

Electronegativity: Mn(1.55); Tc(1.9); Re (1.9)

*Note* – technetium does not occur terrestrially in nature and has no stable isotopes.

Most common oxidation states.

Mn: +2 >> +1, +3 > +4, +6, +7

Re: +4 > +6 > +2, +7

ca. 90% of the stable crystalline compounds of these elements are 18 e-

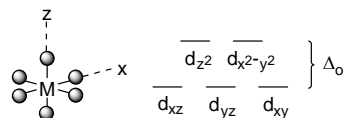
Approximate bond strengths

(OC)<sub>5</sub>Mn-H 59 kcal/mol

(OC)<sub>5</sub>Mn-CH<sub>3</sub> 45 kcal/mol

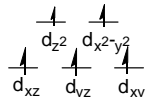
(OC)<sub>5</sub>Re-CH<sub>3</sub> 53 kcal/mol

Octahedral ligand field splitting



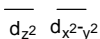
$\Delta_o$  increases going down group  
 $\Delta_o$  increases with oxidation  
 $\Delta_o$  increases with the spectrochemical series:  
 $I^- < Cl^- < H_2O < H_3N < bipy < R_3P < CO$

For example: Mn(II) is not highly oxidized so it will have a small  $\Delta_o$  with ligands like halides. Thus the splitting of MnCl<sub>2</sub> (in THF) will resemble:

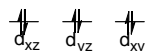


Note: a small  $\Delta_o$  favors "high spin"

However, strong field ligands like CO can favor "low spin" even with low oxidation state metals. i.e. (CO)<sub>5</sub>MnBr



Note: a large  $\Delta_o$  favors "low spin"



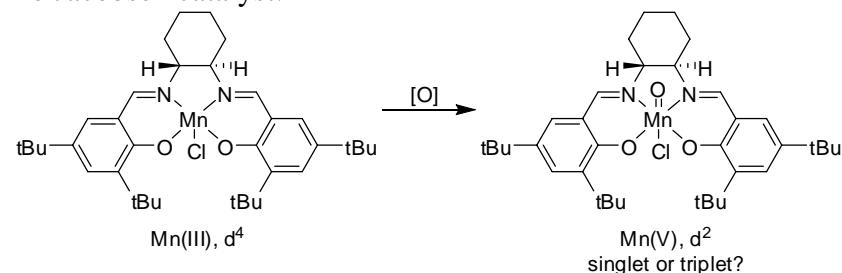
## Manganese:

Manganese-catalyzed oxidations (usually using Mn(III)) are the most widely used reactions.

### Jacobsen-Katsuki epoxidation:

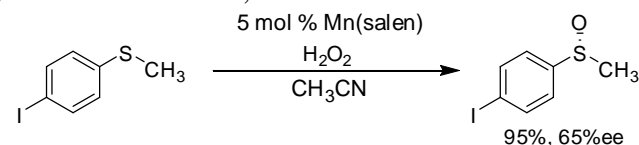
See Chad Schroeders notes: 11/15/07

The Jacobsen catalyst:

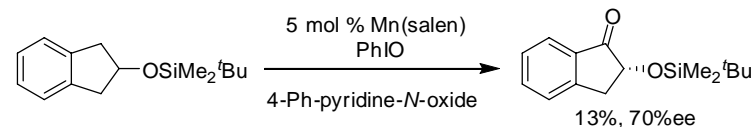


The Mn oxo complex can epoxidize olefins, but it can also oxidize C-H bonds and sulfides.

Sulfide oxidation: Jacobsen, E. N. *TL* **1992** 7111. Higher ee's Katsuki, *Tetrahedron* **1994**, 9609.



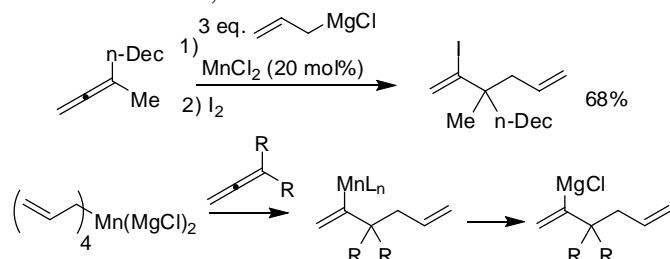
Murahashi, S.-I. *TL* **1998** 7921. (poor turnover) "rebound mechanism?"



