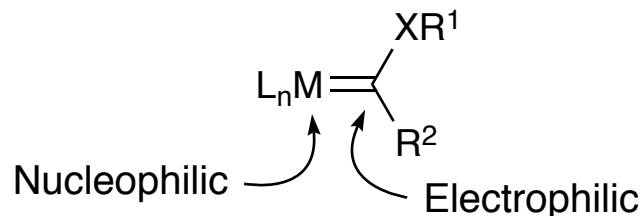


Three Type Of Carbene Complexes

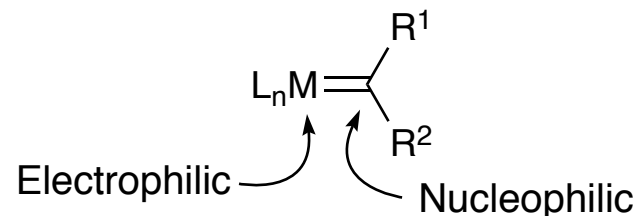
Carbene complexes have formal metal-to-carbon double bonds. Several types are known. The reactivity of the carbene and how it contributes to the overall electron counting is dependent on the substituents and metal involved.

Fischer carbenes



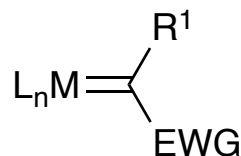
- X = O, NR, S
M = low-valent, middle or late transition metals
- L-type ligand
 - donating 2 electrons

Schrock carbenes



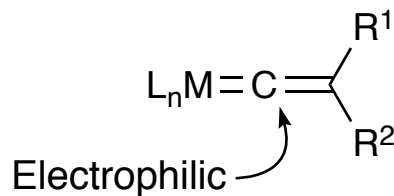
- R¹, R² = alkyl or H
M = high-valent carbyl or middle transition metals
- 2X-type ligand (−2 charge)
 - donating 4 electrons

Carbenoids



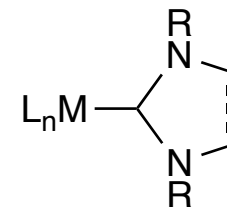
- $L_nM = Rh_2(O_2CR)_4, N_4Ru, (N_2O_2)Ru, \text{ or } (N,N)Cu$
- L-type ligand
 - donating 2 electrons

Vinylidenes



- R¹, R² = alkyl, aryl, or H
- L-type ligand
 - donating 2 electrons

N-Heterocyclic carbenes

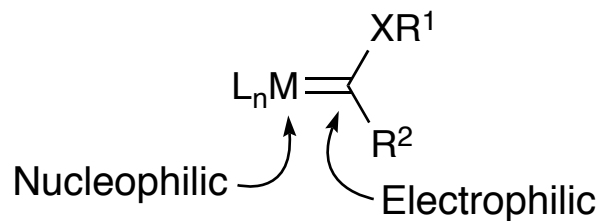


- R = alkyl or aryl
- generally a spectator ligand
 - L-type ligand
 - donating 2 electrons

Hartwig, *Organotransition Metal Chemistry*, 2010, pp 481–504.

Semmelhack, *Organometallics in Synthesis*, Schlosser, Ed., 2002, pp 1024–1041.

Fischer Carbenes

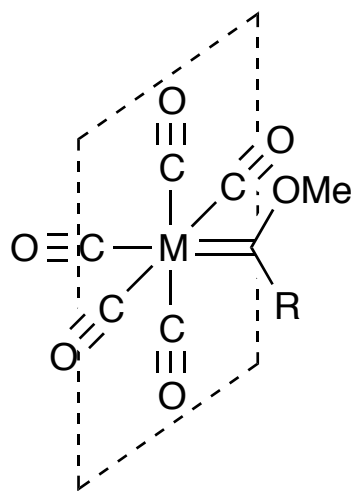
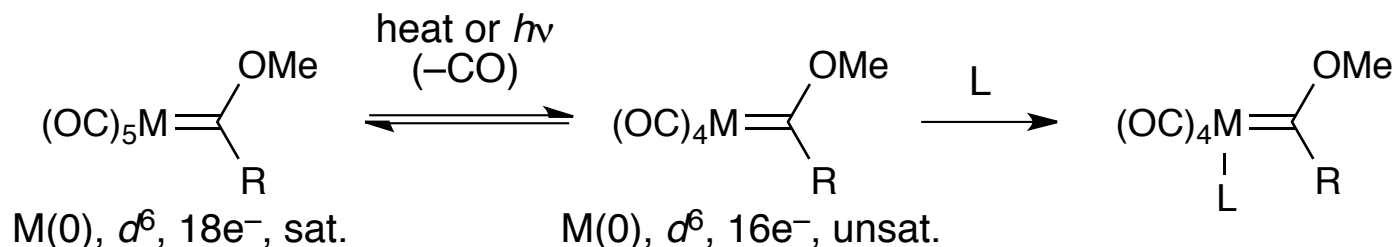


X = O, NR, S

M = low-valent, middle or late transition metals

- Most developed carbenes are those of Cr, Mo, and W.
- Usually synthesized from commercially available and stable $M(CO)_6$.
- Usually crystalline solids, easily purified by recrystallization or silica gel chromatography.
- Air stable as solids, slight sensitive in solution. The stability is due to the heteroatom. Dialkyl complexes decompose at low temps.
- The metal is d^6 and zero valent, coordinatively saturated.

- To react at the metal, one of the carbonyls must be removed with high temps or photolysis.

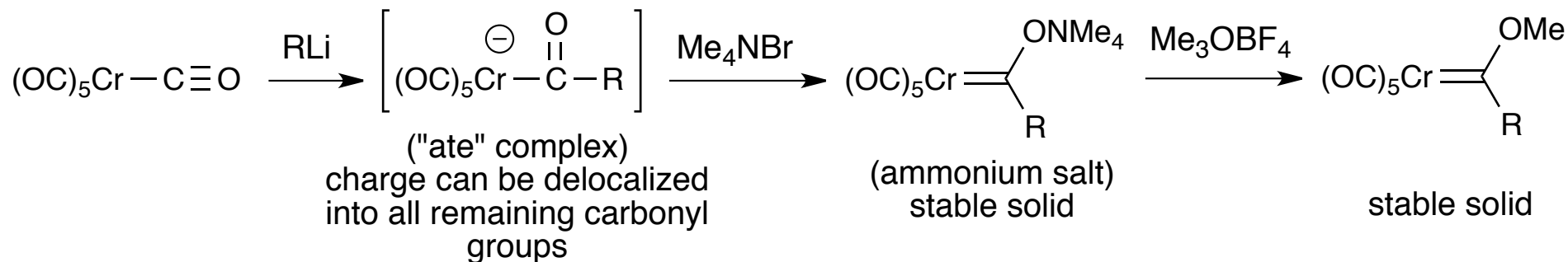


The "CO Wall" can destabilize some complexes with α -branching on the R group.

