 4

R Gree, R. Lellouche, J. P. *Adv. Met.-Org. Chem.* **1995**, 4, Ch.4

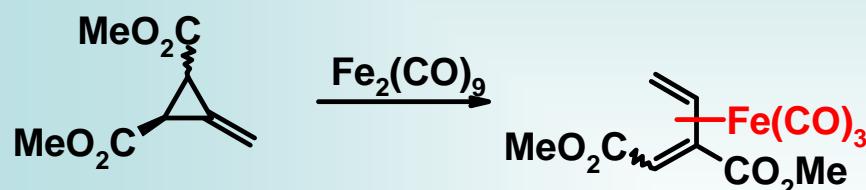
R King, R.B. 'The Organic Chemistry of Iron', Vol. 1, 1978.

## Rare/specialty methods



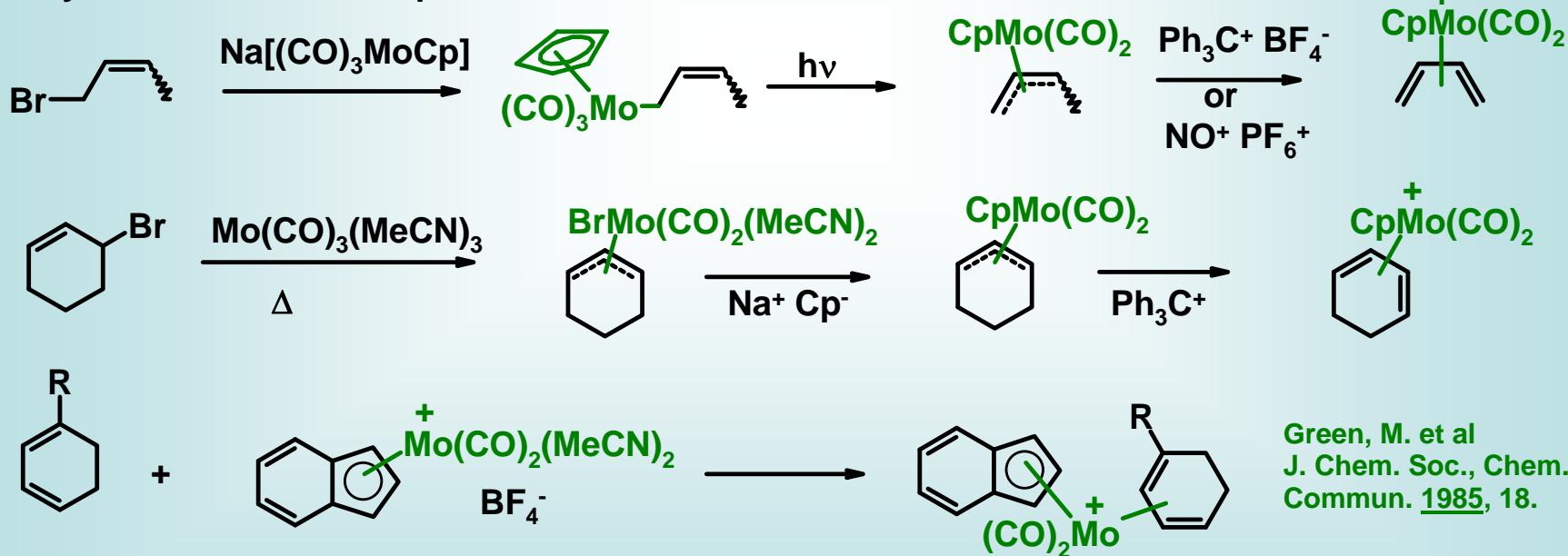
Agar, J.; Kaplan, F.; Roberts, B. W. *J. Org. Chem.* **1974**, *39*, 3451.

**Very stable complex**  
-by contrast, free cyclobutadiene is not at all stable



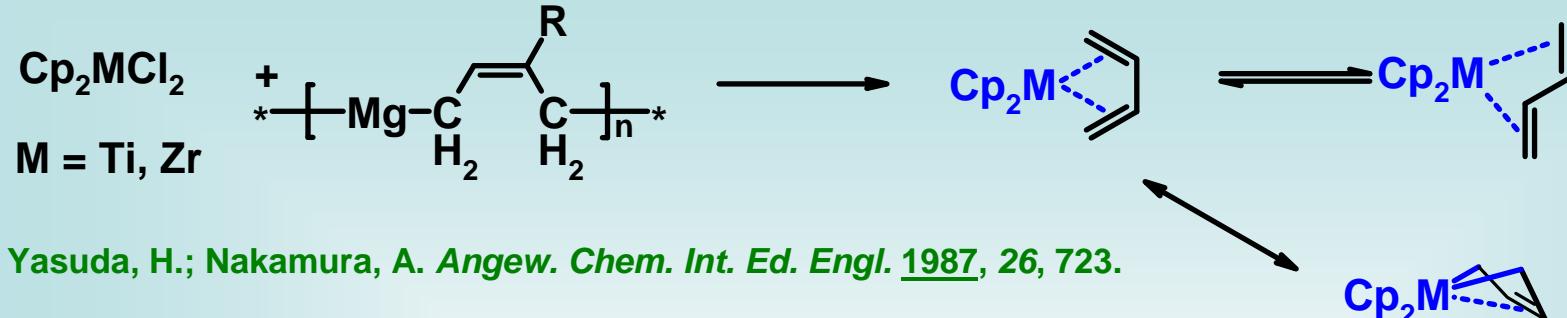
rare: ring opening is actually stereospecific  
Whitesides, T.H. *J. Organomet. Chem.* **1974**, *67*, 99.

## Molybdenum dienes complexes



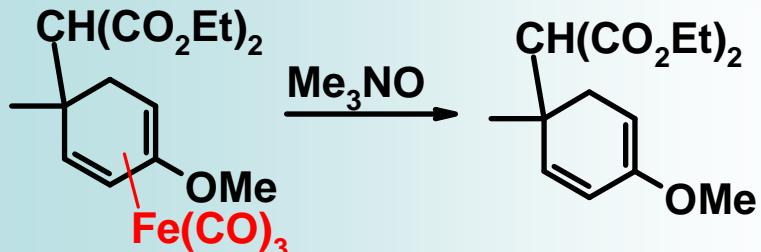
Green, M. et al  
*J. Chem. Soc., Chem. Commun.* **1985**, 18.