Desymmetrization of disilylethers. Murahashi *Synlett* **2004** 1739.

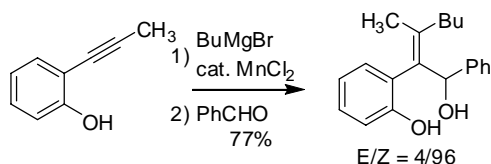
**Carbomagnesiation** *Catalysis Surveys from Asia* **2003**, p 39 (yes we have this electronically).

Allenes *OL* **2003** 4623.;



Note: Mn "ate" complex is the active species

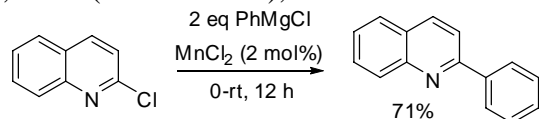
Most examples are with *alkynes*. Aryl, alkyl, allyl, and silyl Grignards all work.



**Manganese-catalyzed cross-coupling reactions.**

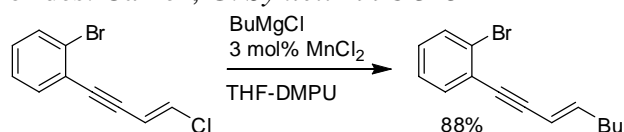
[Mn(II)-Mn(IV) cycles?]

*Synlett* **2007**, 247. (Kumada-like),



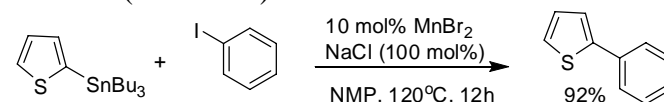
Must have *o*, or *p*-EWG, but alkyl and aryl Grignards work fine. *Synthesis* **1999** 2138.

Vinyl-chlorides: Cahiez, G. *Synlett* **1998** 325



Note: 49% yield without Urea cosolvent.

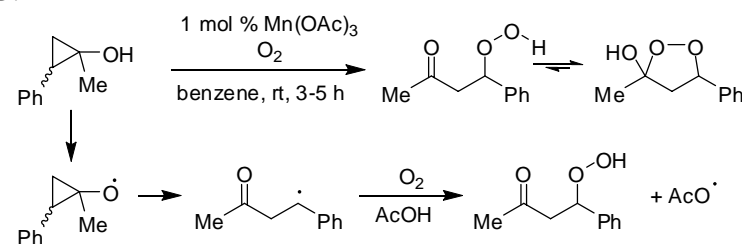
*JOC* **1997** 4208 (Stille-like)



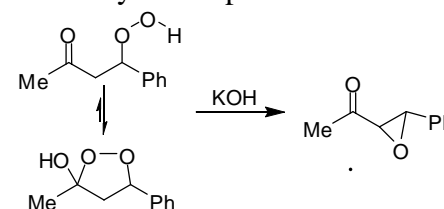
Cross-coupling of stannanes with iodonium salts *TL* **1998** 2131.

**Mn-catalyzed radical chemistry.** Mn(III) is an excellent radical initiator via H-atom abstraction. However most reactions are stoichiometric in Mn.

Opening of cyclopropanols: Kulinkovich, O. G. *Synthesis* **2001**, 1453.

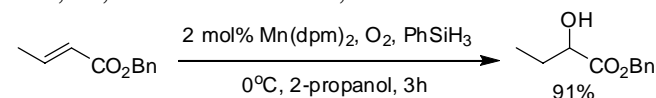


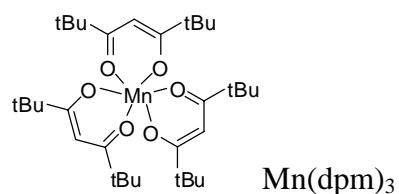
Product peroxides readily form epoxides.



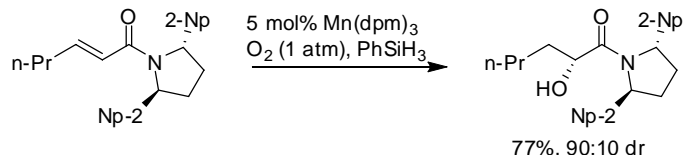
**Anti-Markovnikov Hydration of olefins.**

Mukaiyama, T.; *Chem. Lett.* **1990**, 1869.