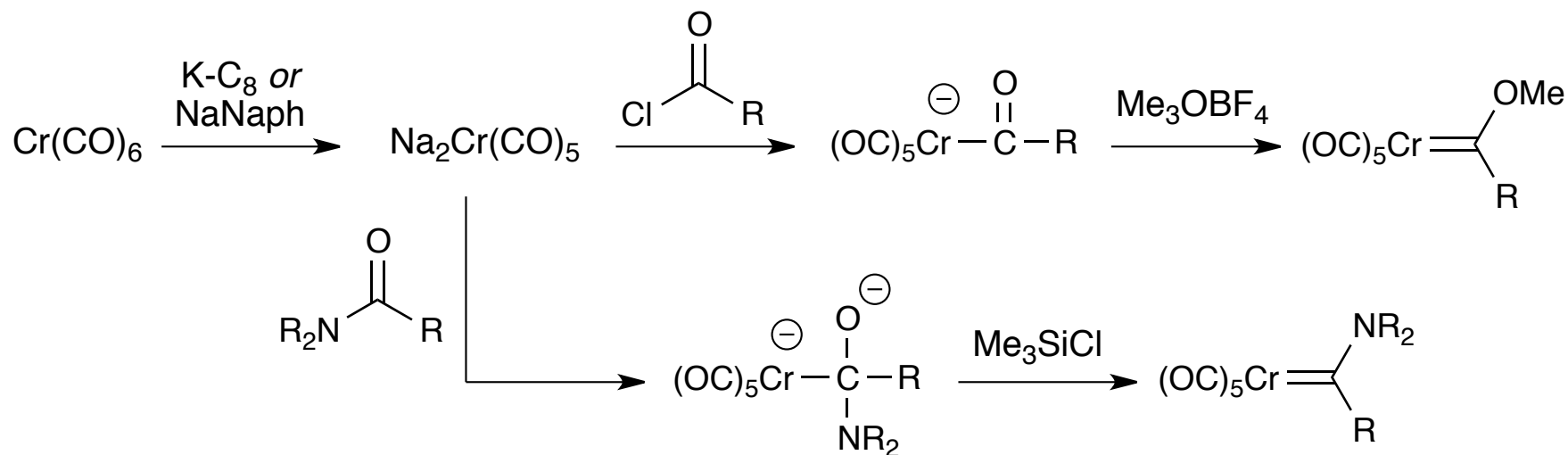
Preparation

Preparation of the Fischer carbene usually proceeds via an anionic acyl "ate" complex.

Alkyl lithium addition: probably most commonly used method

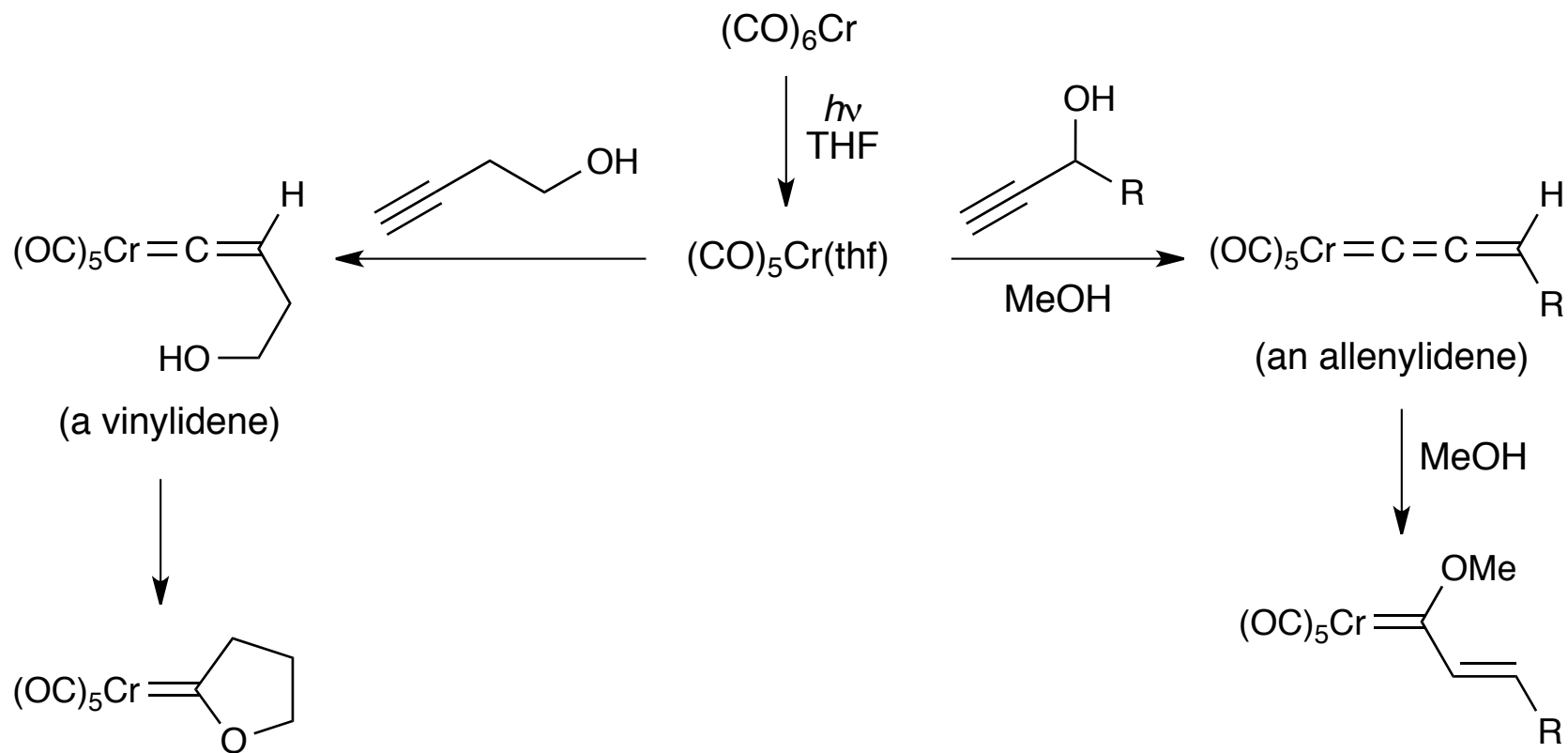


Reductive routes:



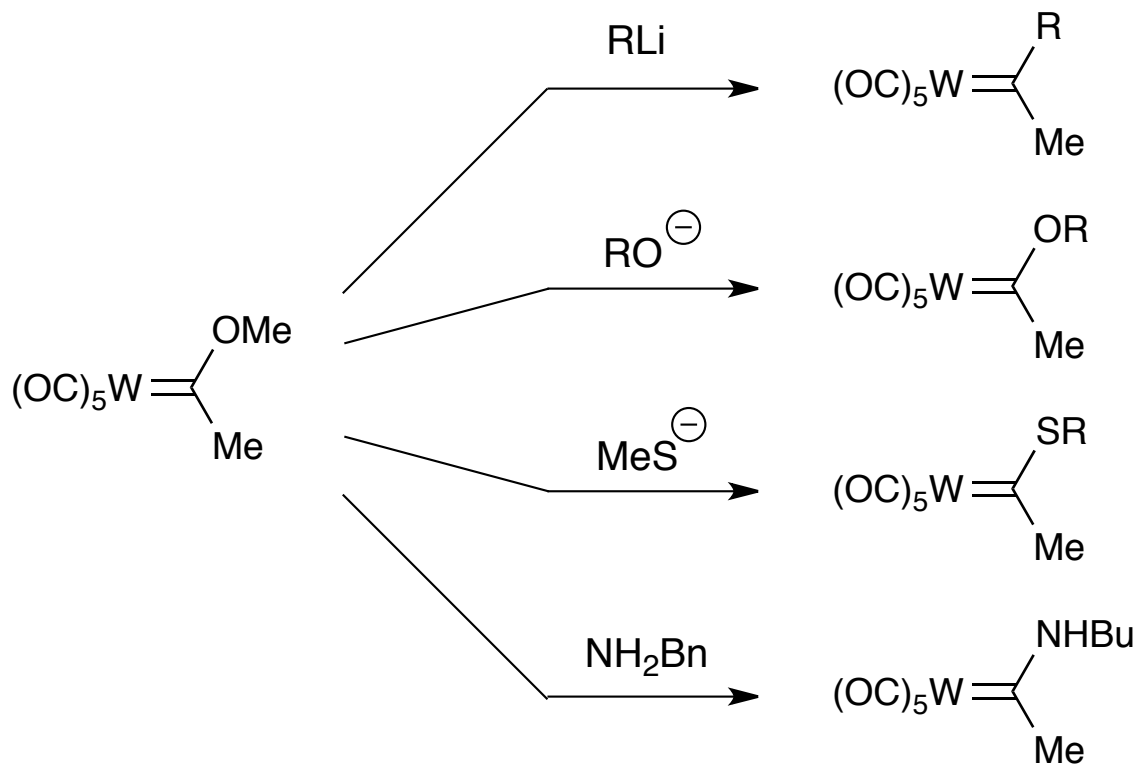
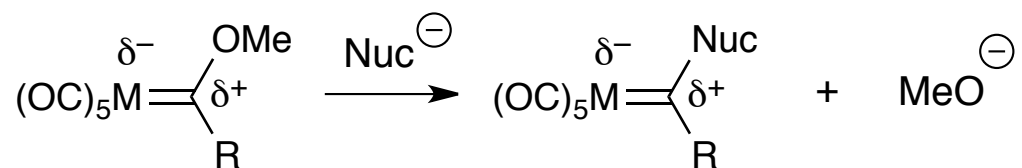
Preparation

Vinylidene and allenylidene intermediates: Neutral conditions



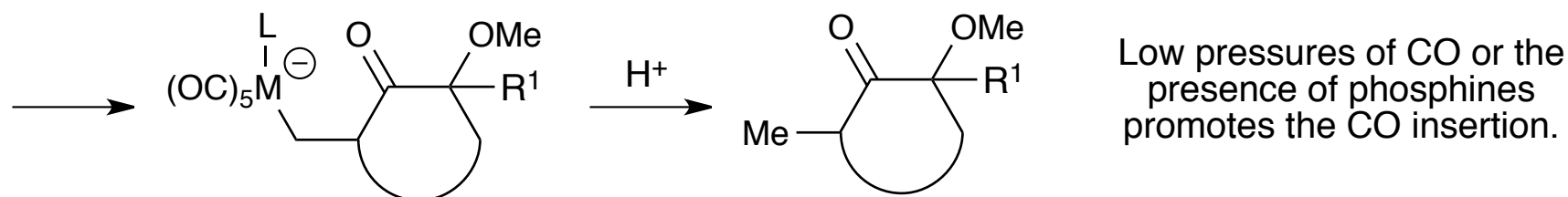
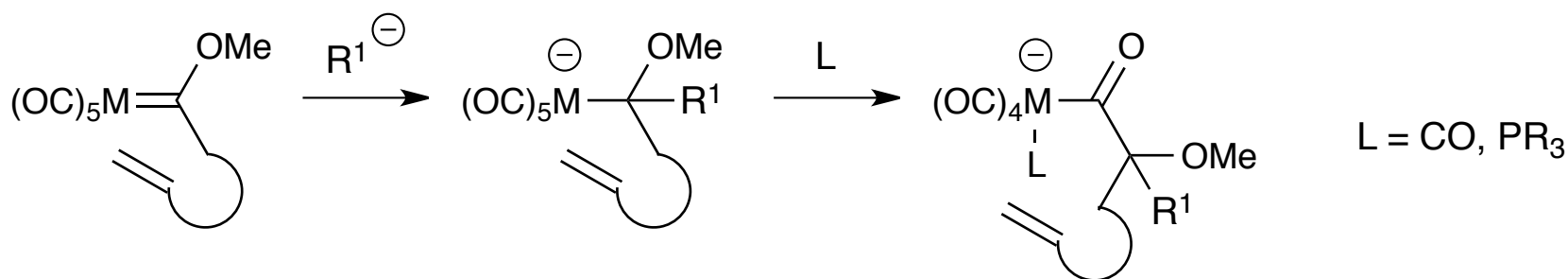
Addition Of Nucleophiles

The carbonyl groups are strongly electron withdrawing. This makes the M–C bond electrophilic. Reaction mechanisms are similar to the reactions of esters.



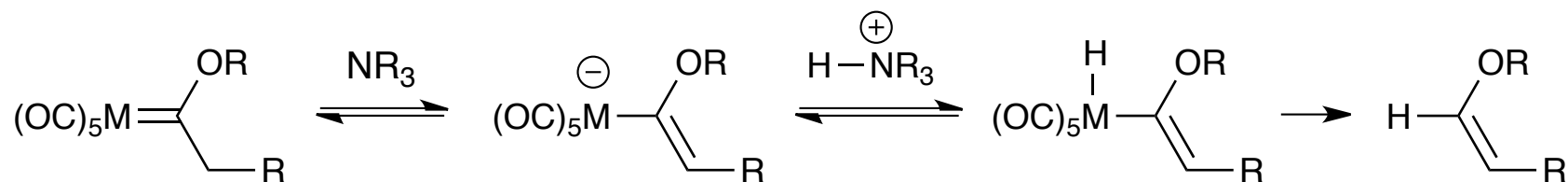
CO Insertions and Carbometallations

With carbon-based nucleophiles or hydrides, the alkoxide can be slow to eliminate. The metal-based anion can then undergo other reactions. Carbonyl migrations and carbometallation of alkenes/alkynes are common. How facile these reactions are is quite dependent on the R group.