## Early Transition Metal Complexes



## 2. Decomplexation of $\eta^4$ -Diene Complexes

### a) Oxidation of Iron-Diene Complexes



Shvo, Y.; Hazum, E. *J. Chem. Soc., Chem. Commun.* 1974, 336.

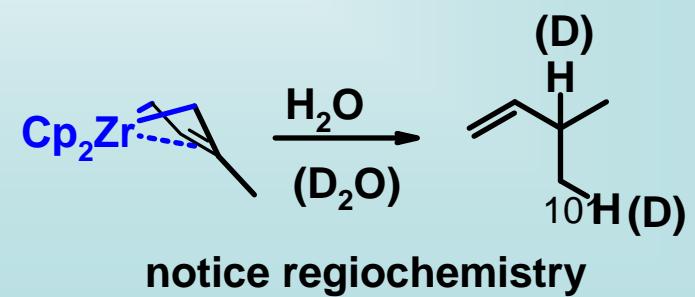
Other oxidants such as Ce<sup>IV</sup>, CuCl<sub>2</sub>, Ag<sup>I</sup> work also

### b) Early Transition Metal Dienes

- have reactivity like.....



and therefore

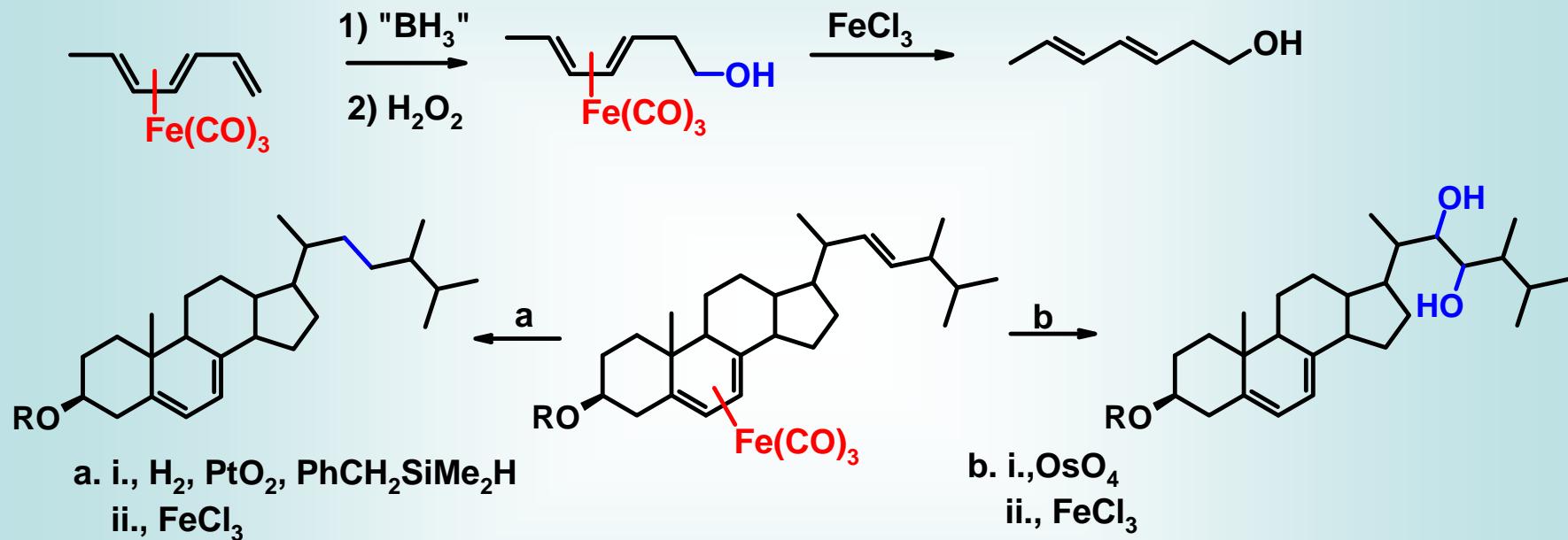


### 3. Use as Protecting/Stabilizing Groups

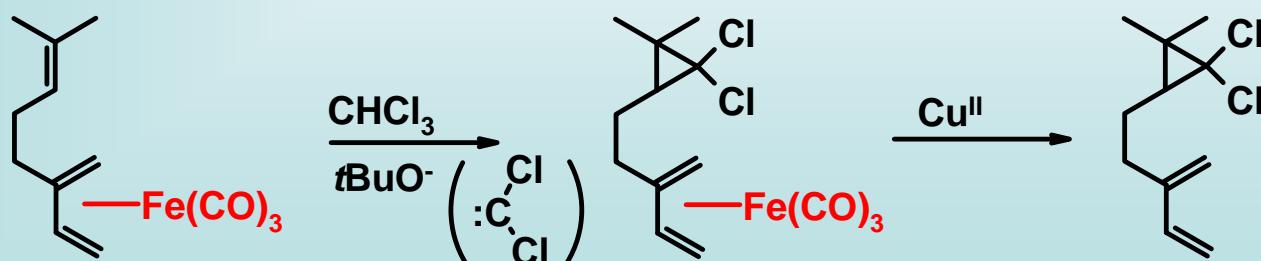
#### a) Protection of Dienes

-although coordination of a diene by  $\text{Fe}(\text{CO})_3$  is inductively a slight electron donor,  
the reactivity of dienes to electrophiles is *reduced*

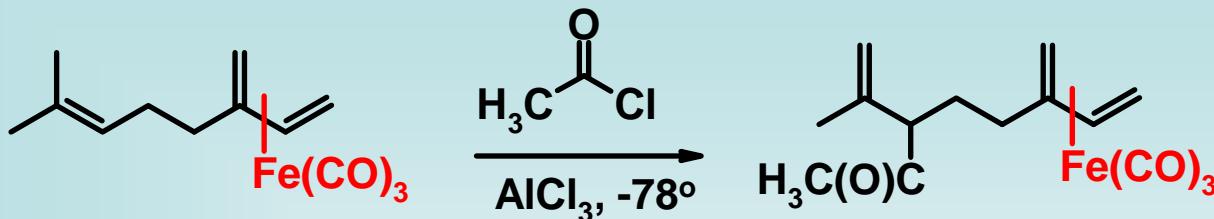
therefore



-Carbenes - normally prefer to add to conjugated dienes over isolated C=C 's, but....

