Electronegativity: Cr(1.66); Mo(2.16); W (2.36)
Note: The Pauling electronegativity *increases* down the row!

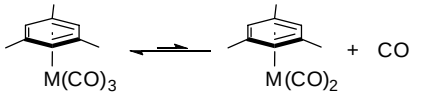
These elements are most commonly found in 0 oxidation state.

Most common oxidation states.

Cr: 0 >> +3, >+2
Mo: lots of common oxidation states
W: 0 >> others

ca. 80% of the stable compounds of these elements are 18 e-

remember:



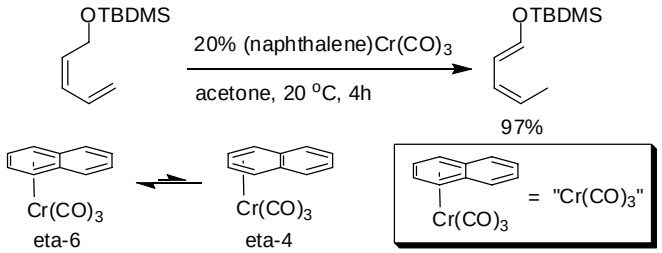
M	BDE (kcal/mol)
Cr	46
Mo	67
W	80

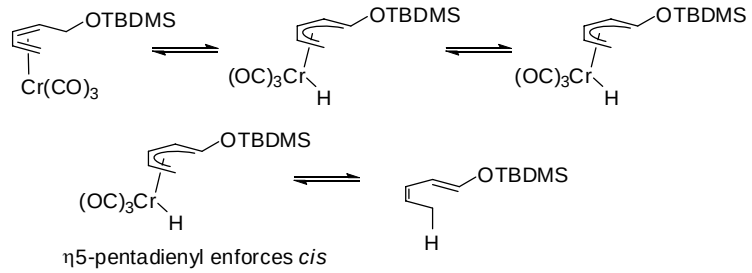
To make a catalytically active species from an 18 e- complex can require the input of significant energy.

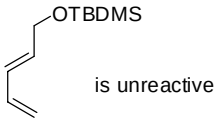
Chromium:

Analogs of Jones oxidation that are catalytic in chromium are relatively common. See Muzart, *Chem. Rev.* **1992** 113.

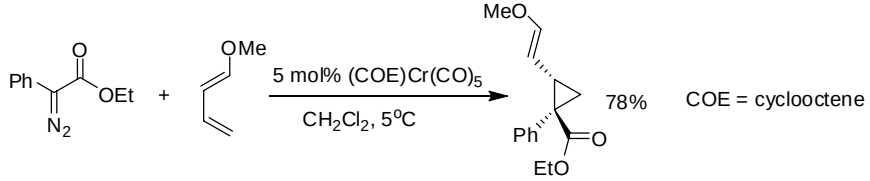
Olefin isomerization: Sodeoka, M.; Shibasaki, M. *JACS* **1990** 4906.:



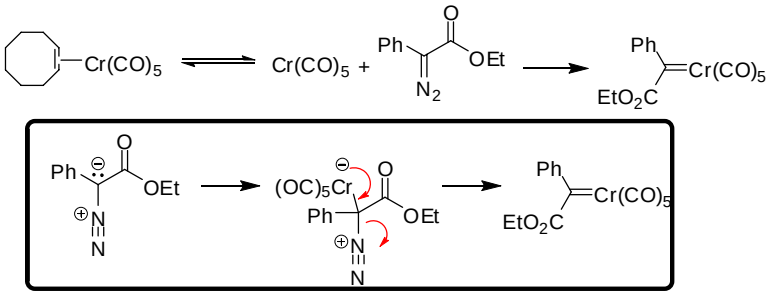




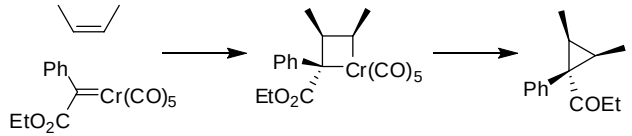
Cyclopropanation: Dotz, *Eur. J. Org. Chem.* **2004**, 1049.



