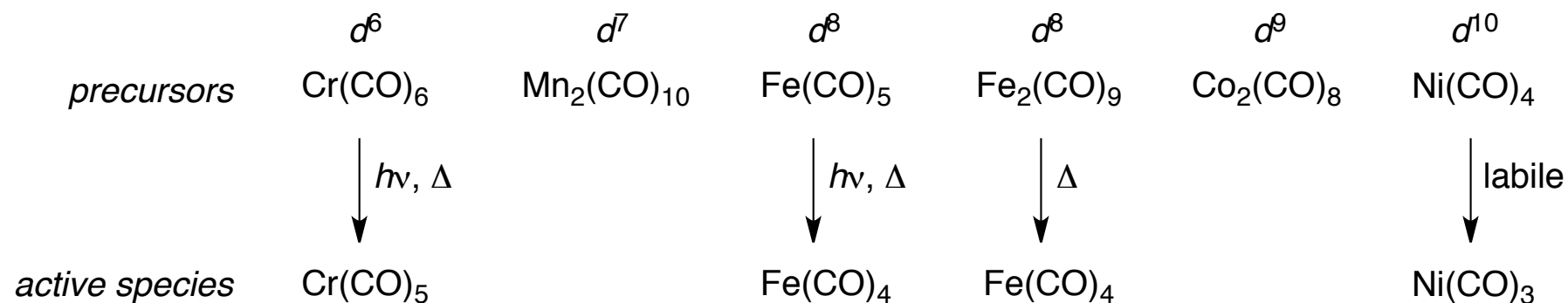


Metal Carbonyl Chemistry

Here we will be talking about, generally, homoleptic ("all CO") complexes of first row transition metals. Discussions about hydroformylation and other carbonylation chemistry will be later.

The chemistry of these metal carbonyls is possible because CO is an excellent π -acceptor, and can stabilize metals with a low oxidation state and high electron density.

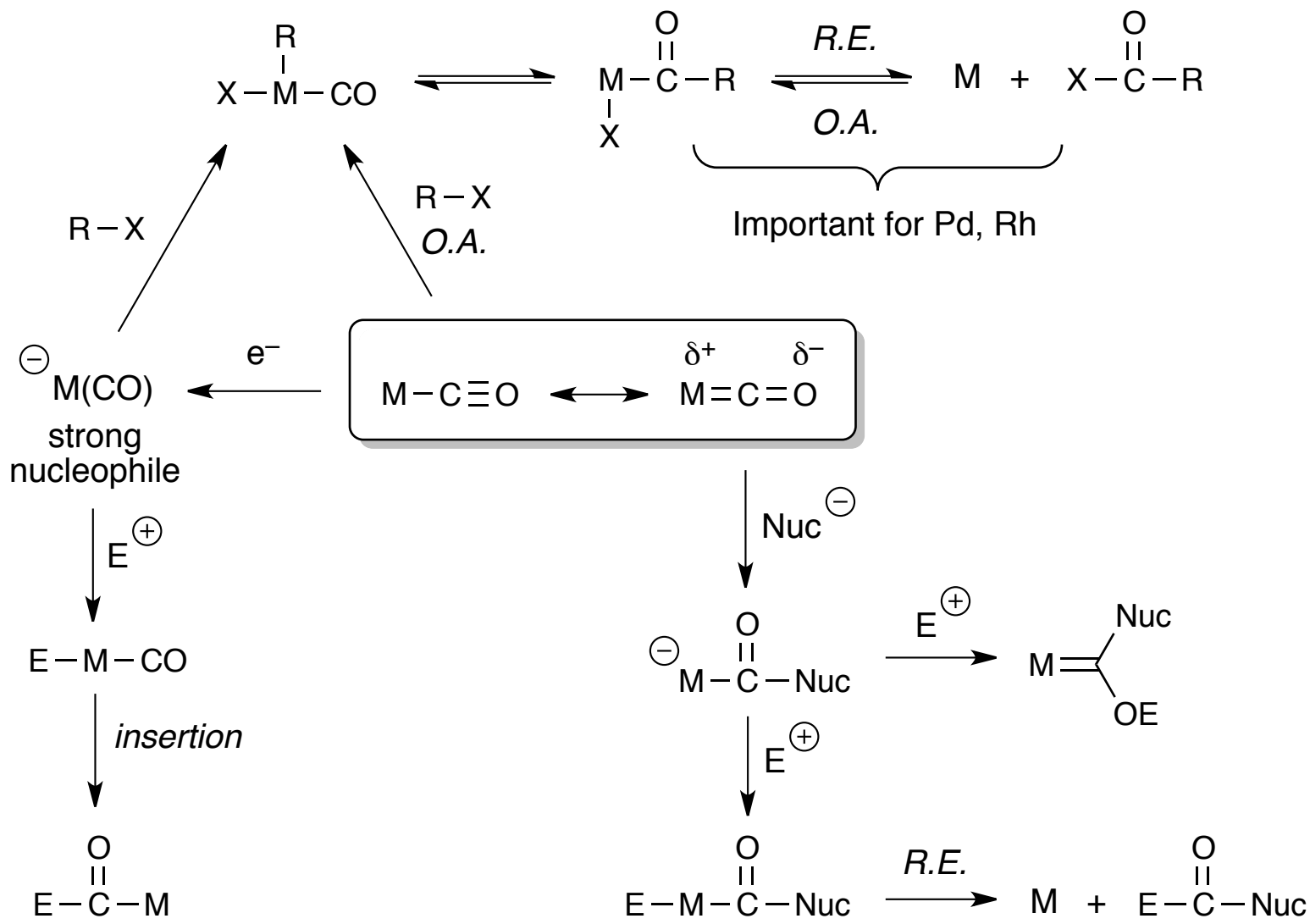
The commercial complexes are generally stable, but are coordinatively saturated and must lose a CO ligand in order to participate. The high affinity of metals for CO means that high temps or photolytic conditions must be used.