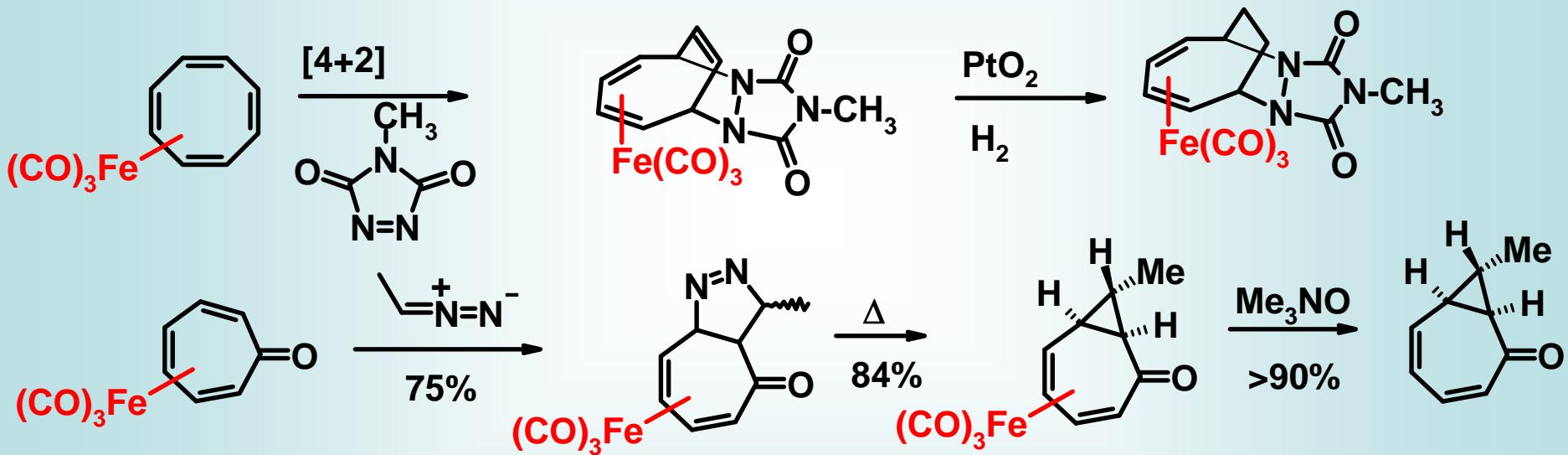


-and acylation\*



\* - diene- $\text{Fe}(\text{CO})_3$  complexes *will* also react, but more slowly

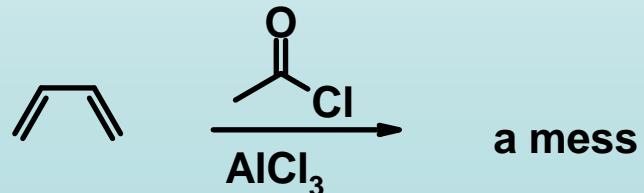
-one can even do cycloadditions on free double bonds in the presence of  $\text{Fe}(\text{CO})_3$  complexes



-also stable to Wittig reaction, aldol condensations, osmylation (dihydroxylation)

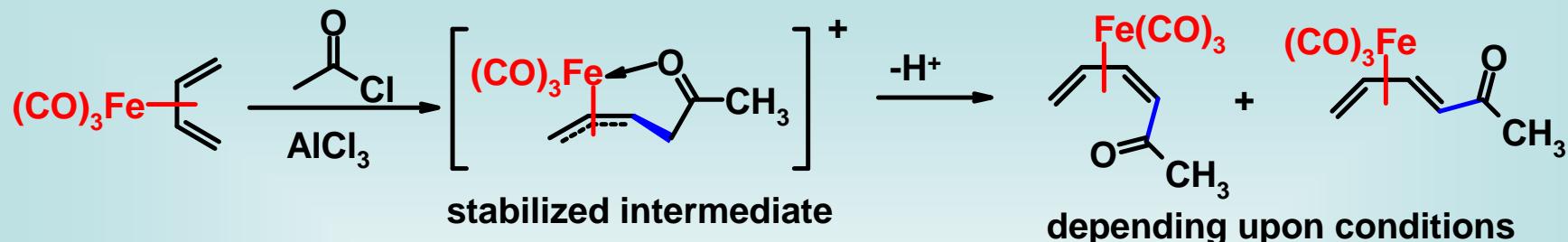
-exception (sort of) - let's say 'controlled' reactivity

consider

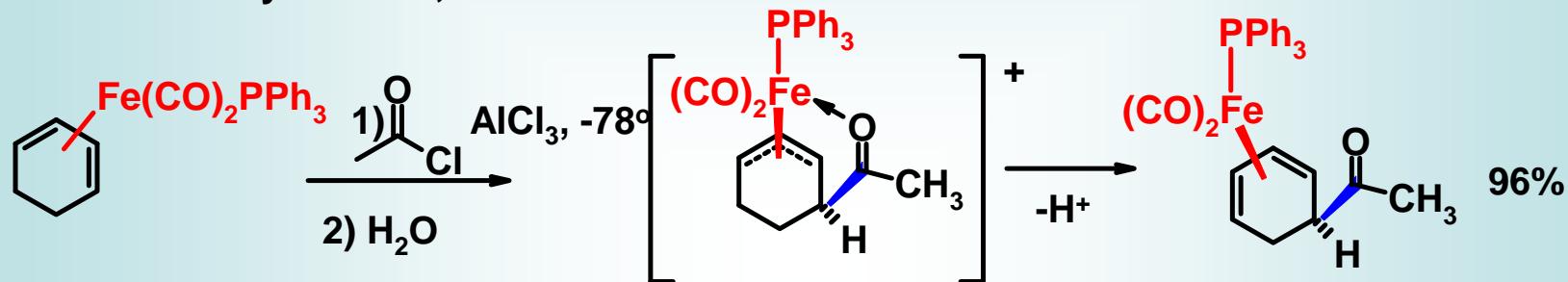


v. non-selective reaction/oligomerization

-conversely,..