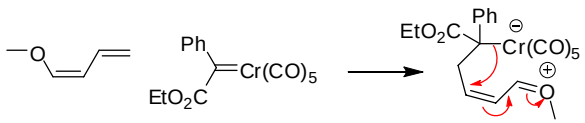
Formation of carbenes from diazocompounds:



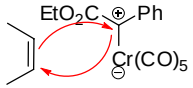
Cyclopropane formation from a metallacyclobutane?: Casey, *JACS* **1976**, 608.



With enol ethers, a zwitterionic mechanism is possible. Wulff, W. D. *JACS* **1988**, 2653.

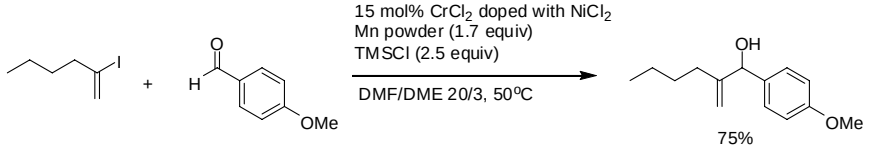


In analogy to other cyclopropanations with diazocompounds, a concerted, asynchronous cyclopropanation may be possible.

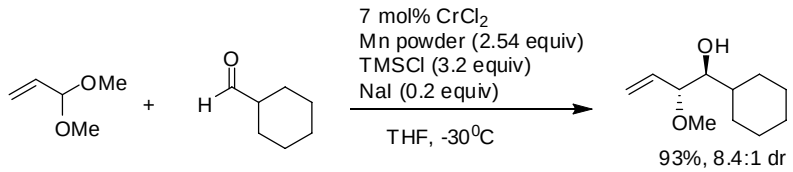


Nozaki-Hiyama-Kishi Reaction: Highly chemoselective coupling of halocarbons with aldehydes. To be described in better detail by Tim Ribelin.

Chromium-catalyzed variant see: Furstner, A. *JACS* **1996** 12349.



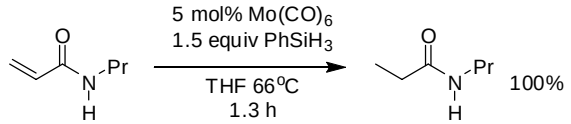
Similarly coupling of acetals is possible: Boeckman, R. K. *JOC* **1998** 3524.



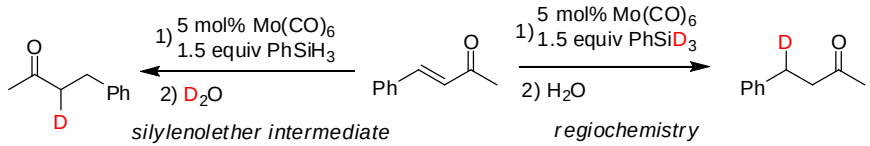
Molybdenum catalysis:

Hydrosilylation and Hydrostannylation:

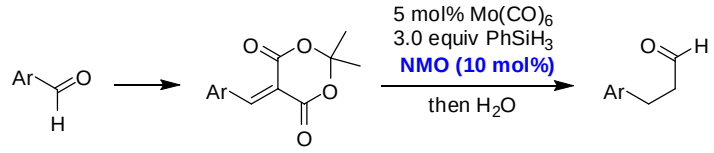
Conjugate reduction. Keinen, E. *JOC* **1987** 2576.



Works well for unsaturated amides, esters, ketones, and nitriles

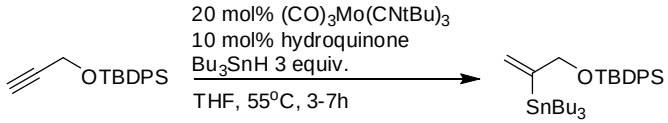


Tandem hydrosilylations: Frost, C. G. *OL* **2007** 4259.

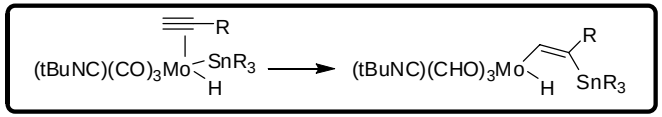


Note: NMO will free a coordination site by oxidizing a CO to CO_2.