Many of the reactions associated with these complexes are stoichiometric. This is due to the preference of the early transition metals to be in higher oxidation states. As a result the chemistry of Fe has dominated ($\text{Fe}(\text{CO})_5$ \$~200/\text{kg})

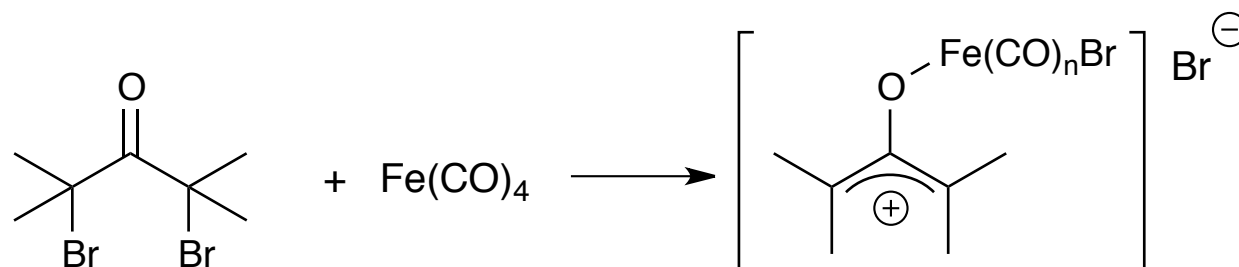
Metal Carbonyl Chemistry

Overview of metal carbonyl chemistry. Some of these pathways will be discussed later.