-the reactivity is lower, but much more controlled



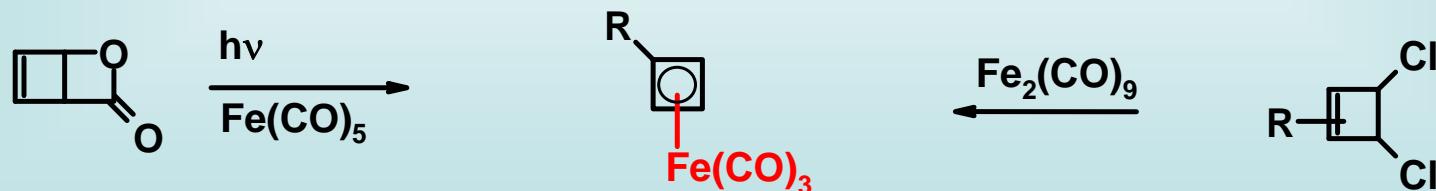
### b) Stabilization of (overly) Reactive Species

i) consider cyclobutane     



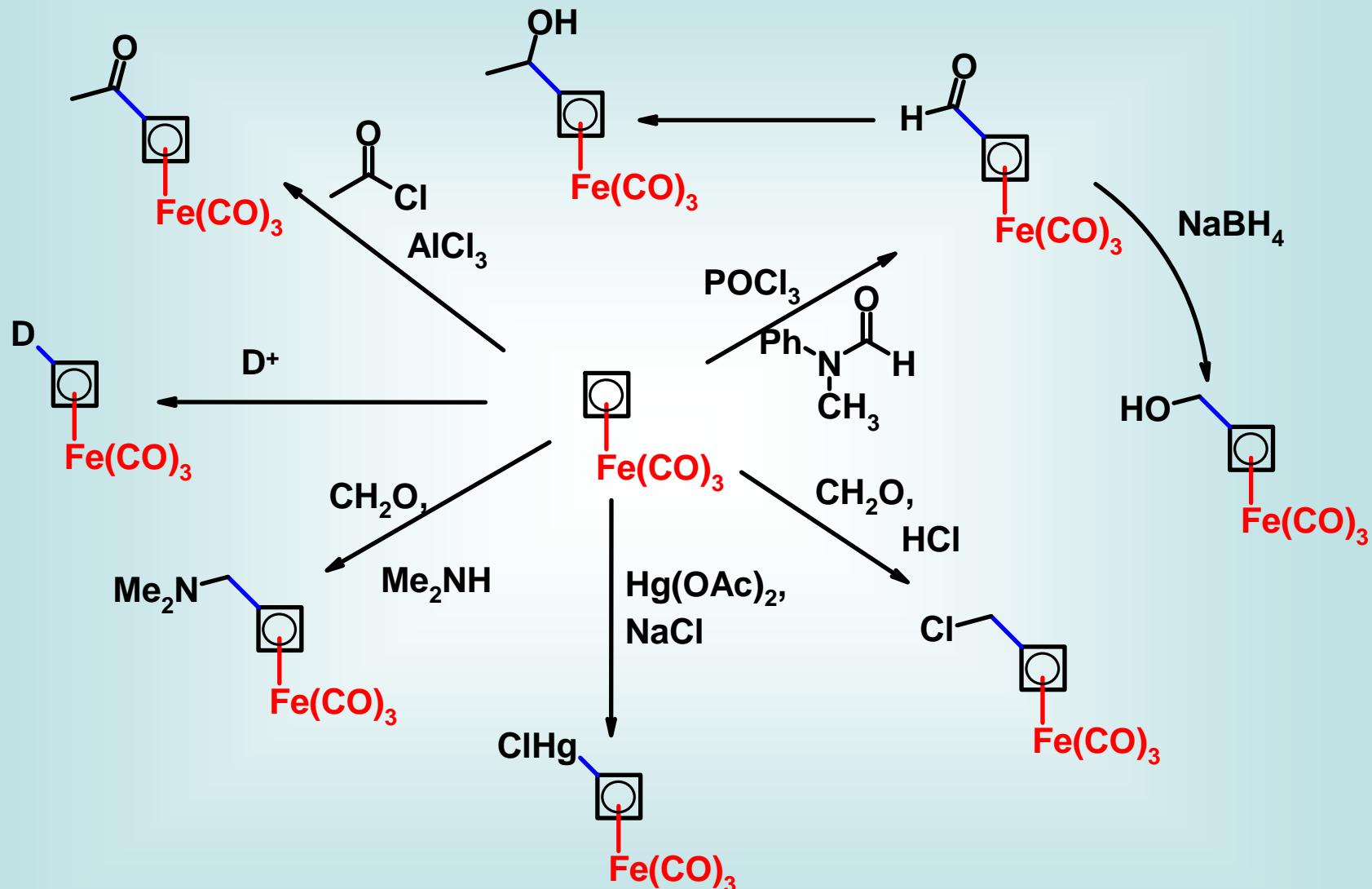
-classic antiaromatic compound  
-'cannot' be isolated

-very stable compounds



-stable enough to allow standard aromatic functionalization reactions - behaves pretty much like benzene

-these cyclobutadiene- $\text{Fe}(\text{CO})_3$  complexes are stable enough to allow standard aromatic functionalization reaction - they behave pretty much like benzene

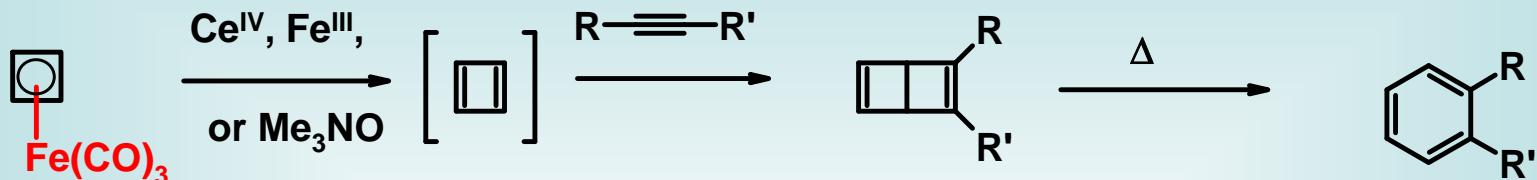


Rosenblum, M.; et al *J. Am. Chem. Soc.* 1972, 94, 1239

Emerson, G.F.; Pettit, R., et al *J. Am. Chem. Soc.* 1975, 97, 3255.