Markovnikov Hydrostannylation: Kazmaier, U. *OL* **1999** 1017.; *JOC* **2004** 468.

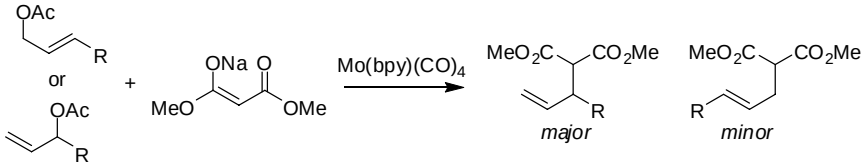


Proposes that stannylmetalation is faster than hydrometalation

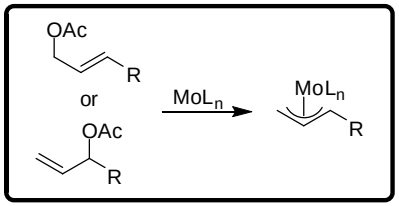


Allylic Alkylation: Trost *JACS* **1982** 5543; **1987** 1469.

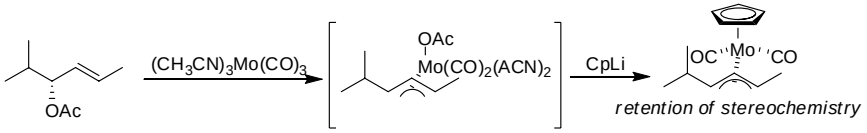
Molybdenum(0) catalysts provide the branched alkylation products selectively (generally >90%).



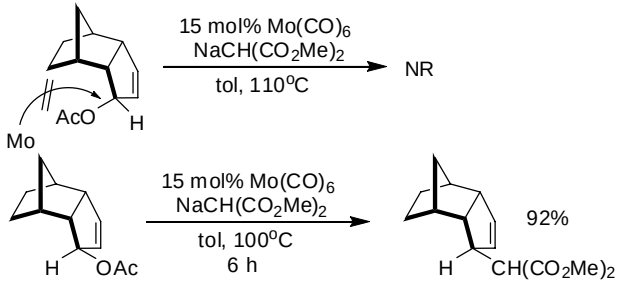
The fact that branched and linear reactants both give branched product (regioselective not regiospecific) suggest π-allyl molybdenum intermediates.



Oxidative addition proceeds with retention! Faller, J. W. *Orgmet* **1988** 1670.

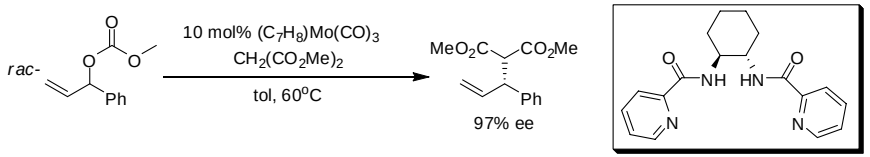


Catalytic alkylation goes by retention-retention mechanism. Kocovsky, P. *JACS* **1995** 6130.

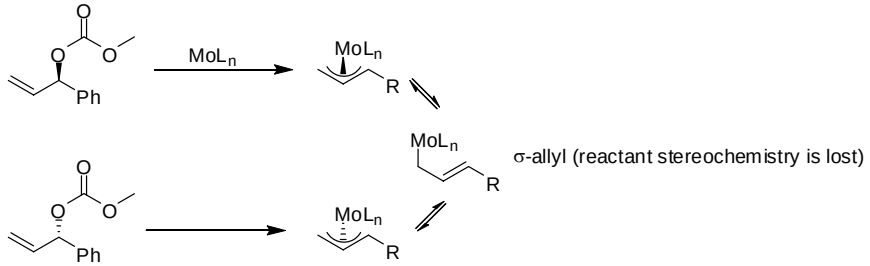


Note: This is in contrast to Pd, Rh, and Ir-catalyzed allylic alkylations which proceed by inversion-inversion mechanisms.

Asymmetric allylic alkylation.

