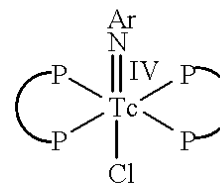
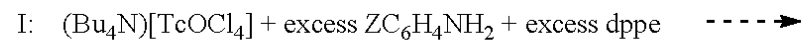
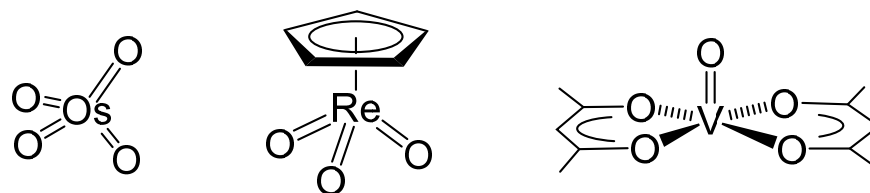


M=heteroatom bonds: terminal **Oxo (M=O)** and **Imido (M=NR)** complexes

- More reactive than bridging oxo or imido species
- Less common than bridging versions
- Commonly act as site of reactivity
- Much more stable in the middle of the d-block



6 Z = CH₃, 60%, violet
7 Z = Br, 64%, maroon
8 Z = Cl, 64%, maroon

Bonding picture

from: Hartwig, 'Organometallic Chemistry'

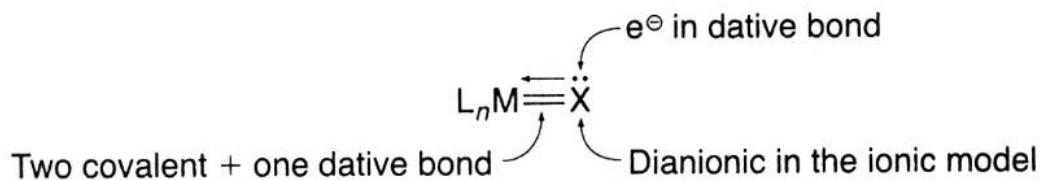


Figure 13.8.

A valence bond description of metal–imido and metal–oxo complexes.