R Green, J. R.; Donaldson, W.A. 'Encyclopedia of Inorganic Chemistry', Vol. 4, 1735, 1994.

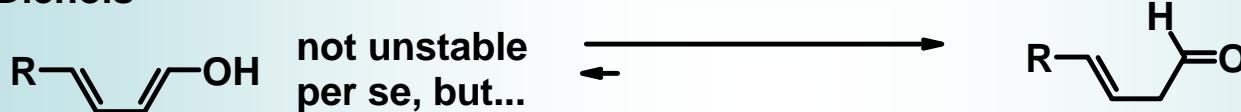
Note: Decomplexation of Fe leads to free cyclobutadiene, which can be trapped by other reagents



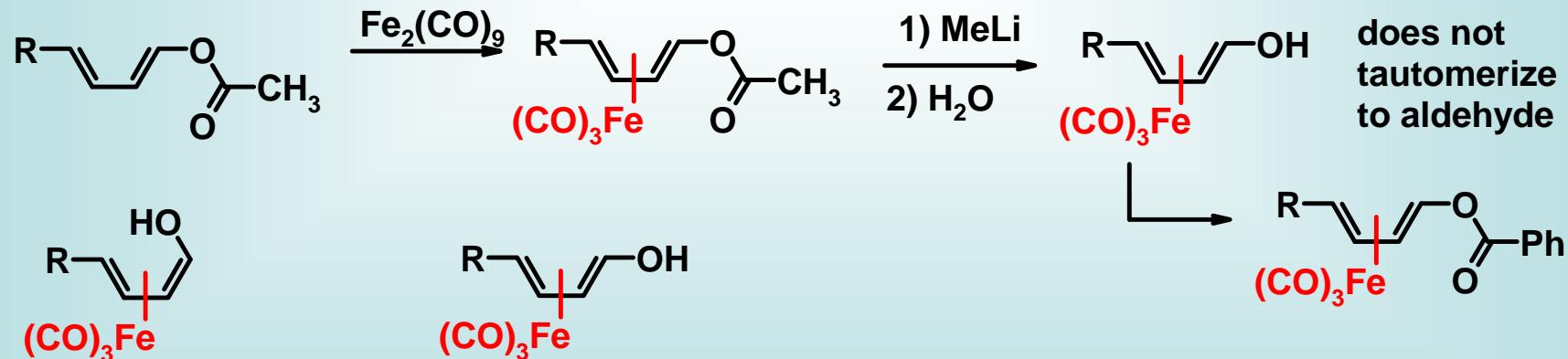
Pettit, R. J. Am. Chem. Soc. 1965, 87, 3253.

Snapper, M.

## ii) Dienols

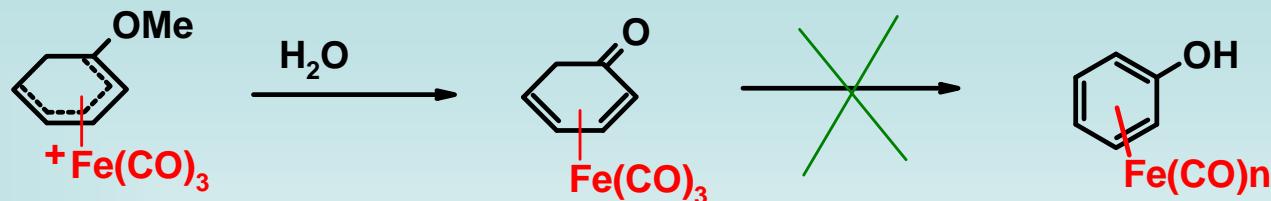


$\text{Fe}(\text{CO})_3$  coordinates more strongly to the  $\pi$ -system of a C=C relative to a C=O, so....



is similar, except it  
isomerizes to....

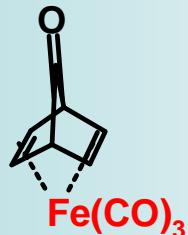
iii)



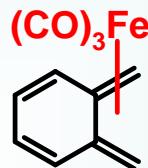
-almost nothing has been done with this, but it has much potential....

see Birch, A.J. *Tetrahedron Lett.* 1975, 119 (*Org. Synth. VI*, 996)

iv) Other examples



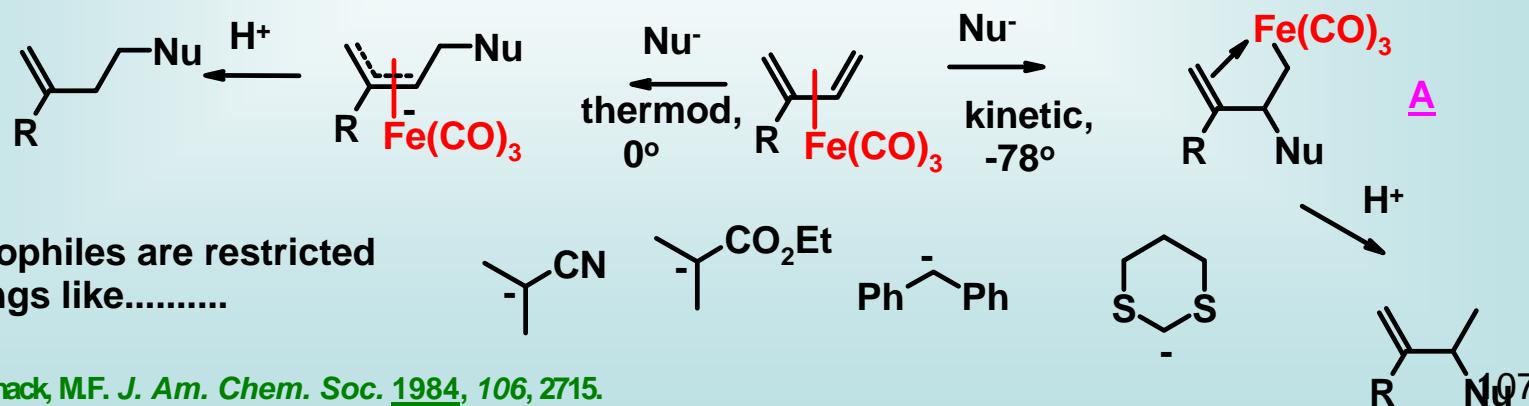
Landesberg, J.M.;  
Sieczkowski, J.  
*J. Am. Chem. Soc.* 1971, 93, 972