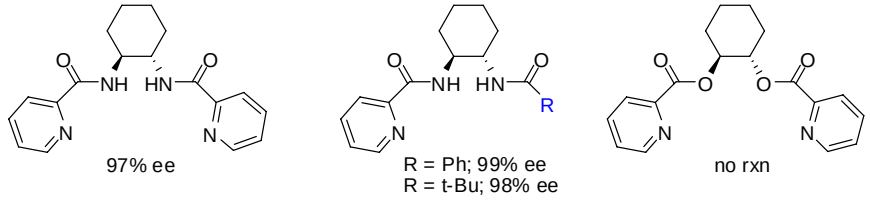


How does racemic starting material give optically active product in a substitution? **π–σ–π isomerization/racemization**



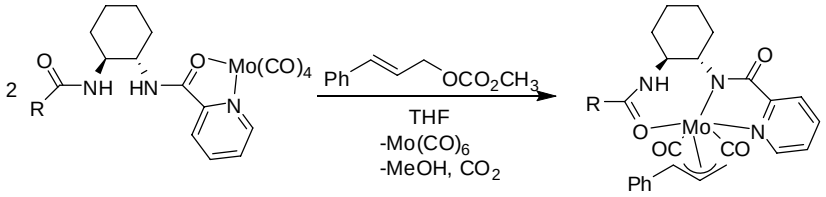
For an elegant analysis that indicates a retention-retention mechanism in asymmetric allylic alkylation see: Llyod-Jones, G. C. *PNAS* **2004** 5379.

Ligand effects: Trost, *ACIEE* **2002** 1929.

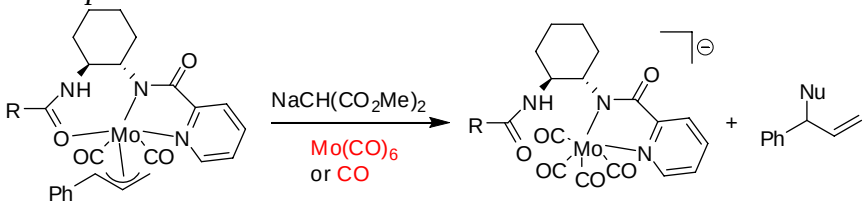


Only one pyridine coordinates; Amide N-H is important

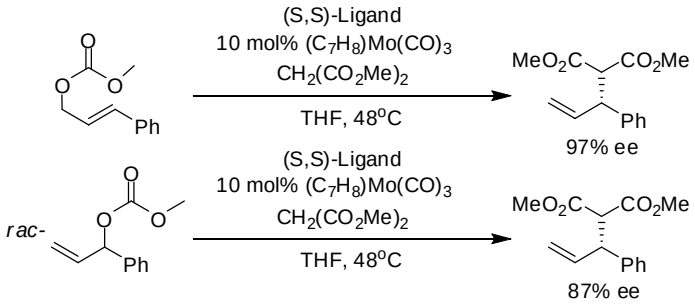
Catalyst Activation: Krska, S. W. *JACS* **2002** 12656; *Pure Appl Chem*. **2004** 625.



Note: You have to lose CO to form active catalyst, but need to add CO for nucleophilic attack. At least one *CO coordinates prior to nucleophilic attack.*



Memory effect. Hughes, D. L. *JOC* **2002** 2762.



Both proceed through the same π-allyl intermediate, so how can they give different ee's?? In the lower case, the product might "remember" the chirality (racemic) of the starting compound.

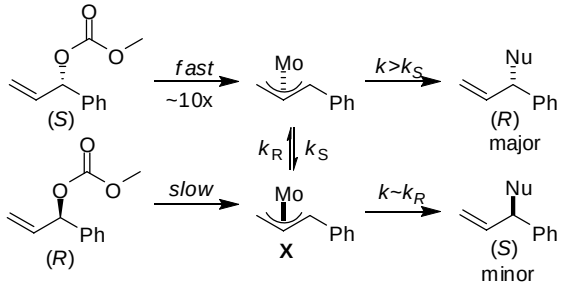
Testing memory (in THF solvent).

substrate config	ligand config	%ee
rac	(S,S)	87(R)
R	(S,S)	70(R)
R	(R,R)	99(S)

Note: The CIP designator of the product was missassigned in the paper.