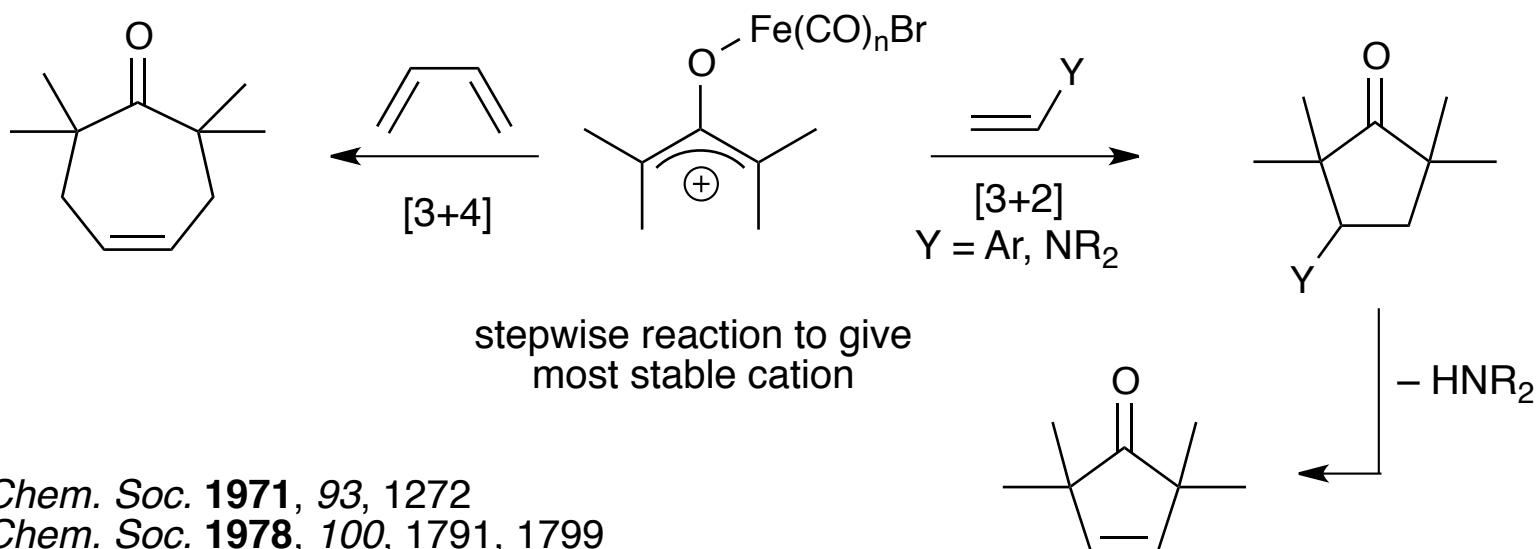
Iron(II) Oxallyl Cations

Electrophilic 3-carbon subunits for [3+N] cycloadditions



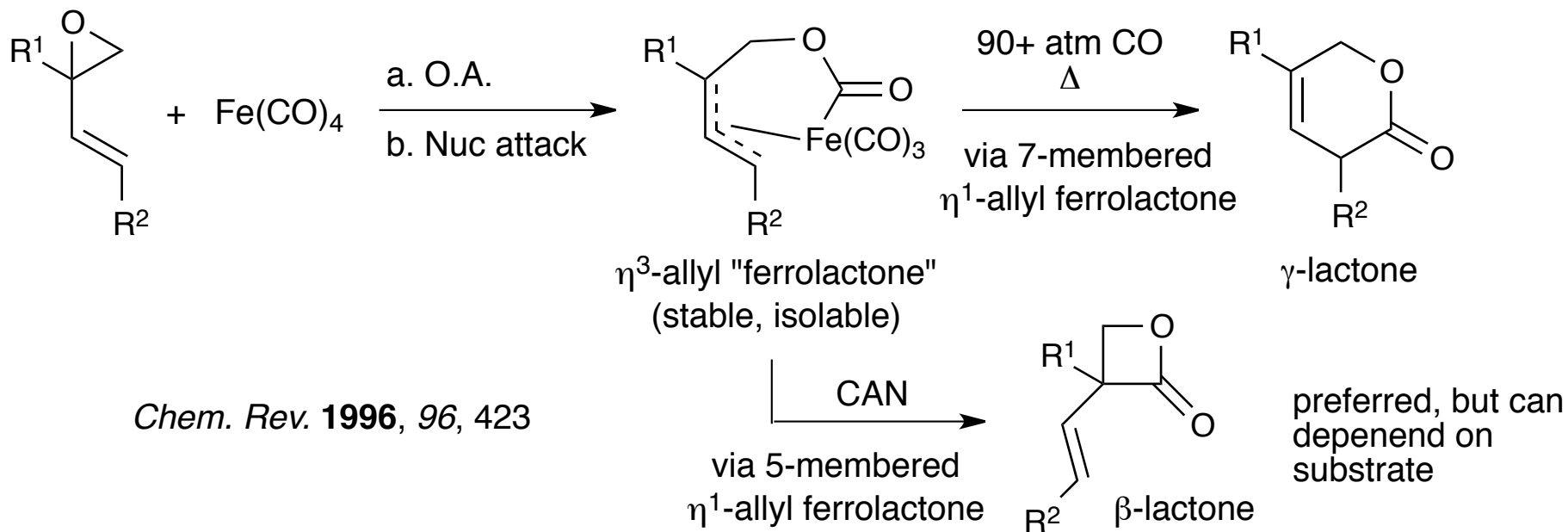
Fe(II) oxallyl cation

must have at least one α -substituent to stabilize allyl cation, dibromoacetone does not react, tetrabromoacetone does