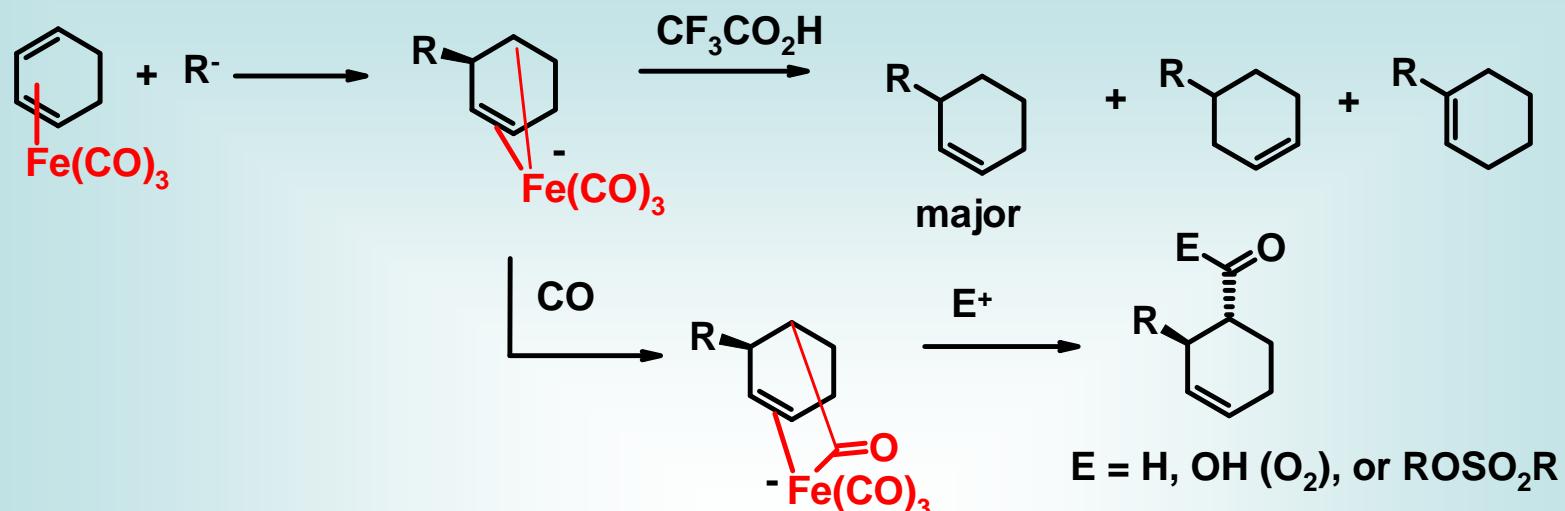
Roth, W.R.; Neier, J.D.  
*Tetrahedron Lett.* 1967, 2053.

#### 4. $\eta^4$ Diene Iron Complexes as Electrophiles

-iron diene complexes will react with nucleophiles, although the pathways are a bit complex



-in cyclohexadiene complexes, species like A do further chemistry



-see R Pearson, A.J. 'Iron Compounds in Organic Synthesis, p. 67-97.

in acyclic dienes, get related but more complicated reaction pathway

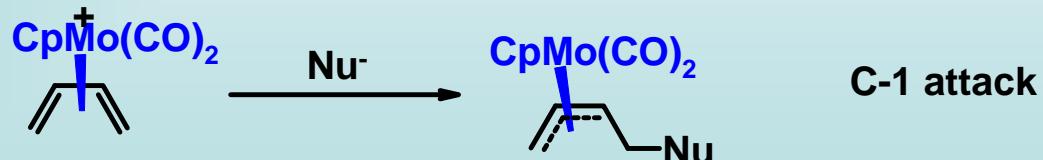
-see Semmelhack, M. F. *Organometallics* **1983**, *2* 1385 ; *J. Am. Chem. Soc.* **1985**, *107*, 1455.

Yeh, M.C.P.; Hwu, C.C. *J. Organometal. Chem.* **1991**, *419*, 341.

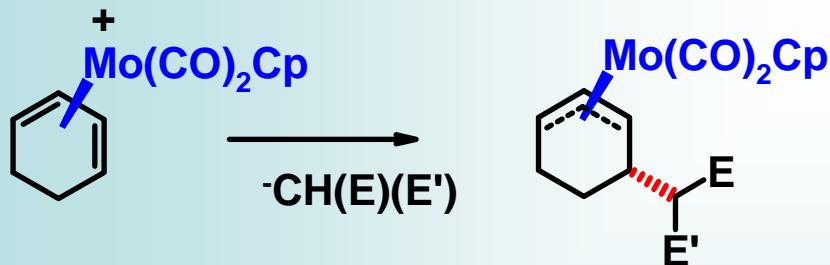
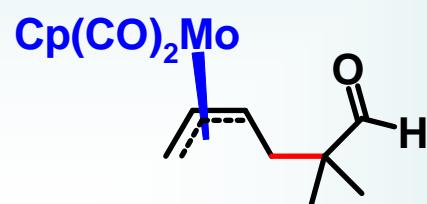
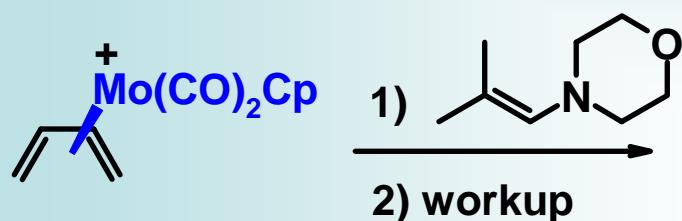
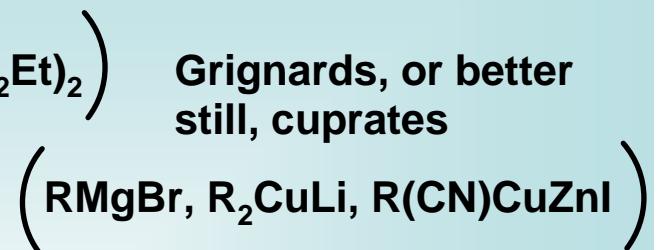
Chang, S. et al (M. Brookhart) *J. Am. Chem. Soc.* **1994**, *116*, 1869.