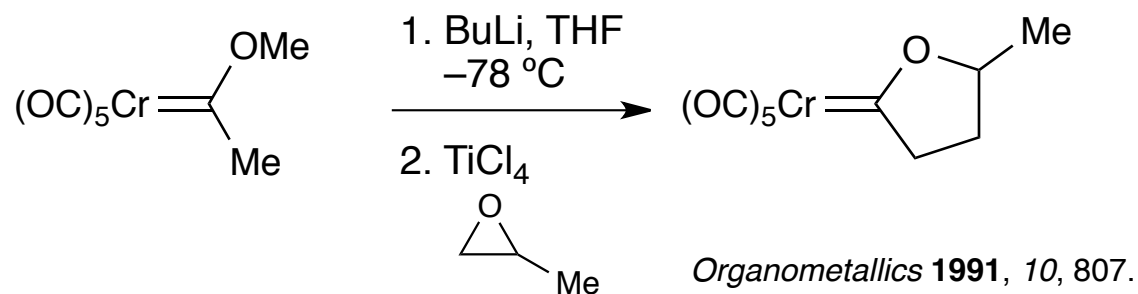
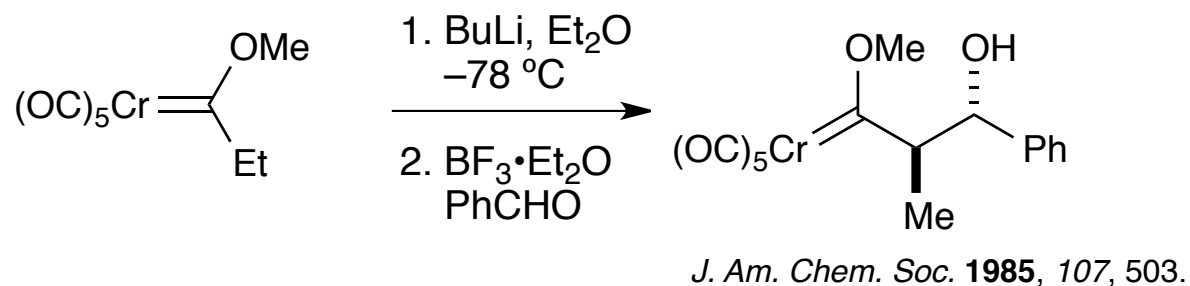


Fischer Carbene "Enolates"

The α -protons of Fischer carbenes are quite acidic ($pK_a \sim 12$). Anionic bases needed for irreversible deprotonation. Weak bases (Pyr, DMAP, Et_3N) can be used, but lead to formation of enol ether.

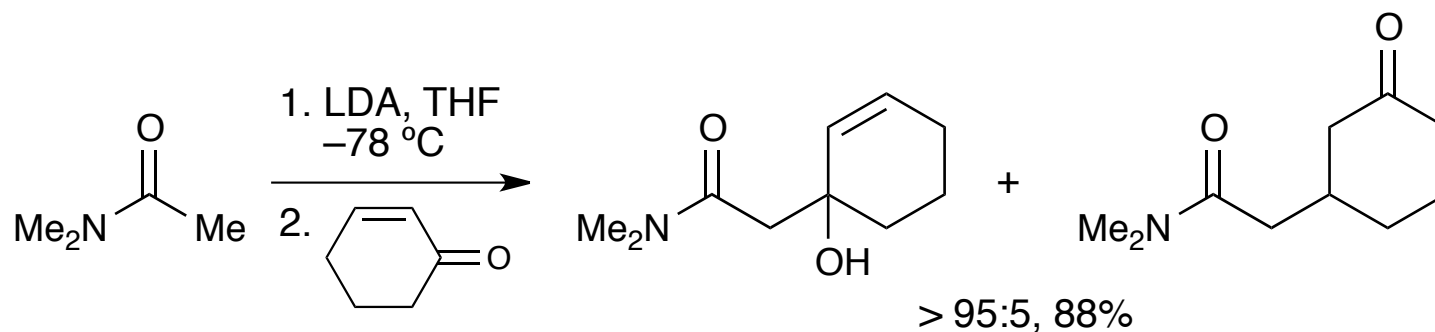
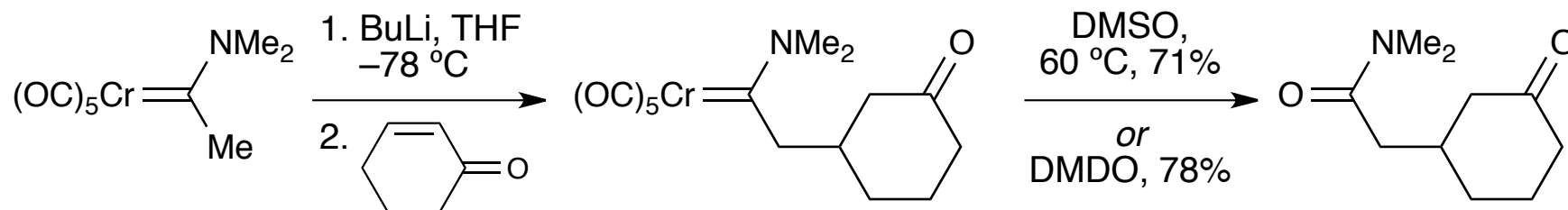
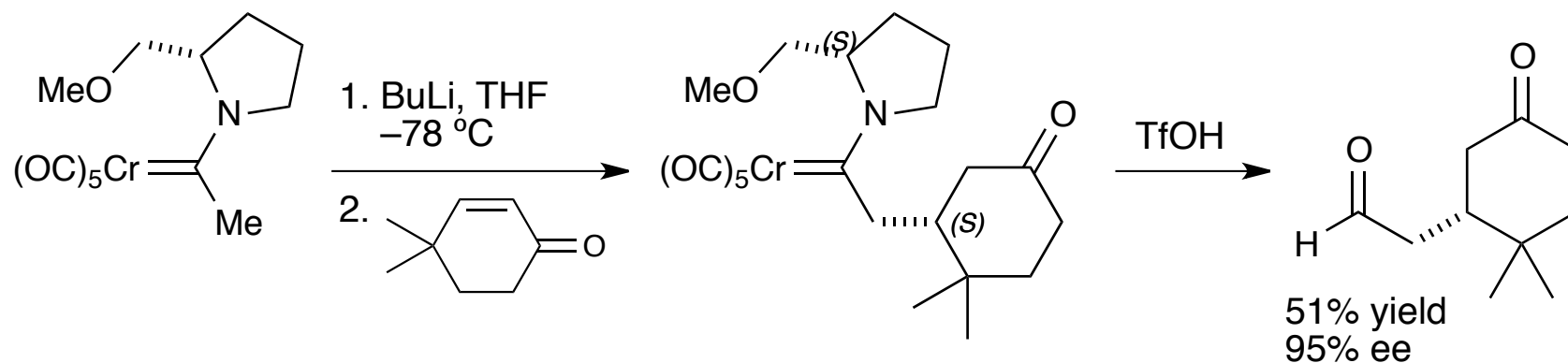