Note: The R substrate is "matched" with the *R,R* catalyst.
Note: Inversion is faster than alkylation, but if inversion of the π-allyl through π–σ–π was *much* faster than alkylation, then there would be no memory effect.

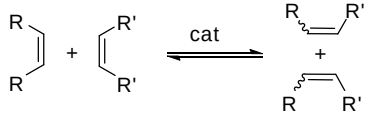
Below is the analysis for the (*S,S*)-Ligand



The fast reacting enantiomer can form the favored product without the need to epimerize the π-allyl.

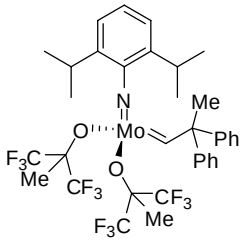
The slow reacting enantiomer (*R*) forms **X**, which has to epimerize to form the favored product. If nucleophilic attack of π-allyl **X** is kinetically competitive with epimerization, then the ee will be reduced from the maximum.

Olefin Metathesis: Excellent review of Mo-cat metathesis see: Schrock, R. R.; Hoveyda A. H. *ACIEE* **2003** 4592.



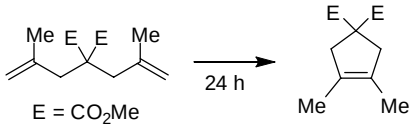
Early system of $WCl_6/EtAlCl_2/EtOH$ produced ill-defined "tungsten oxo" complexes that catalyzed metathesis.

Schrock's catalyst design: A prime example of modular catalyst design.



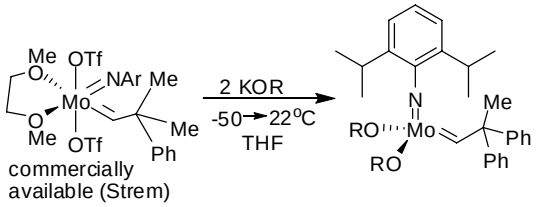
π-bonding spectator ligand
hard, electron deficient, alkoxide ligands
sterically encumbered (12 e-) metal

Advantages: Highly reactive (especially for sterically hindered internal olefins). Tolerant of thioethers and phosphanes.



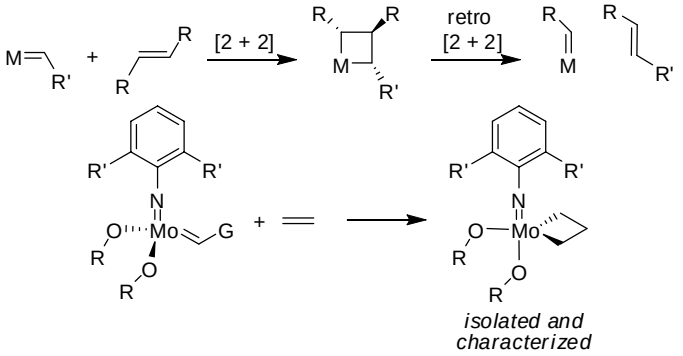
Schrock cat.	93%
Grubbs I	0%
Grubbs II	31%

Easily modified with chiral alkoxides.

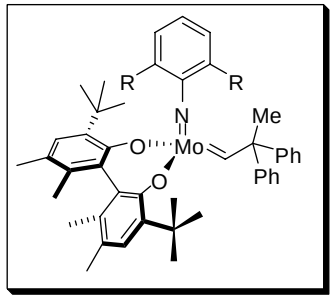


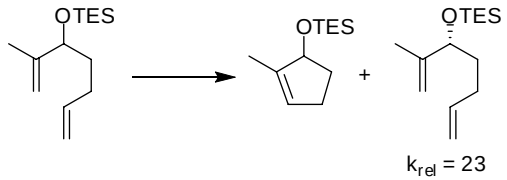
Disadvantages: Air sensitive. Generally not tolerant of protic functional groups, aldehydes, ketones, or amines.