**d⁰, d¹ or d²
electron counts
favoured:**

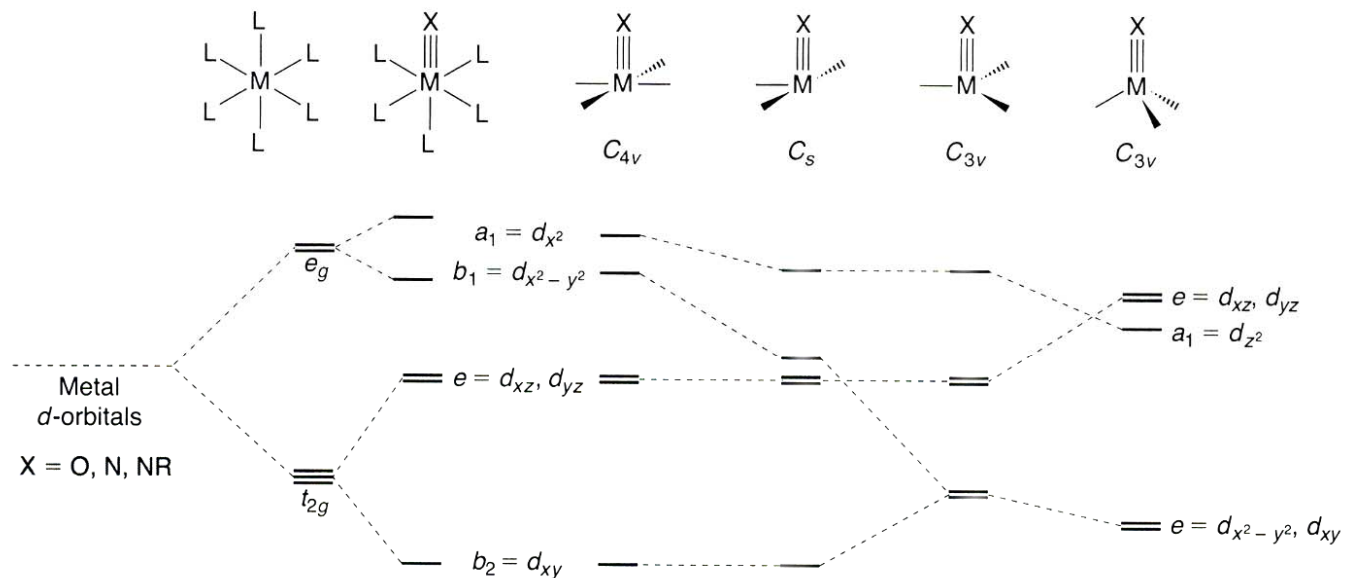
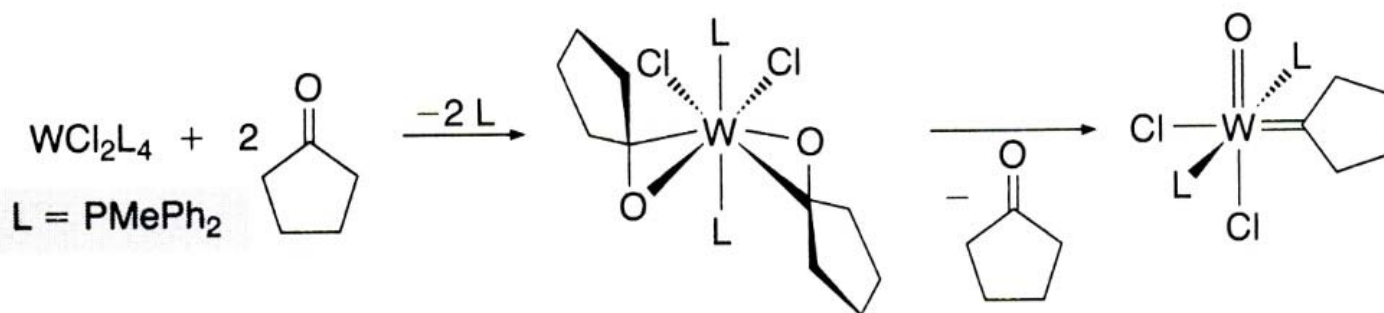
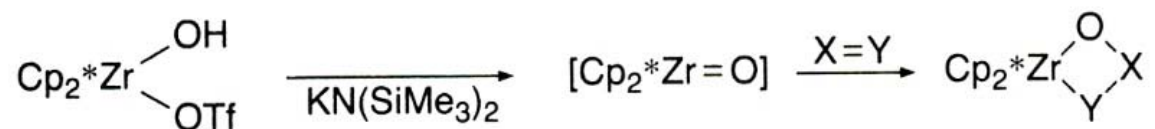
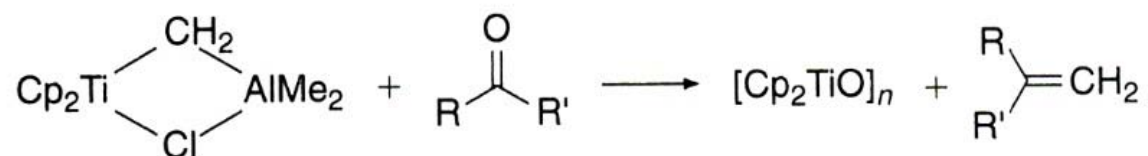


Figure 13.9.

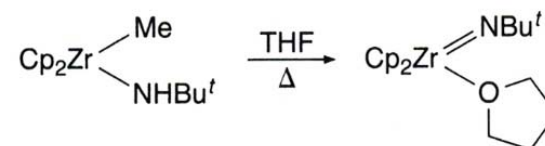
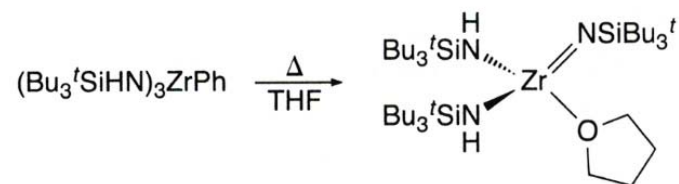
Qualitative molecular orbital diagrams of oxo, nitrido, and linear imido complexes of various geometries. Adapted with permission from Figure 4 of Mayer, J. M., Thorn, D. L., Tulip, T. H. *J. Am. Chem. Soc.* **1985**, *107*, 7454.