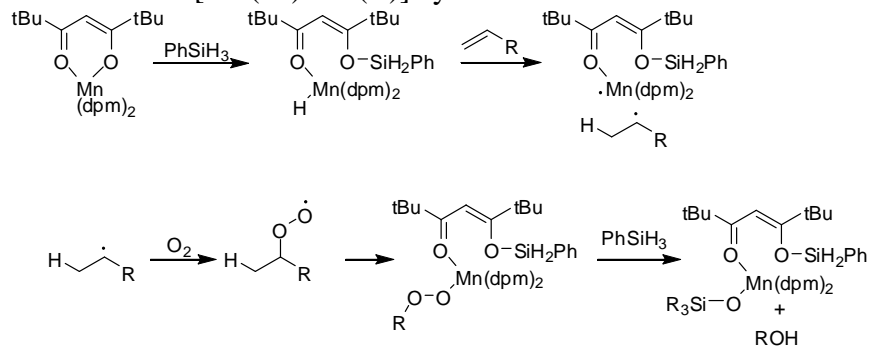




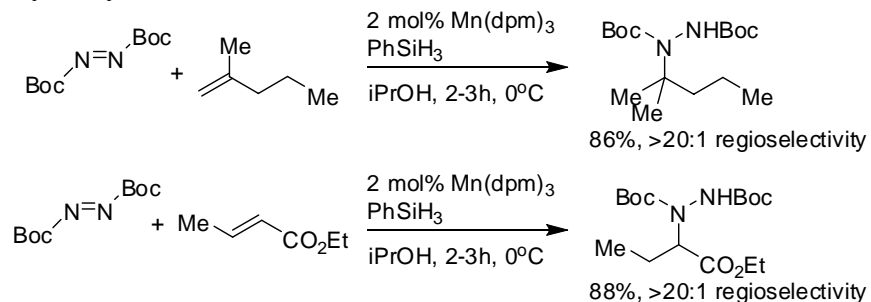
Diastereoselective: Yamada, T. *Chem. Lett* **2004** 1304.



Mechanism?? [Mn(III)-Mn(II)] cycle

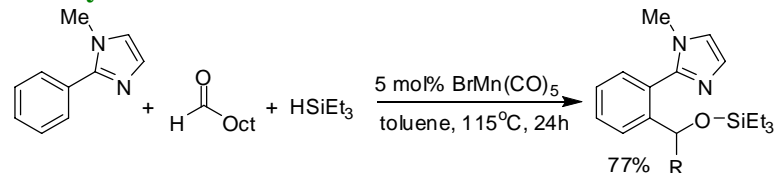


Hydrohydrazination: Carreira, E. *ACIE* **2004**, 4099.

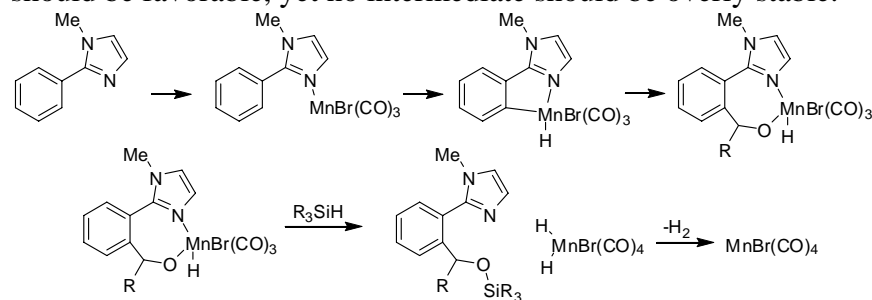


*Note:* Works well for the amination of unactivated alkenes.

**Mn-catalyzed C-H insertion.** *ACIEE* **2007** 6638.

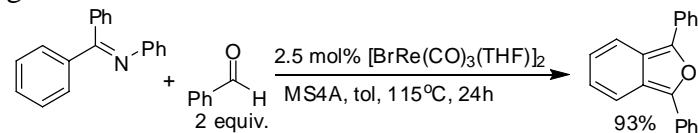


*Note:* Mn(I) precursor allows for favorable oxidative addition should be favorable, yet no intermediate should be overly stable.