Anionic bases required for irreversible deprotonation. The "enolates" of alkoxy-carbenes are only weakly nucleophilic, but can react with electrophiles in the presence of a Lewis acid.



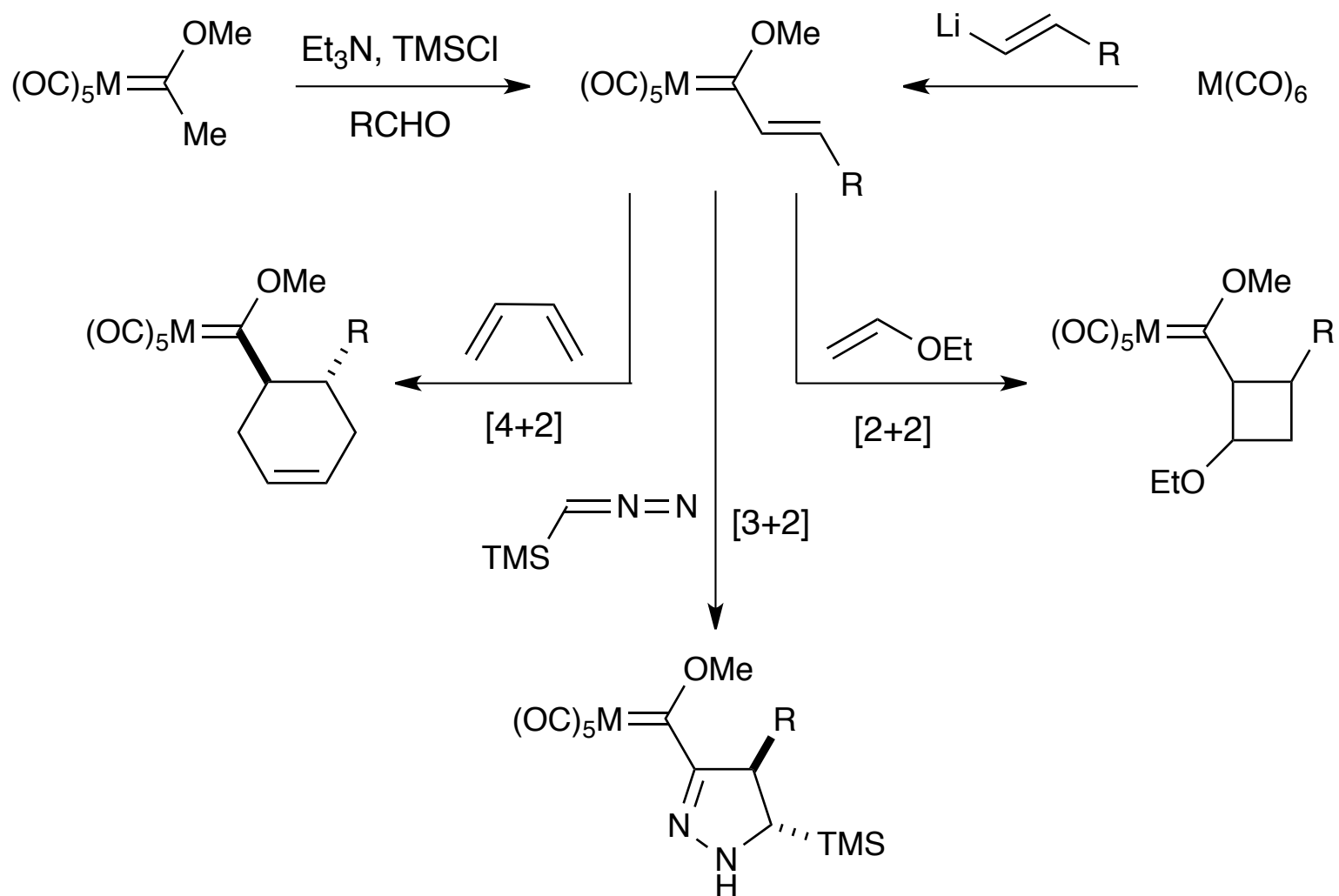
Fischer Carbene "Enolates"

The "enolates" of aminocarbenes are only more nucleophilic (compare ester enolates to amide enolates), and do not require Lewis acids to react.