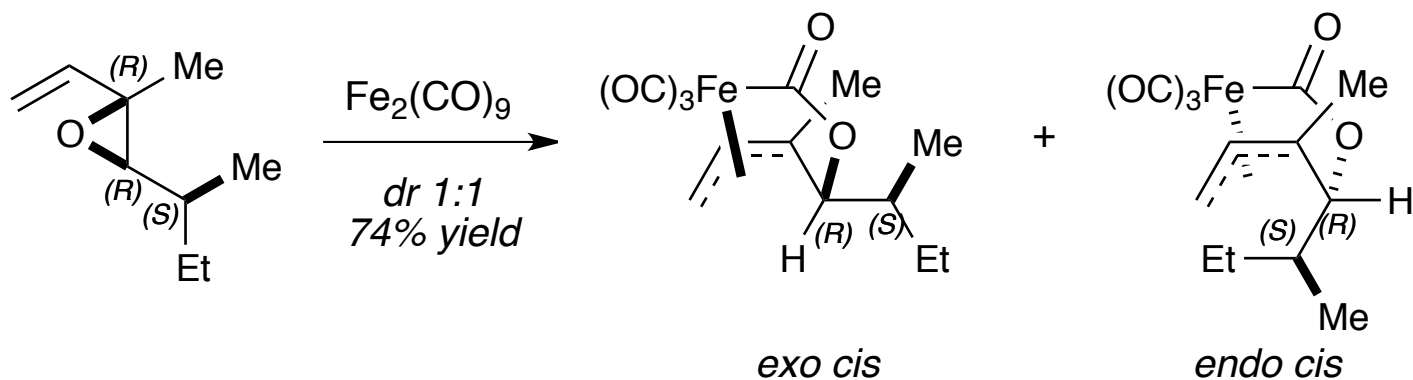
J. Am. Chem. Soc. **1971**, *93*, 1272
J. Am. Chem. Soc. **1978**, *100*, 1791, 1799
Acc. Chem. Res. **1979**, *12*, 61

Reactions of Vinyl Epoxides With $Fe(CO)_4$



Chem. Rev. **1996**, *96*, 423

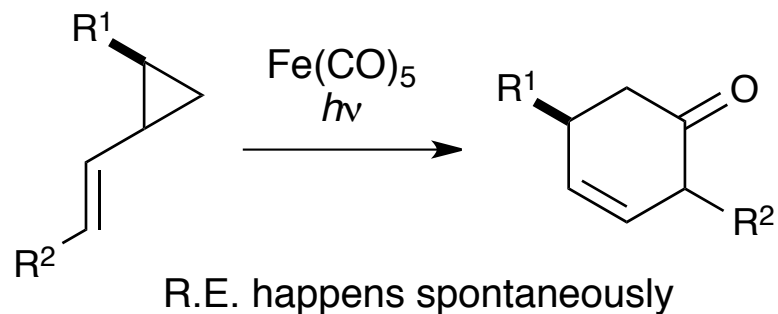
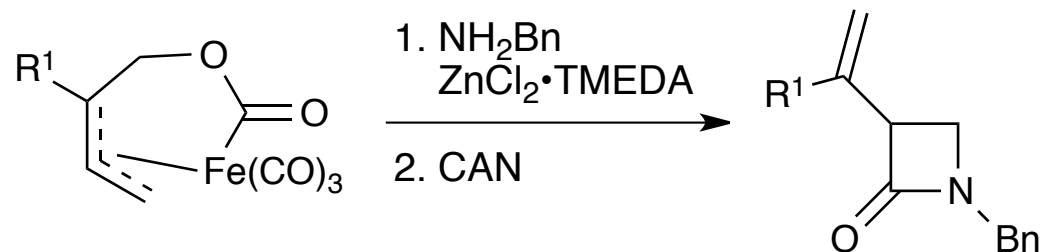
The η^3 -allyl ferrolactone can be present in multiple stereoisomers, but they can be separated by chromatography and carried forward to give diastereomerically pure lactones.



Reactions of Vinyl Epoxides With $Fe(CO)_4$

The η^3 -allyl ferrolactones are stable to a wide range of reaction conditions (H_2O , Me_3SiCN , MnO_2 , $CuCl_2$, $FeCl_3$, $t-BuOOH$, amine oxides, CrO_3 , PCC, PDC, O_3 , Swern, dilute acids, Et_3N , cat. H_2 , Wittig, Tebbe, Sml_2 , Lewis acids). Reaction sequences can therefore be accomplished, before decomplexation. The ferrolactone is a large group that can influence stereoselective reactions.

Lactams and ketones are also possible:



Collman's Regent – $\text{Na}_2\text{Fe}(\text{CO})_4$

Disodium tetracarbonylferrate – d^{10} , Fe(-II) – highly nucleophilic