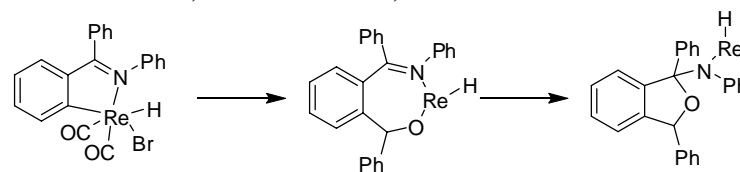


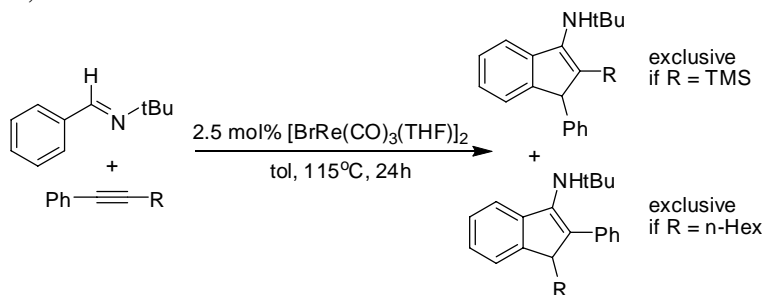
**Re-catalyzed C-H insertions**

Highlight: *ACIE* **2007** 2144.

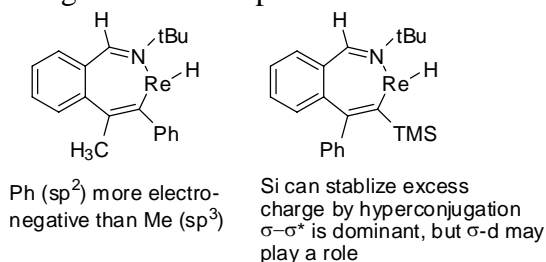
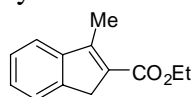
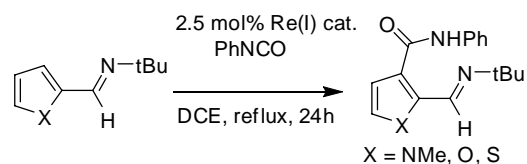
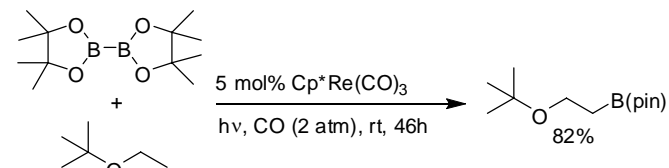


*Note* 1 equiv of aldehyde is necessary to react with the amine that is liberated. Takai, K. *JACS* **2006**, 12376. *Tet* **2007** 8463

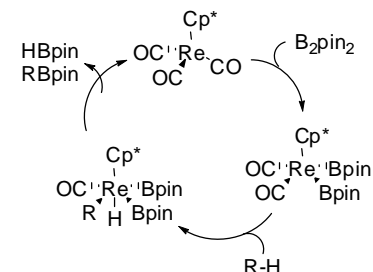
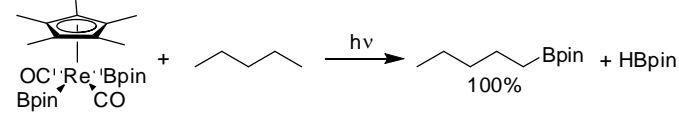
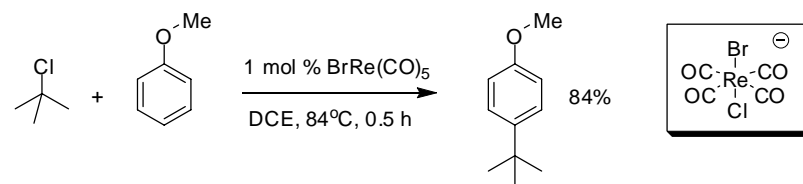


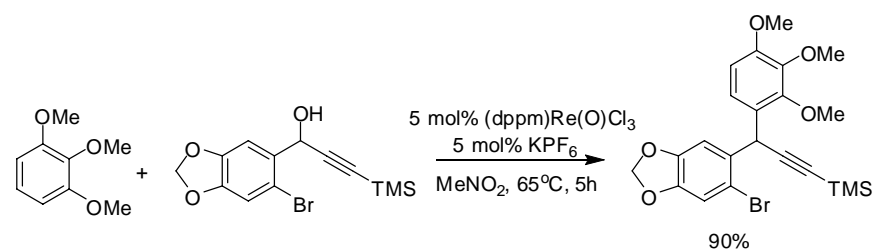
Takai, K. *JACS* **2005** 13498.