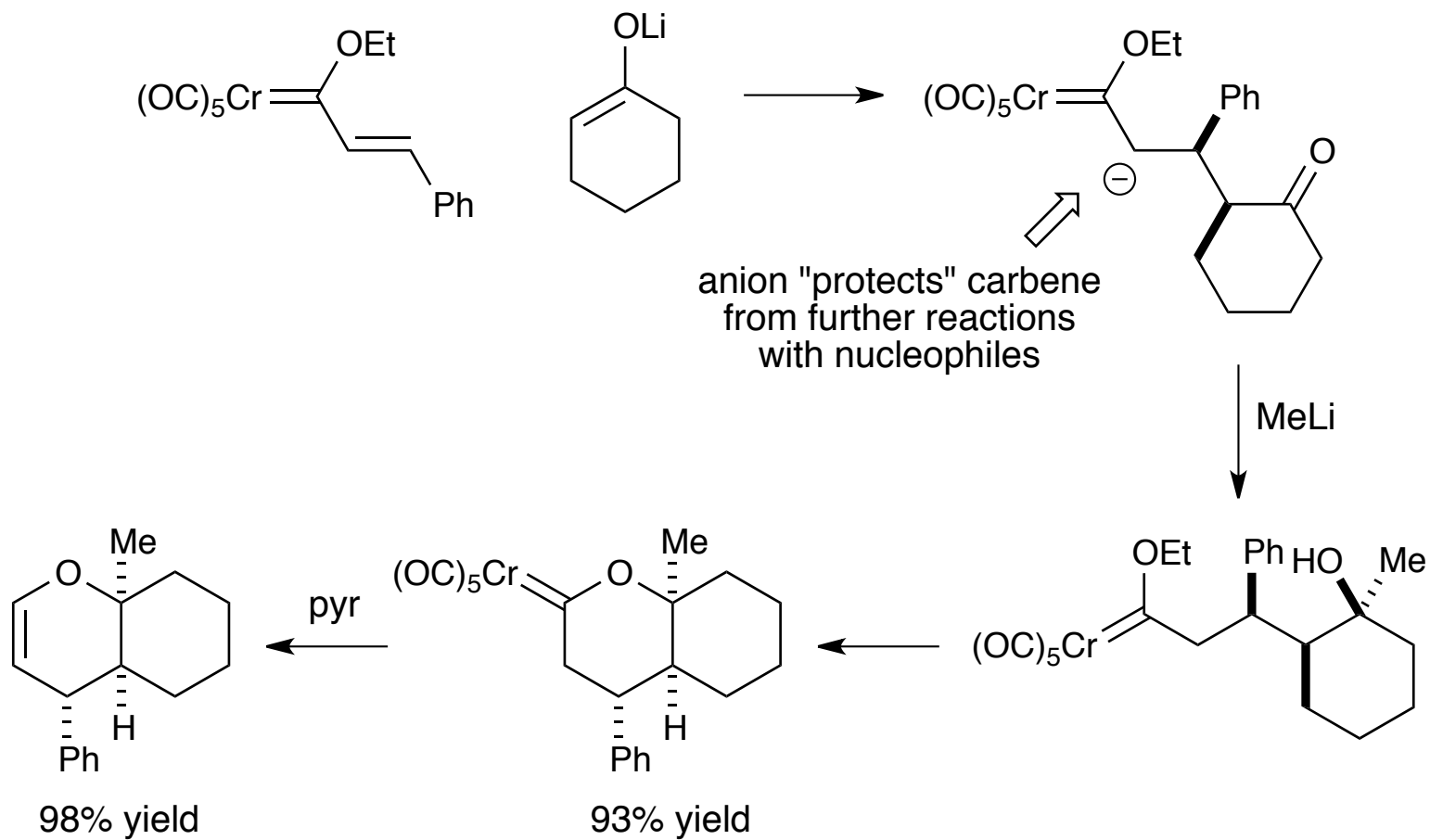
Cycloadditions

α,β -Unsaturated Fischer carbenes undergo cycloaddition reactions but are much more reactive than the corresponding ester.



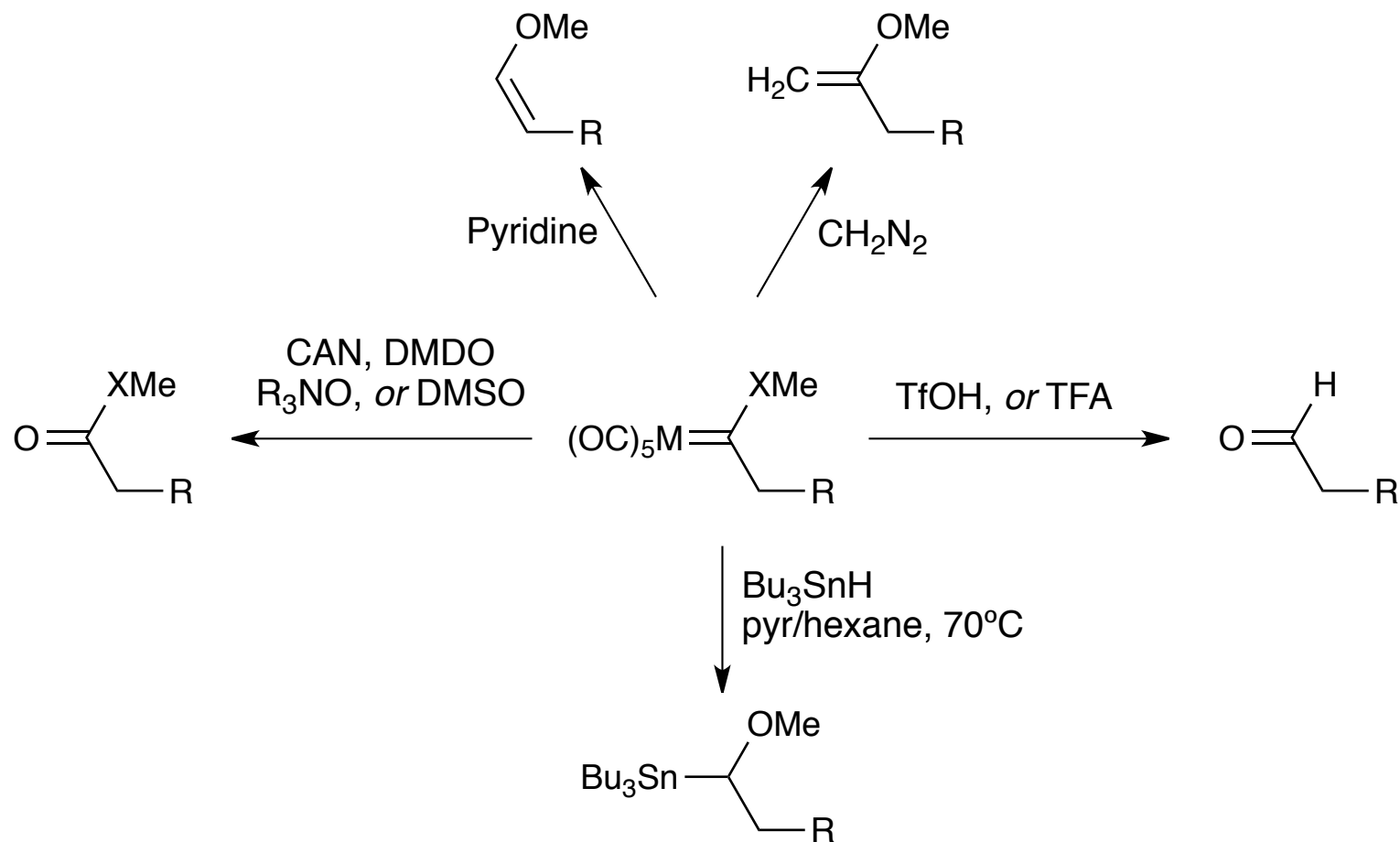
Conjugate Additions

α,β -Unsaturated Fischer carbenes can also serve as Michael acceptors.