Synthesis

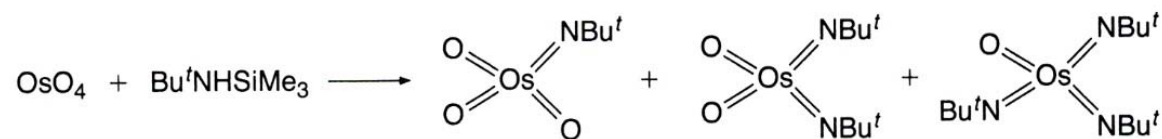
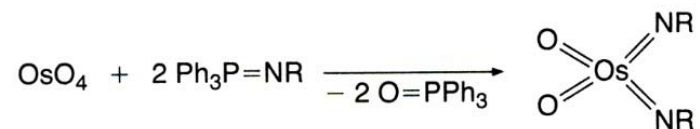
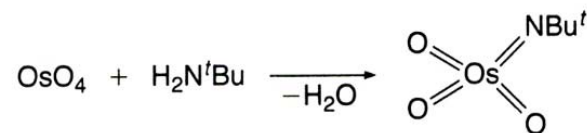
Oxo often by oxidation, but a few other routes exist:



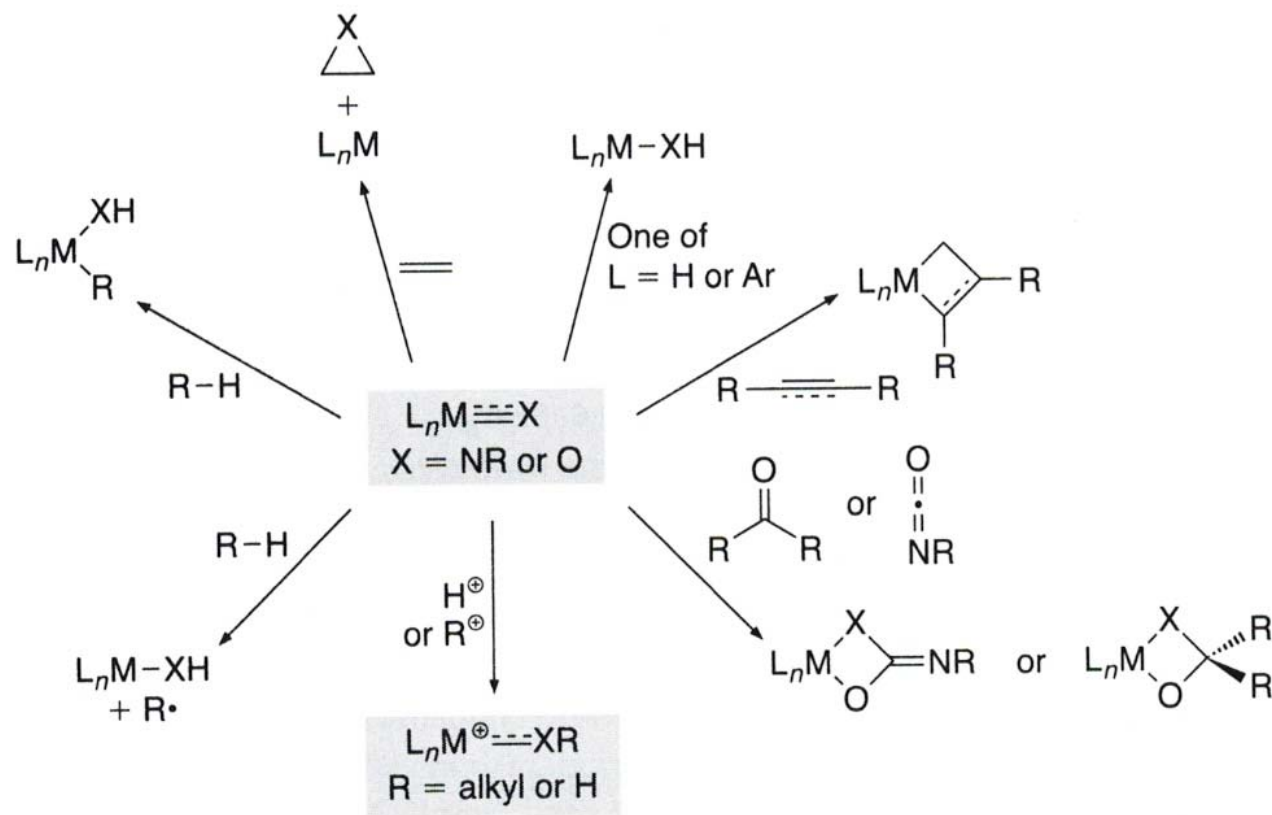
Common route to imides is internal deprotonation of secondary amides:



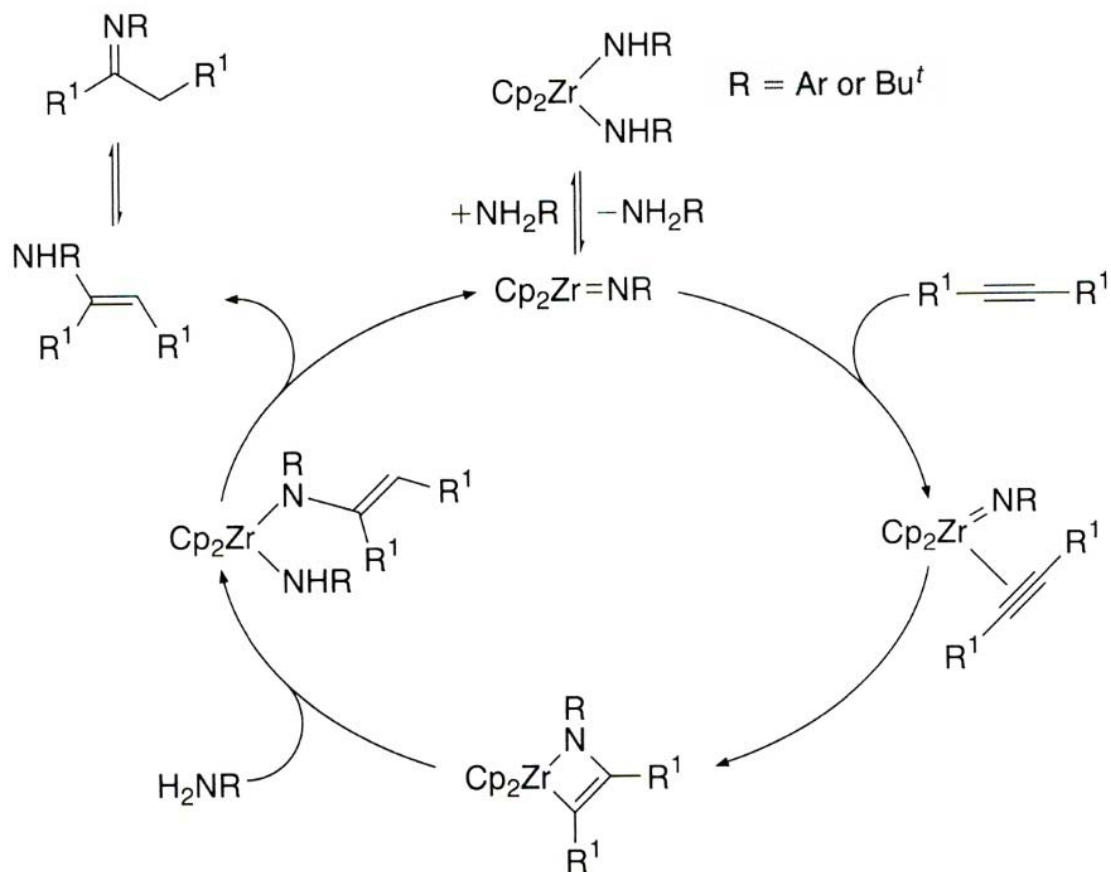
Imido ligands often form from oxo in a metallo-equivalent of the Schiff base reaction:



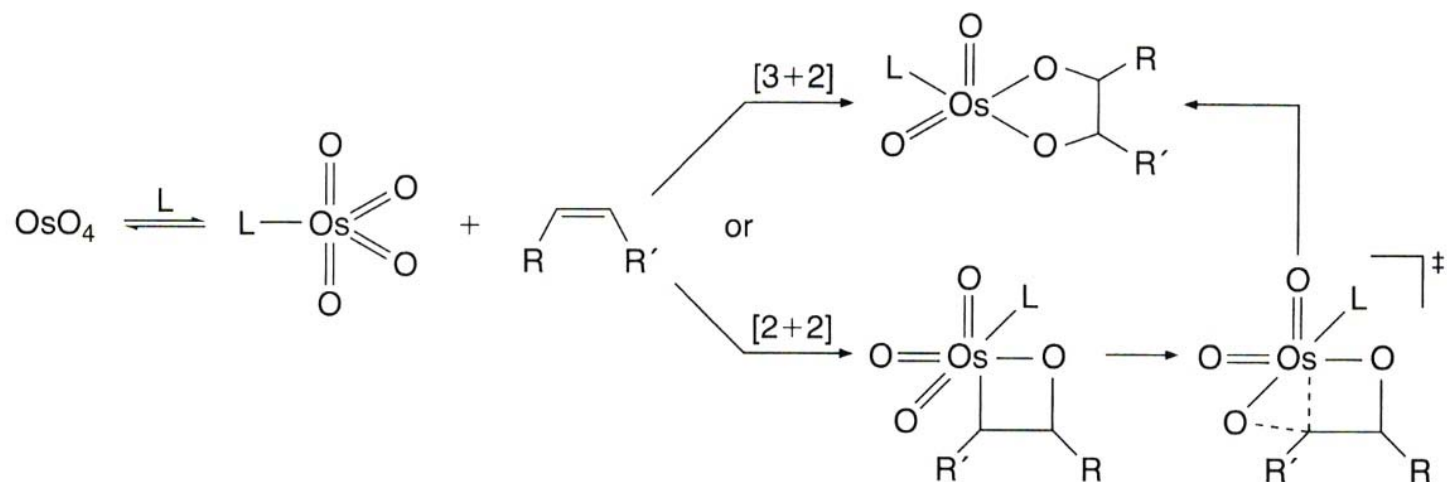
Summary of Imido and Oxo reactions:



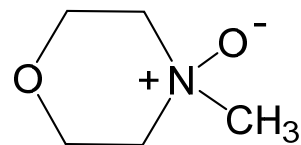
[2+2] Cycloadditions: e.g. Zr-catalyzed hydroamination



[3+2] Cycloaddition: e.g. Os cis-dihydroxylation

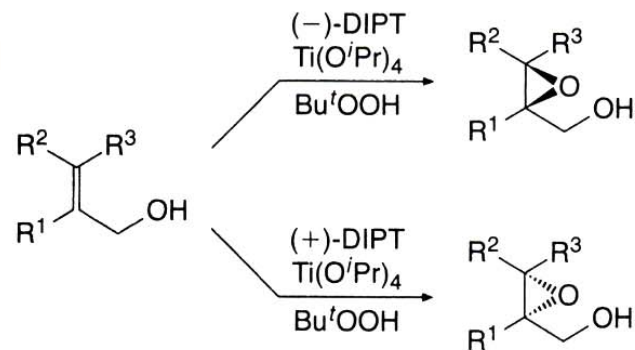


Catalytic version uses **NMO** as stoichiometric oxidant in a biphasic system



Atom transfer reactions: e.g. Sharpless epoxidations

Nobel Prize 2001



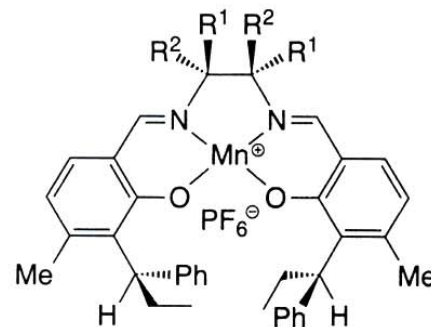
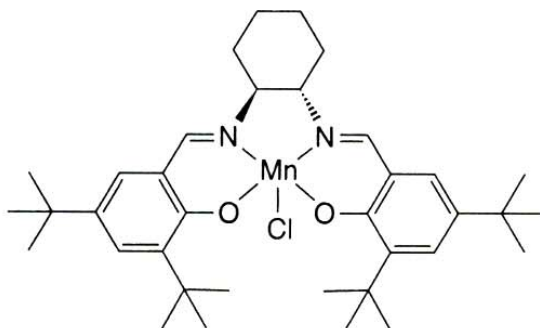
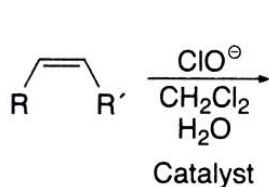
Probably via a Ti-O-O-H

DIPT = diisopropyl tartrate

Scheme 13.22

Likely to be via a true Mn(V) oxo

Note: *R.E.* possible here



If $\text{R}^1 = \text{Ph}$ then $\text{R}^2 = \text{H}$
If $\text{R}^1 = \text{H}$ then $\text{R}^2 = \text{Ph}$

Katsuki's catalyst

Related macrocyclic systems of Fe, Mn