Why are these regiochemistries preferred?

Si-stabilization of  $\alpha$ -anions see: *Chem. Eur. J.* **2002**, 2324.Hyperconjugation is more important than backbonding into d-orbitals. *JACS* **1999** 5737.Electron-deficient olefins cyclize similarly: *ACIEE* **2006** 2766.*Chem Lett* **2007** 872.*Note:* There is no cyclization after carborehenation.**C-H activation/Borylation** Hartwig, J. F. *JACS* **1995** 11357; *ACIE* **1999** 3391; *Orgmet* **1999** 3383.*Note:* can activate simple hydrocarbons selectively at unhindered methyl positions.

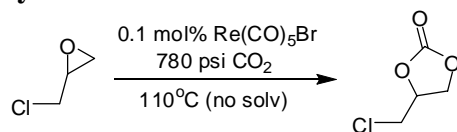
Mechanism:

*Note:* an oxidative addition/reductive elimination mechanism is shown, but products could be formed by  $\sigma$ -bond metathesis/reductive elimination.**Re-catalyzed Friedel-Crafts Alkylation:** *BCS Jpn.* **2000**, 2779.Propargylation: Toste, F. D. *OL* **2004**, 1325.

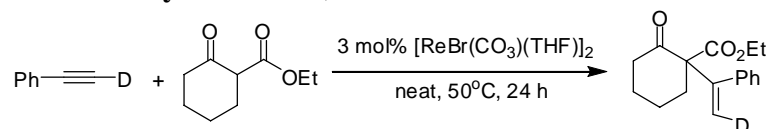


Allylsilane nucleophiles, see: Toste, F. D. *JACS* **2003** 15760.

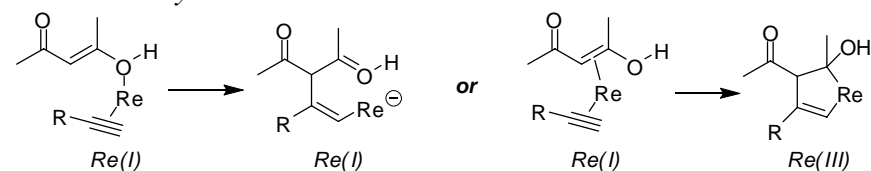
**Epoxide carboxylation.** *JOC* **2005** 381.



**Addition to alkynes:** Takai, *OL* **2005** 4823.

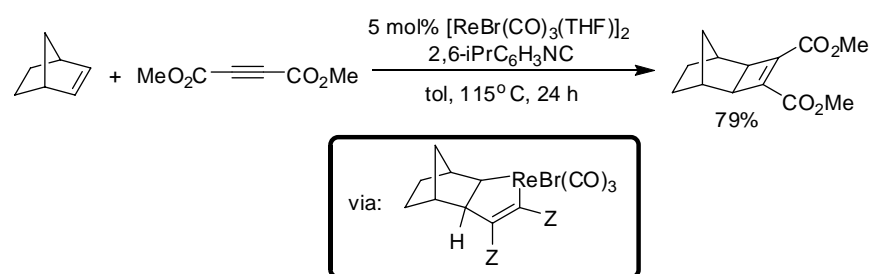


*Note:* alkyl and aryl alkynes give good yields and same regiochem  
Addition is *syn*



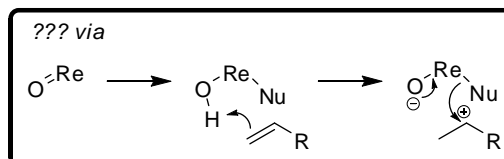
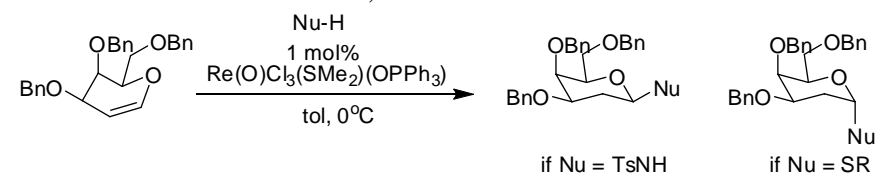
The latter mechanism may be supported by....