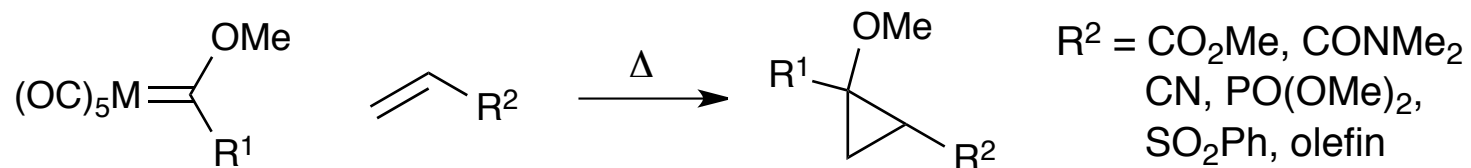
Removing the Metal

There are several methods available for removing the metal and converting the carbene into a different functional group.

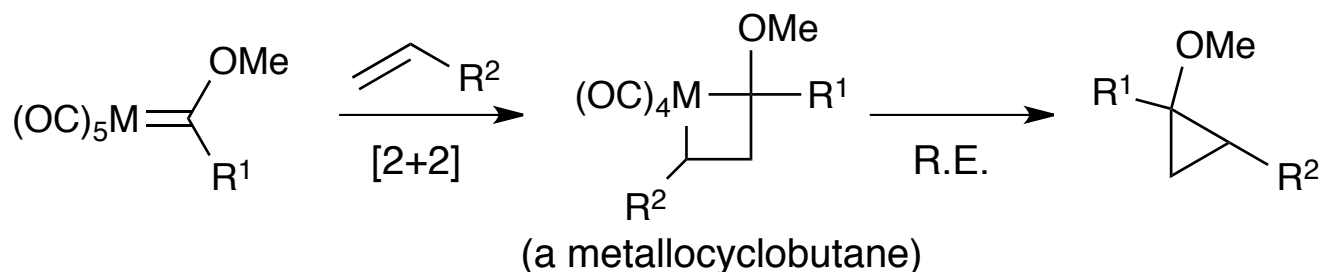


Cyclopropanation

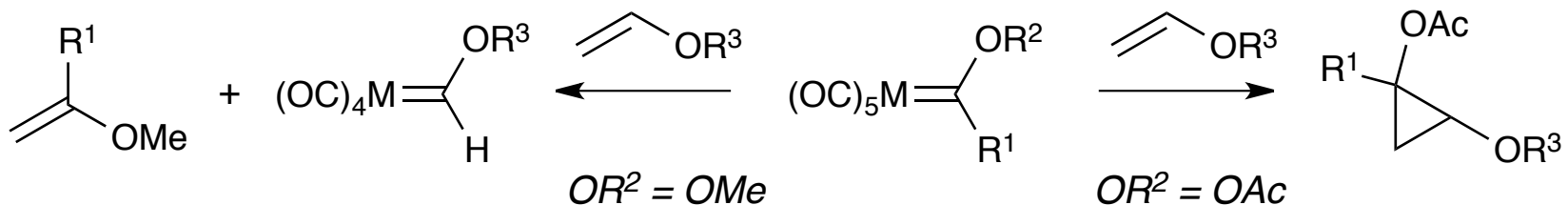
Fischer carbenes will react with electrophilic olefins to form cyclopropanes. The yields can vary, but generally work well.



Reaction is suppressed by CO pressure. This points to formation of a metallocyclobutane intermediate.

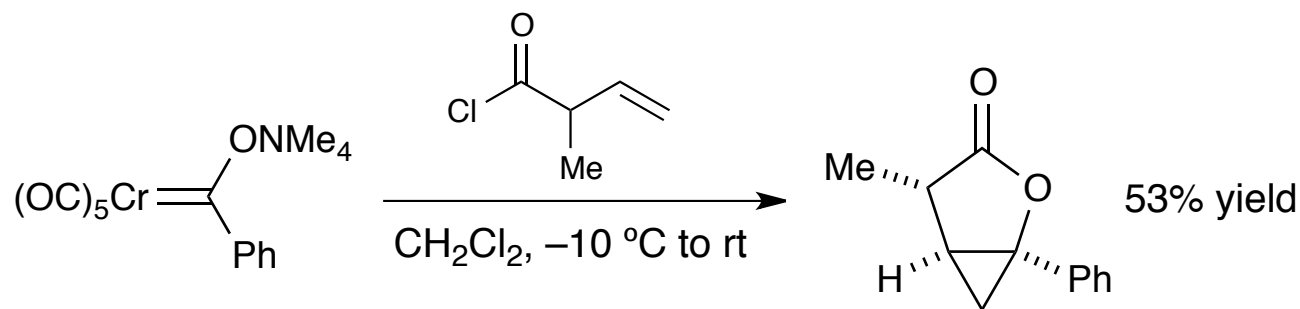
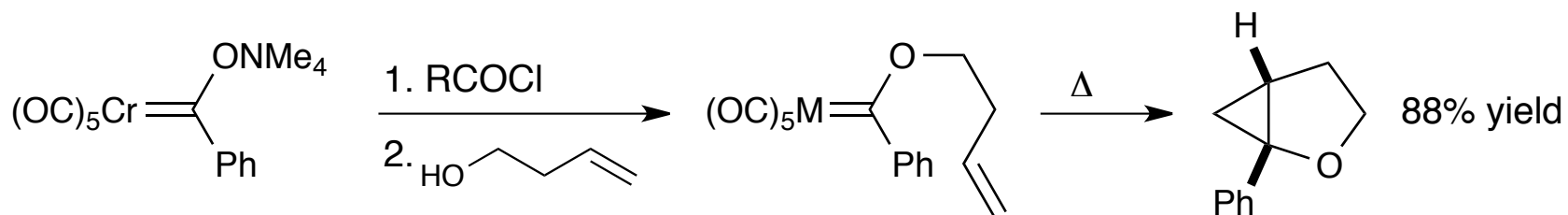


In order to cyclopropanate electron-rich olefins, acyloxycarbenes must be used. Likely involves a different (polar) mechanism.

