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
- 
  \[(OC)_2\text{Mn-H} \quad 59 \text{ kcal/mol}\]
  \[(OC)_2\text{Mn-CH}_3 \quad 45 \text{ kcal/mol}\]
  \[(OC)_5\text{Re-CH}_3 \quad 53 \text{ kcal/mol}\]

Octahedral ligand field splitting
- \[\Delta_o \text{ increases going down group}\]
- \[\Delta_o \text{ increases with oxidation}\]
- \[\Delta_o \text{ increases with the spectrochemical series: } I^- < Cl^- < H_2O < H_3N < \text{bipy} < R_2P < CO\]

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\(_2\) (in THF) will resemble:
- \[\frac{d_{x^2}}{d_{xz}} \quad \frac{d_{y^2}}{d_{yz}} \quad \frac{d_z}{d_{sy}} \quad \text{Note: a small } \Delta_o \text{ favors "high spin"}\]

However, strong field ligands like CO can favor "low spin" even with low oxidation state metals, i.e. (CO\(_5\))MnBr
- \[\frac{d_{x^2}}{d_{xz}} \quad \frac{d_{y^2}}{d_{yz}} \quad \frac{d_z}{d_{sy}} \quad \text{Note: a large } \Delta_o \text{ favors "low spin"}\]

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


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.;

\[
\text{3 eq. } \overset{\text{n-Dec}}{\text{Me}} \text{MgCl} \quad 1) \text{MnCl}_2 (20 \text{ mol\%}) \\
\overset{\text{R}}{\text{Me}} \quad \overset{\text{I}}{\text{Me}} \text{n-Dec} \\
\text{MnLn}_4 \text{R}_4 \quad \text{MnCl}_2 \\
\text{MnCl} \quad \text{MgCl}
\]

*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),

\[
\text{2 eq. } \text{PhMgCl} \\
\text{MnCl}_2 (2 \text{ mol\%}) \\
\text{0-rt, 12 h}
\]

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.


**Anti-Markovnikov Hydration of olefins.**

Catalysis by Group VII Elements


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


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.

\[
\begin{align*}
\text{Ph} & \xrightarrow{2.5 \text{ mol\% } \text{[BrRe(CO)₃(THF)]}_2, \text{tol, 115}^\circ\text{C, 24h}} \text{R} \\
\text{N} & \quad \text{exclusive if } R = \text{TMS} \\
\text{N} & \quad \text{exclusive if } R = \text{n-Hex}
\end{align*}
\]

Why are these regiochemistries preferred?


\[
\begin{align*}
\text{Me} & \quad \text{Cl} \\
\text{CO}_2\text{Et} & \quad \text{O}
\end{align*}
\]

Note: There is no cyclization after carborhenation.

**C-H activation/Borylation** Hartwig, J. F. *JACS* 1995 11357; *ACIE* 1999 3391; *Orgmet* 1999 3383.

Note: an oxidative addition/reductive elimination mechanism is shown, but products could be formed by σ-bond metathesis/reductive elimination.

**Re-catalyzed Friedel-Crafts Alkylation** *BCS Jpn.* 2000, 2779.

Note: There is no cyclization after carborhenation.

**Propargylation** Toste, F. D. *OL* 2004, 1325.
Catalysis by Group VII Elements

**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*


**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.


MTO is great at activating hydrogen peroxide and is soluble in nearly all solvents.
**Good replacement for MCPBA. E.g.**

**Epoxidation:** review *Synlett* 2004 1849

MTO 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 diperoxorhenium 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):**


**Note:** $2^\circ>1^\circ$ and radical traps do not affect the reaction.

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)


O₃ReOSiPh₃ 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.

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 1º alcohol, one can isolate 89% of the isomerized product after hydrolysis.

Hydrosilylation
Toste, F. D. JACS 2003 4056.
Catalysis by Group VII Elements

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)

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

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

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


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11/15/2007