**[2+2] Cycloaddition:** *ChemLett* **2007** 1162.



*Note:* normally metallacyclopentenes do not undergo reductive elimination, rather they insert a second alkyne then eliminate the 6-membered ring.

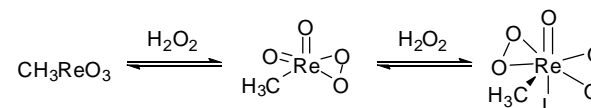
**Additions to olefins.** Toste, F. D. *JACS* **2004** 4510.

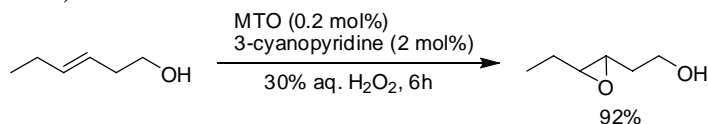
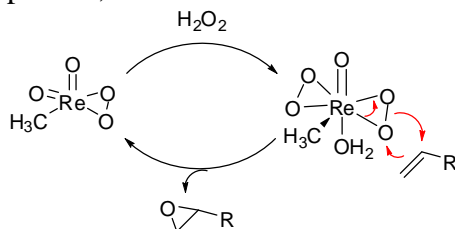
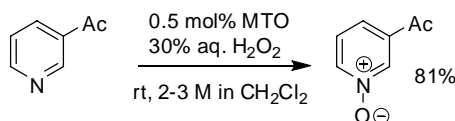
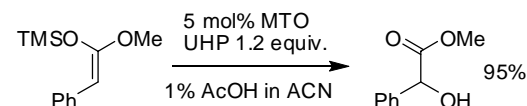
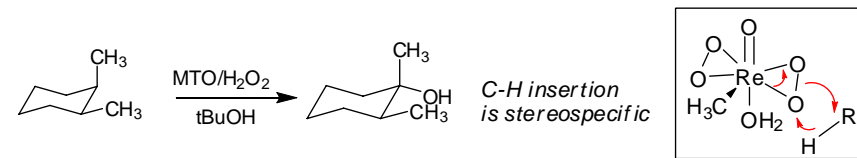
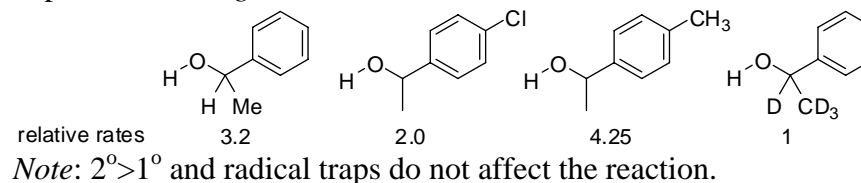


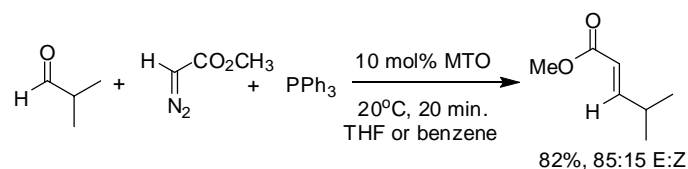
*Note:* This may go via general base catalysis without formation of a Re-Nu bond.

**Methyltrioxorhenium (MTO)-Catalyzed Oxidations** Review of Re oxo chemistry: *ChemRev* **1997** 3197.

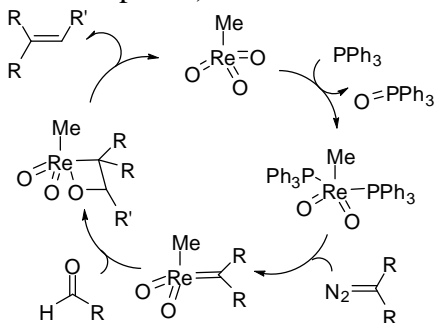
MTO is great at activating hydrogen peroxide and is soluble in nearly all solvents.