Mechanism – standard Chauvin mechanism



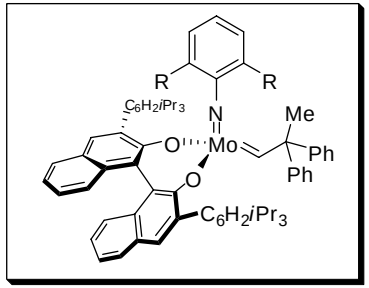
Kinetic resolution via RCM

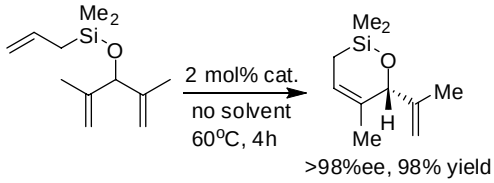




Desymmetrization:

Note: A big advantage of modularity is the ability to modify the catalyst to achieve high ee's.

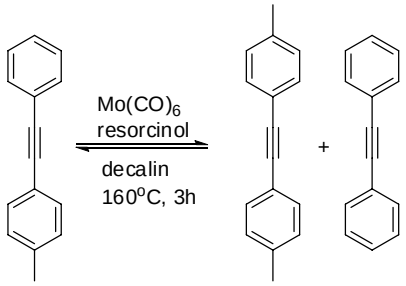




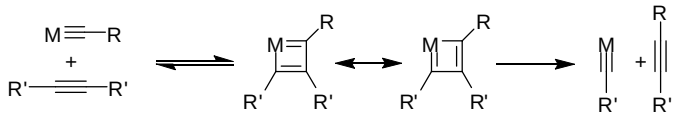
>98%ee, 98% yield

Alkyne Metathesis: Reviews - Moore, J. S. *Adv. Synth. Catal.* **2007** 93.; Furtstner, A. *Chem. Comm.* **2005**, 2307.

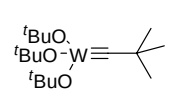
Initial observation:



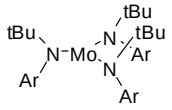
Metal carbyne catalysts. Proposed by Katz (*JACS* **1975**, 1592). Experimentally proved by Schrock (*JACS* **1981** 3932). Mechanism similar to Chauvin mechanism for olefin metathesis.



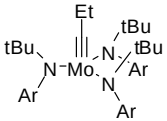
Popular catalysts:



Schrock
JACS 1981 3932



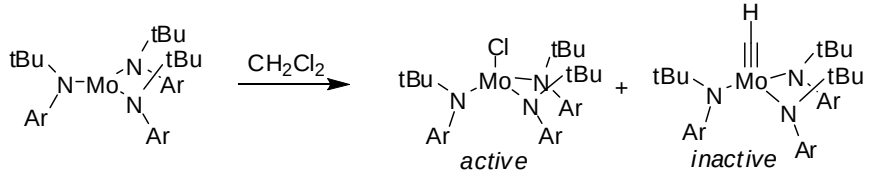
+ CH_2Cl_2
Ar = 3,5-dimethyl
Furstner
JACS 1999 9453



+ p-nitrophenol
Moore
JACS 2004 329

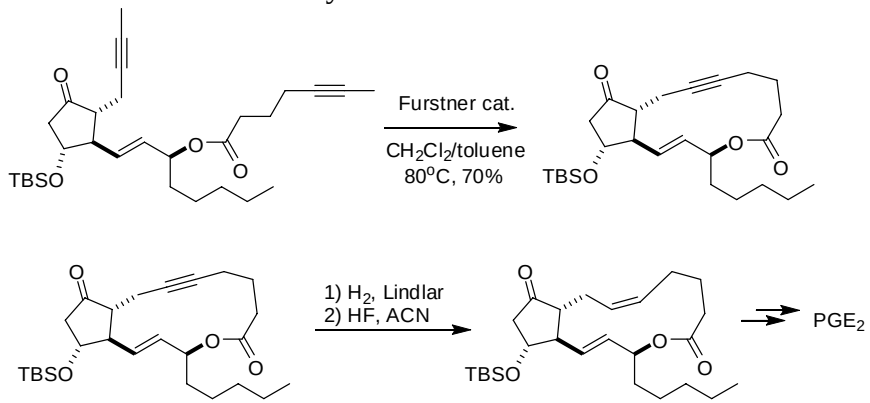
$Mo(CO)_6$
2-fluorophenol
Grela
JOC 2004 7748

The sensitivity of Schrock's catalyst to various functional groups (amines, thioethers, and polyethers) led Furstner to investigate molybdenum amide complexes. These complexes are inactive unless treated with CH_2Cl_2.