### b) Molybdenum Diene Complexes

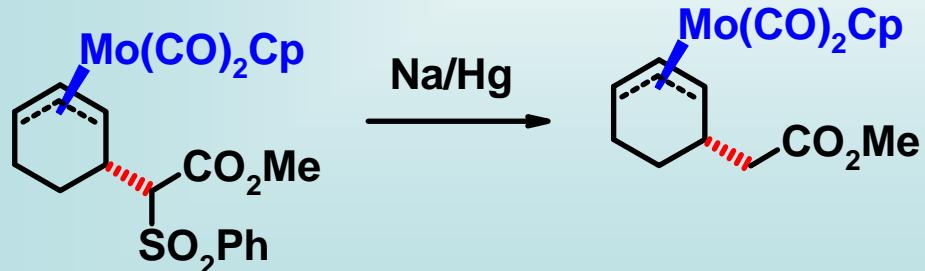
-these complexes are cationic, so that they obviously are a good choice for being more reactive as electrophiles

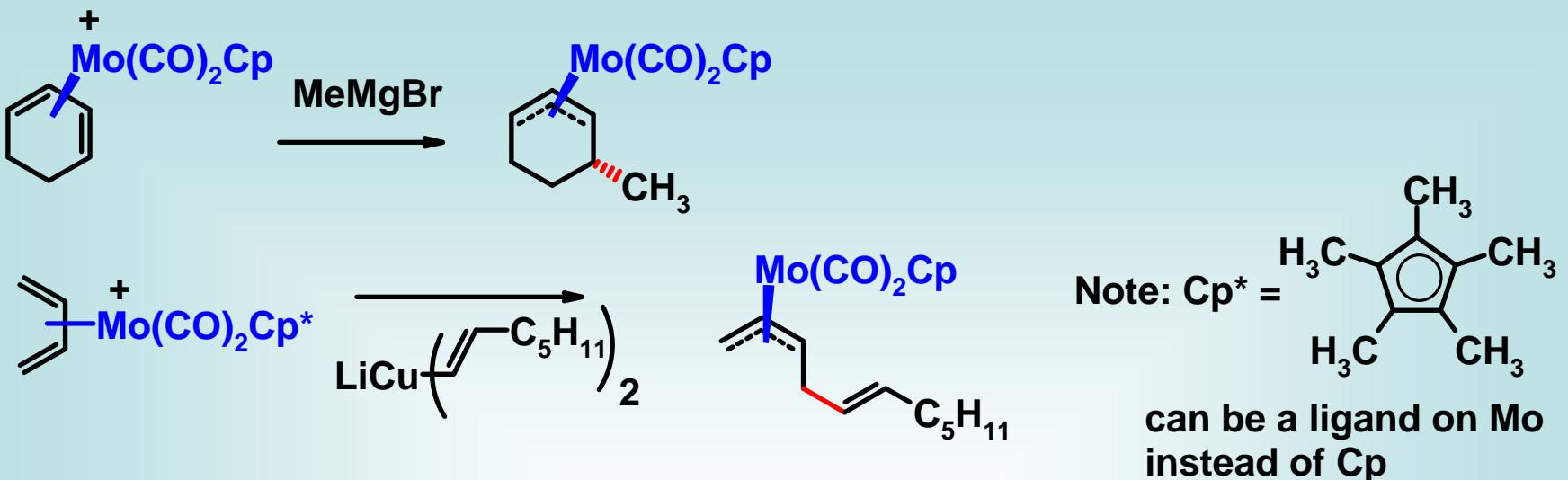


-range of nucleophiles should start looking familiar



Note:



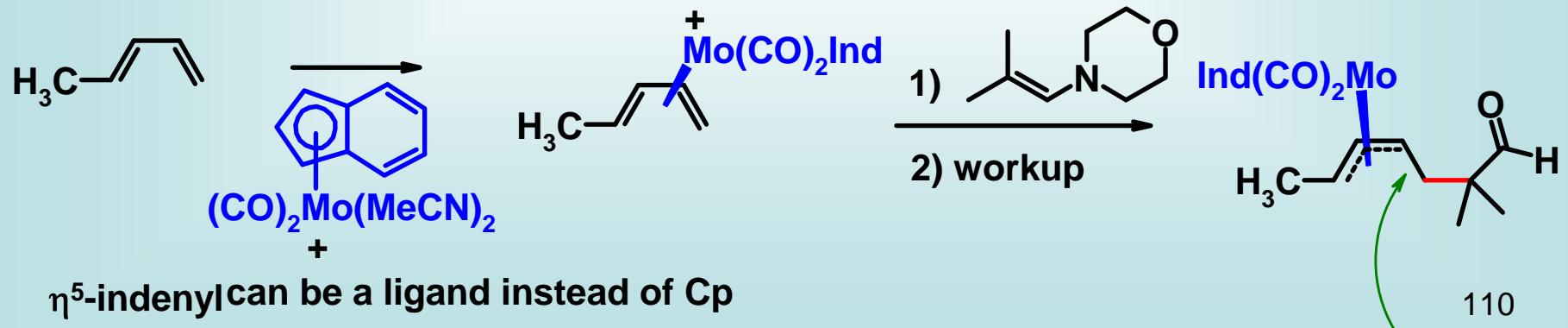


## Stereochemistry

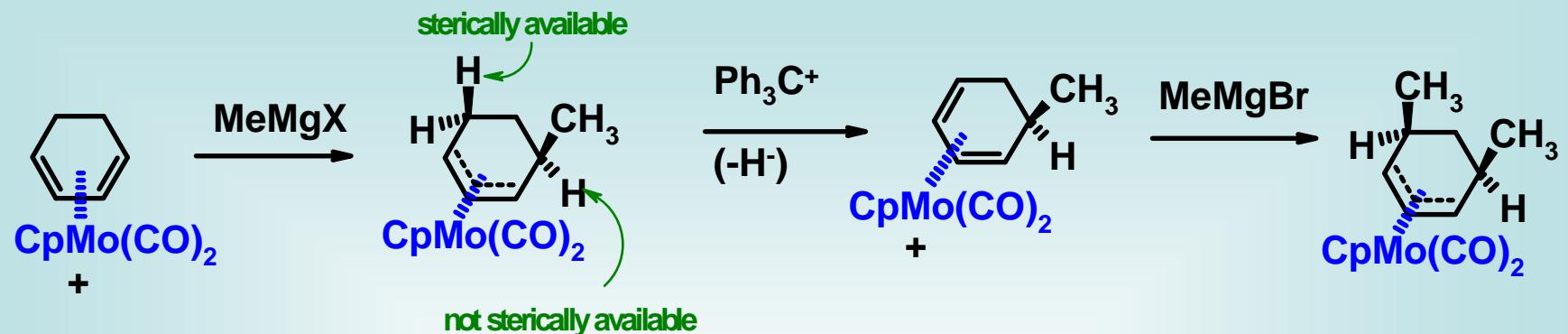
-it is apparent from the above examples that the addition is routinely *anti* to Mo

## Regiochemistry

-the nucleophile's attack is generally at the less substituted end of the diene

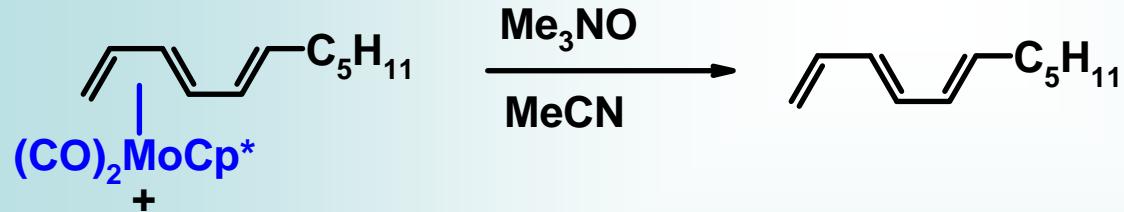


-tandem reactions are also feasible

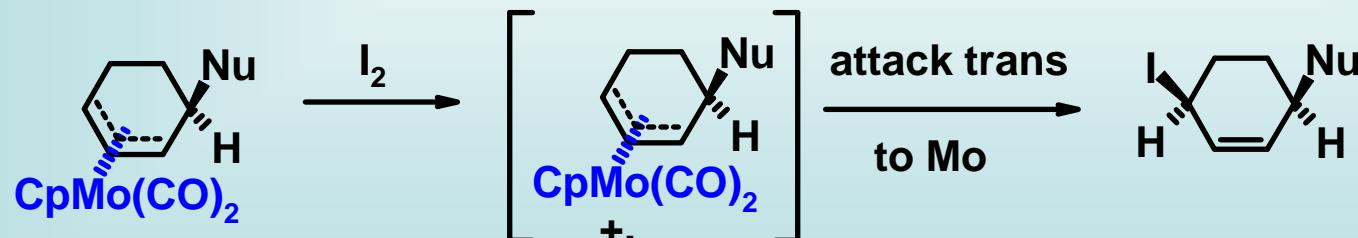


### Decomplexation Reactions of molybdenum Complexes

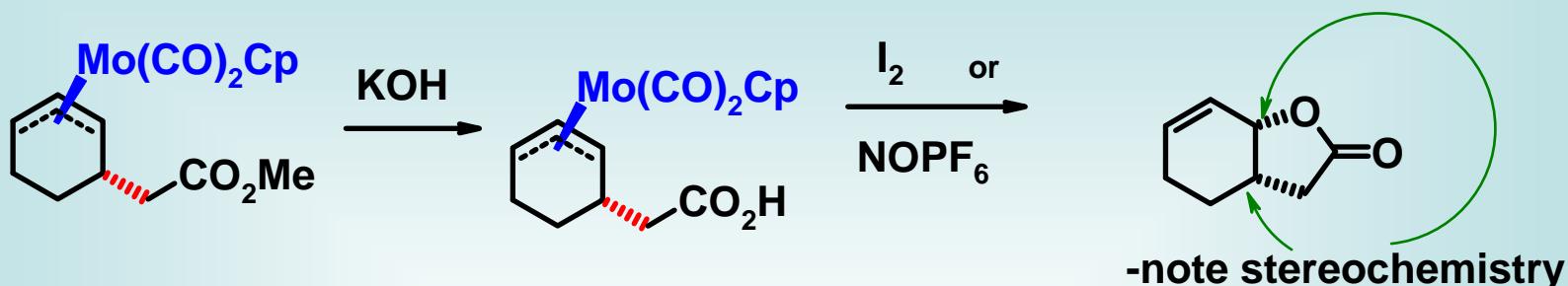
-straight oxidative decomplexation does occur for diene complexes



-oxidative decomplexation of allylMo's with nucleophilic attack



-oxidative decomplexation can occur with nucleophilic addition



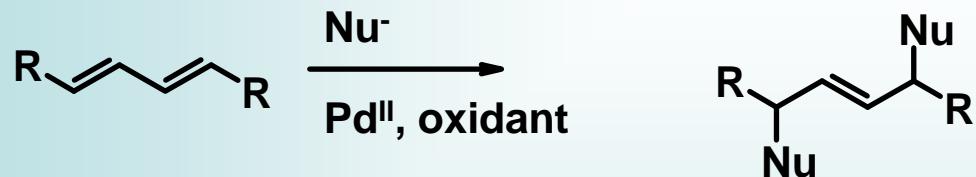
R Pearson, A.J. Adv. Met. Org. Chem. 1989, 1, 1.

R Backvall, J.-E. Adv. Met. Org. Chem. 1989, 1, 135.

(mostly Pd catalyzed addns)

asymmetric addns Pearson, A.J. et al *Tetrahedron Lett.* 1987, 28, 2459

c) we will not discuss this in detail, but Pd<sup>II</sup> catalyzed additions to dienes is known



Nucleophile is usually  $\text{R}_2\text{N}^-$  or  $\text{AcO}^-$ ; oxidant is usually benzoquinone

some cases of C-C bond formation

-see Backvall review