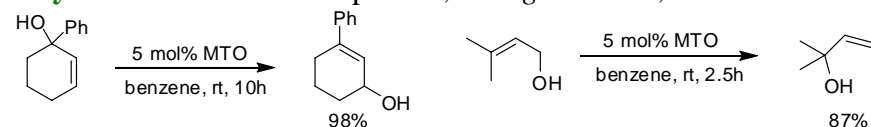
**Good replacement for MCPBA. E.g.****Epoxidation:** review *Synlett* **2004** 1849MTO is very efficient. Epoxidation can be improved by added ligands like 3-cyanopyridine (Espenson *JACS* **1998** 11335; *JOC* **2000** 8651).2-methylpyrazole can provide TON (turn over numbers) of up to 7200. *Org. Biomol. Chem.* **2007** 2109.performing reactions water-free using bis-trimethylsilylperoxide (Sharpless, *JACS* **1997** 11536) can also extend catalyst lifetime [because hydrolysis of the diperoxorehnenium species leads to catalyst deactivation]Mechanism: Espenson, J. *JOC* **1996** 3969.Arenes can be similarly oxidized: *JOC* **1994**, 8281.**Oxidation of amines:** pyridines see Sharpless, K. B. *JOC* **1998** 1740.**Rubottom-type Oxidation:** Espenson, J. *JOC* **2000** 5528.**Baeyer-Villiger:** *TL* **2001** 5401.*Note:* Baeyer-Villiger oxidations are often best with nucleophilic oxidants – here it utilizes a typically electrophilic oxidant.**Alcohol oxidation and C-H insertion (like DMDO):**Alcohol oxidation goes by O-atom insertion/Hydride abstraction. Espenson, J. *Inorg. Chem.* **1998** 6827.MTO readily oxidized phosphines as well. This can be utilized in catalytic olefination of aldehydes with diazoalkanes: Herrmann, W. A. *ACIEE* **1991** 1641.



Perhaps not so useful, but it can be used where Wittig chemistry fails (i.e. malonate nucleophiles)

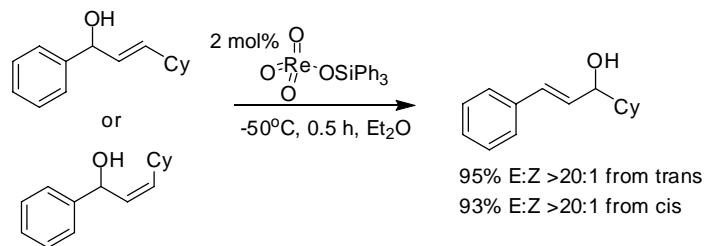


**Allylic isomerization:** Espenson, J. *Orgmet* **1998**, 1835.

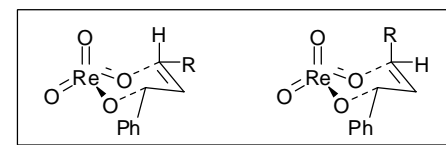


$O_3ReOSiPh_3$  is a superior catalyst – equilibration takes ca. 5 min at 0°C. Osborn, J. A. *ACIE* **1997** 976.

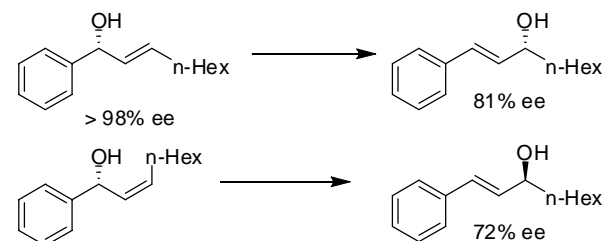
Applied to selective rearrangements: Grubbs, R. H. *JACS* **2005**, 2842.



Aryl group stays equatorial, thus both reactants produce the E isomer.

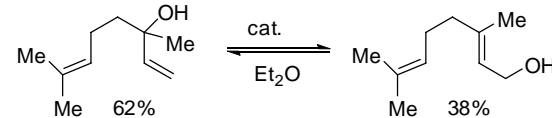


but...