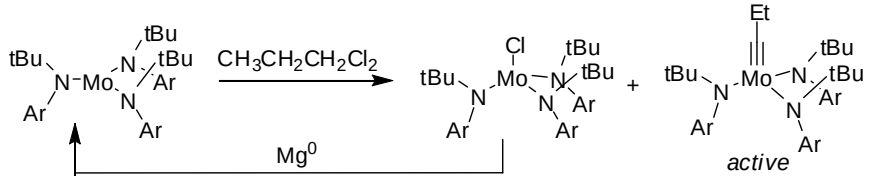


Note: The alkylidyne complex is inactive (terminal alkylidynes are not productive catalysts)

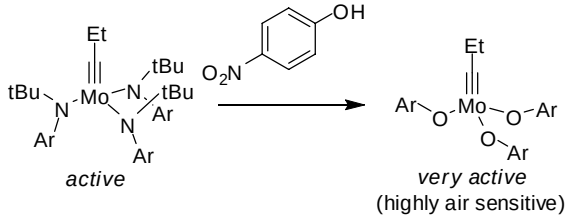
RCAM-Lindlar: Macrocycles with Z-olefins.



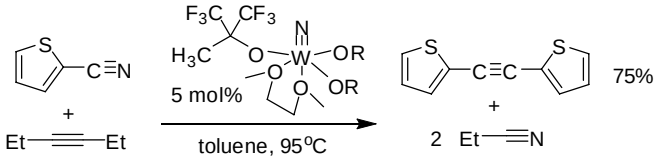
Moore: Active *room temperature* catalyst by reductive recycle.



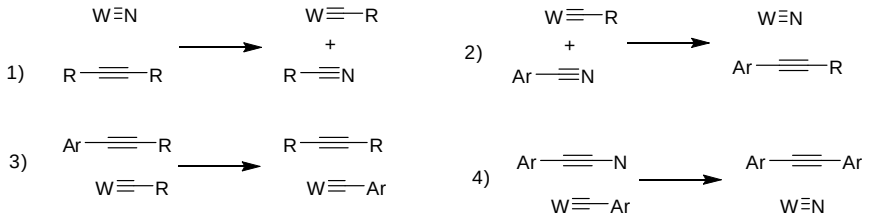
Treament with *p*-nitrophenol generates a very active catalyst.



Alkyne-Nitrile Metathesis: Marc Johnson *JACS* **2007** 3800.

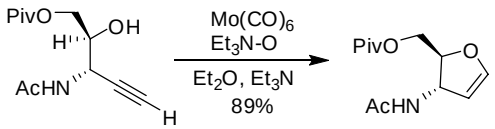


A lot has to happen to get to the diaryl alkyne.



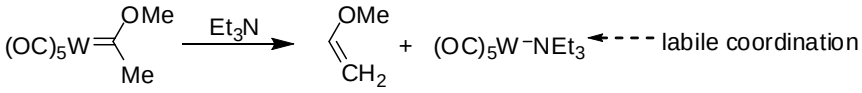
Activation of alkynes with Molybdenum and Tungsten.

Molybdenum is good for 5-membered: McDonald, F. *JACS* **1996** 6648.

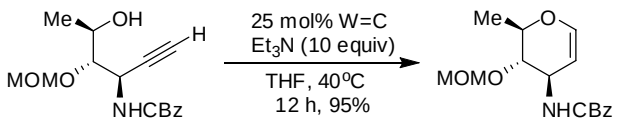


Tungsten is better for 6- and 7-membered. McDonald, F. *JACS* **2000**, 4304; *OL* **2004** 3877.