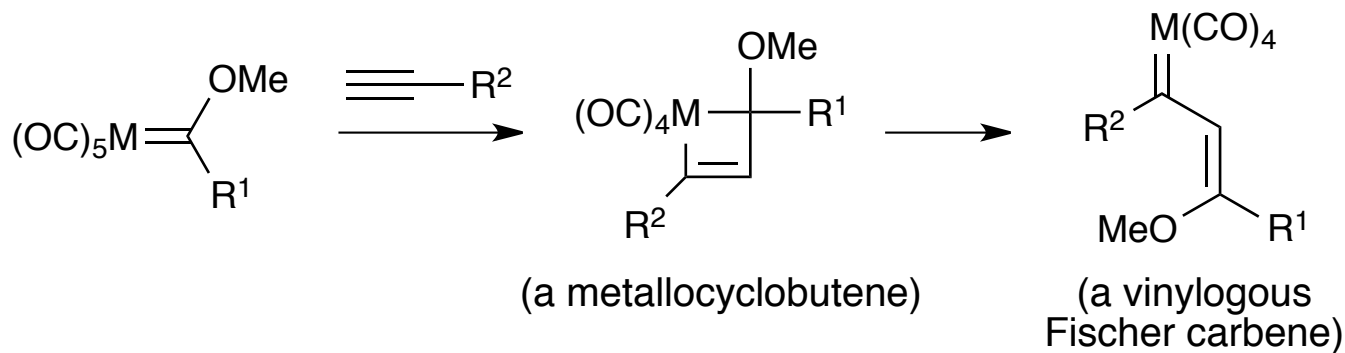


Cyclopropanation

Neutral alkenes are usually poor substrates, but can react in an intramolecular sense. More complex alcohols can be introduced using acyloxycarbenes (triflates would be difficult to handle/prepare).

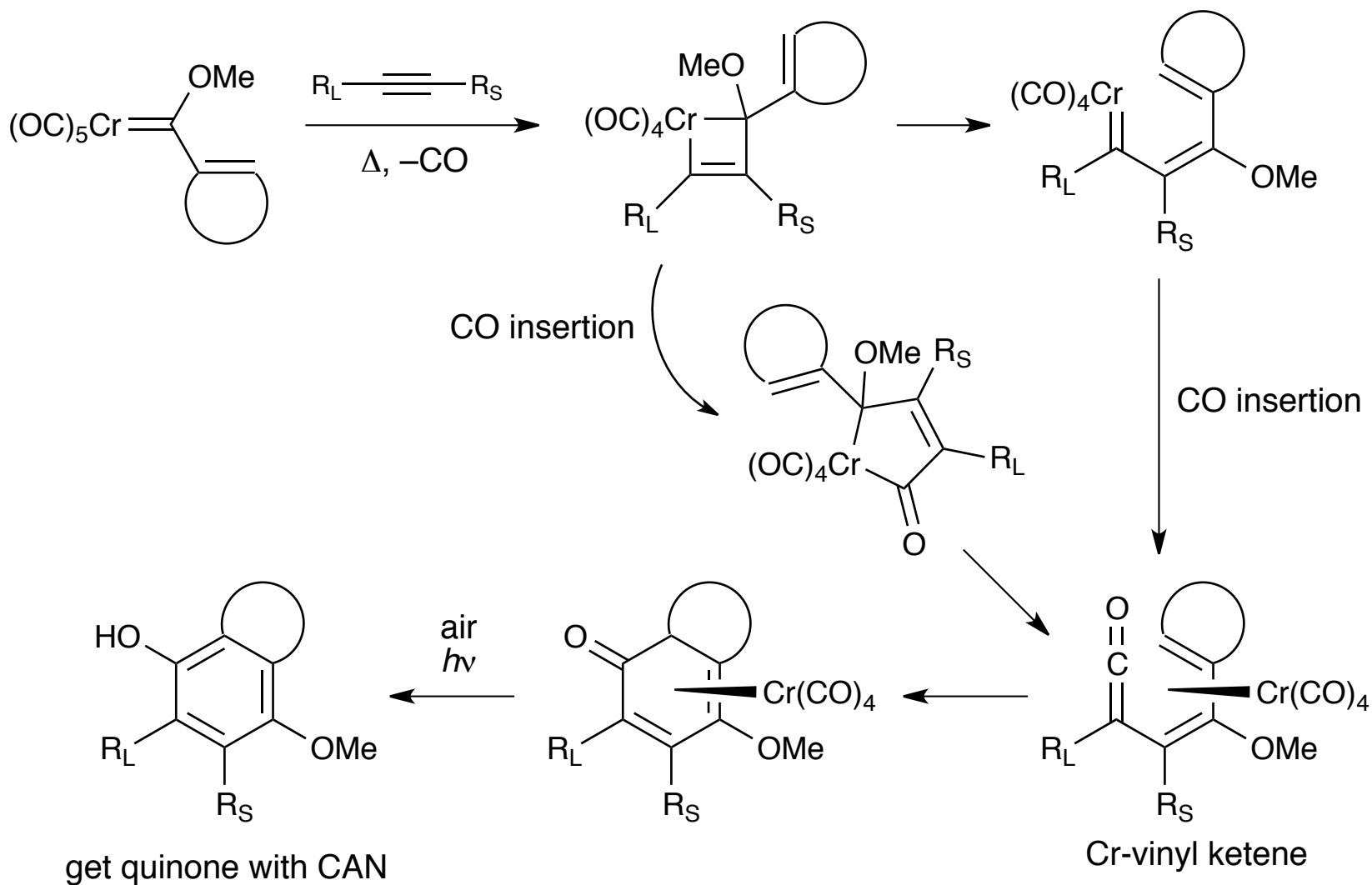


Reactions with alkynes are more facile than with alkenes, but gives an α,β -unsaturated carbene. This can go on and do other chemistry.



Dötz Reaction

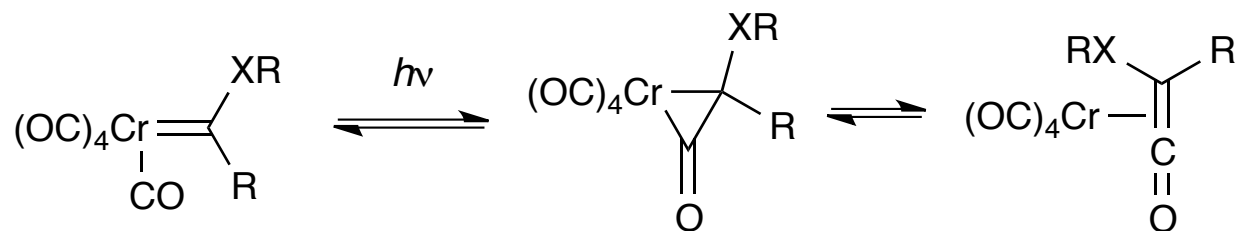
Reaction of alkenyl and aryl alkoxy-carbenes with alkynes produces highly substituted benzene rings or quinones, depending on work-up conditions.



The intermediates in this process can be intercepted by other functional groups before the final ring closure, leading to cascade processes and complex products.

Cr-Bound Ketenes

The formation of Cr-bound ketenes can be used to explain a number of synthetic transformations. The ease of formation appears to be dependent on the substitution around the carbene and can be promoted by photochemical means (in the visible). The process of inserting CO is quite reversible and, unless trapped, will deinsert CO and return to the carbene.



The ketene is generated in low concentrations and is metal-bound. This prevents many of the side reactions commonly encountered with ketenes. The reactivity pattern still mimics that of normal ketenes.