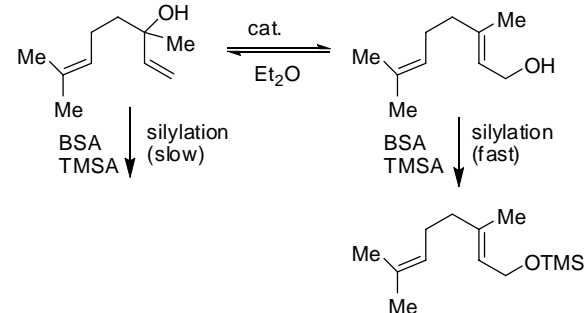


*Note:* There is some loss of stereochemistry, presumably due to ionization to an allylic cation. Near perfect chirality transfer is observed for electron deficient substrates that disfavor ionization.

**Problem:** catalysis only establishes equilibrium



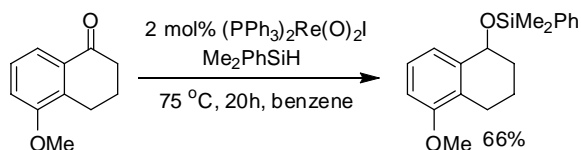
Simple, but clever solution: Grubbs, R. H. *JOC* **2006** 7813.



*Note:* by trapping the 1° alcohol, one can isolate 89% of the isomerized product after hydrolysis.

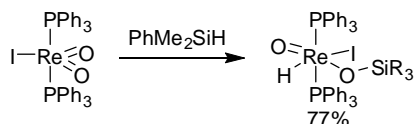
**Hydrosilylation**

Toste, F. D. *JACS* **2003** 4056.



*Note:* can be performed under air, aldehydes provide higher yields.  
*Note also:* This is an unusual case of using an oxidant for reductions.

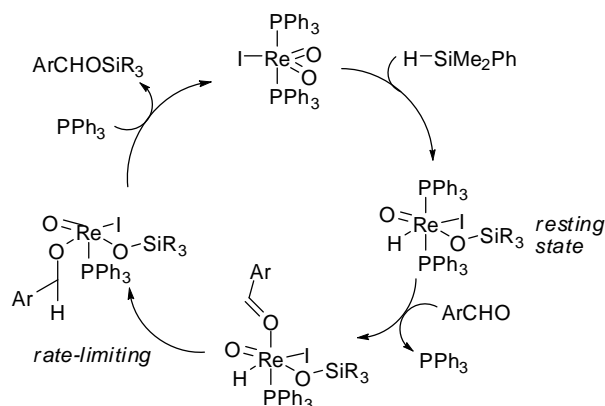
A very elegant mechanistic study of this reaction see: Toste, F. D. *JACS* **2007** ASAP.



*Note:* The formation of silyloxy hydride is irreversible (negative crossover of product with added silane).

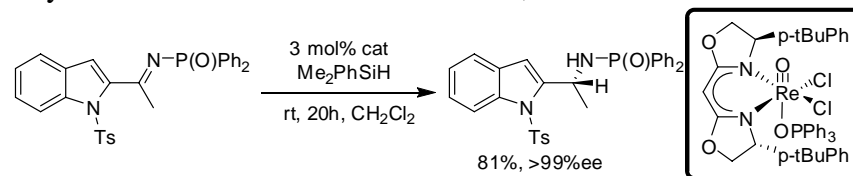
Stoichiometric hydrosilylation with the isolated Re-hydride has a rate law of: (First-order in Re-hydride (**2b**) and aldehyde, inverse first-order in phosphine)

$$\text{rate} = \frac{k_1 k_2 [\mathbf{2b}] [p\text{-anisaldehyde}]}{k_{-1} [\text{PPh}_3] + k_2} = k_{\text{obs}} [\mathbf{2b}]$$

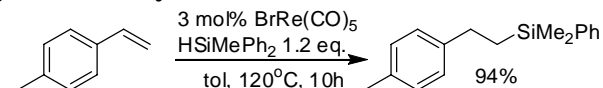


*Note:* The resting state is  $(\text{PPh}_3)_2\text{Re}(\text{O})_2\text{I}$  when  $\text{Ph}_2\text{MeSiH}$  is used.

Asymmetric reduction of imines. Toste, F.D. *JACS* **2005** 14262.



Hydrosilylation of styrenes. *EurJOC* **2006** 5495.



**Techneium-catalyzed reaction?** *Zeitschrift fur Chemie* **1985** 25 150.