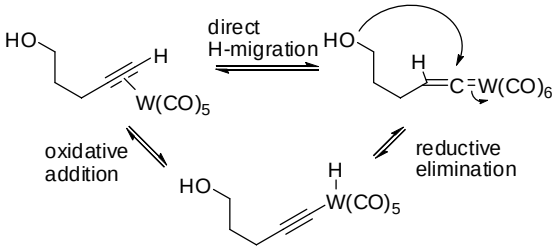
Stable carbenes as precursors to unsaturated carbonyl compounds. McDonald, F. *Org. Lett.* **2007**, 1737.



Endocyclization

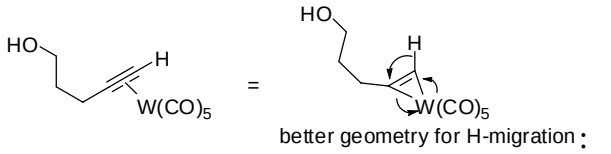


Vinylidene intermediates are key.

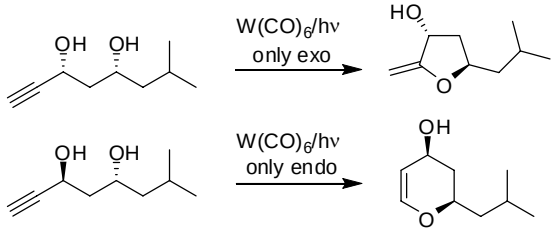


Note: This mechanism requires a terminal alkyne.
Helv. Chim. Acta. **1985** 1461 (direct) *ACIEE* **1983** 414 (stepwise) - calculations support direct hydride migration in this case Morokuma, K. *JACS* **2002**, 4149.

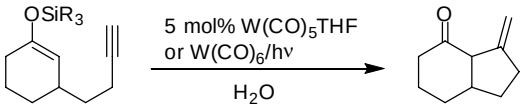
Remember back-bonding is very important

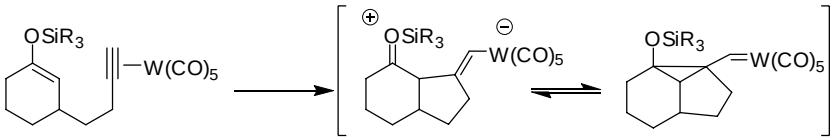


Endo:exo selectivities in cyclizations see: Wipf, P. *JOC* **2003** 8798.



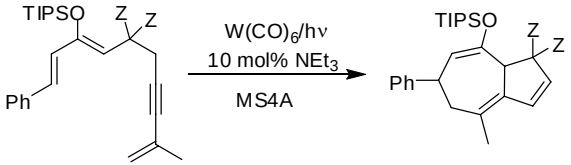
Electrophilic activation of alkynes with tungsten. E.g. Iwasawa, N. *JACS* **2006** 16500.



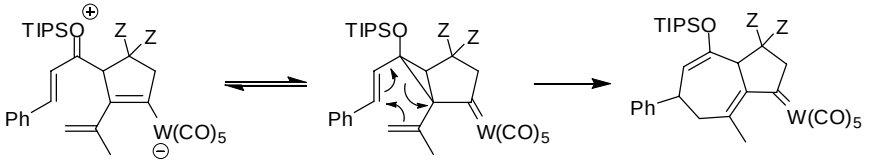


Note: 5-exo is relatively rare for W-catalyzed additions to alkynes.

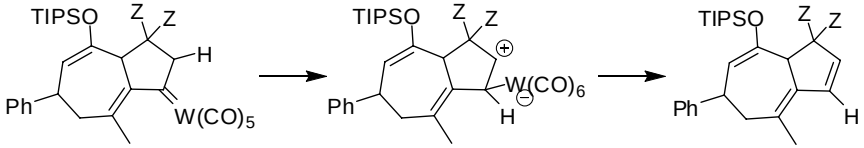
Cascade cyclizations:



C-C bond formation



Demetalation of carbenes via 1,2-hydride shift.



Activation of allenes: formal Cope rearrangement Iwasawa, N. *OL* **2005** 1445.