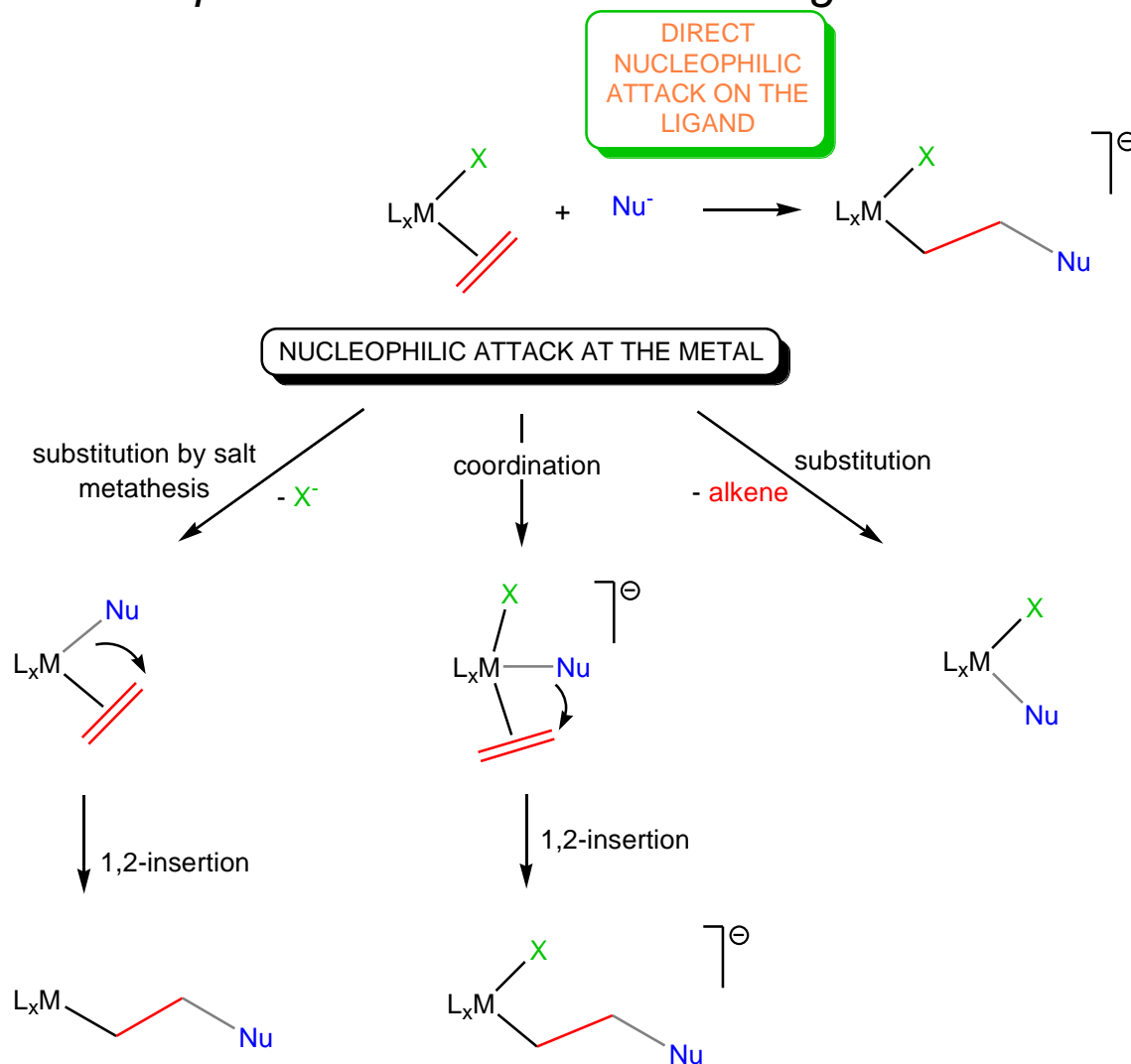


# REACTIONS WITH NUCLEOPHILES – ATTACK AT THE METAL

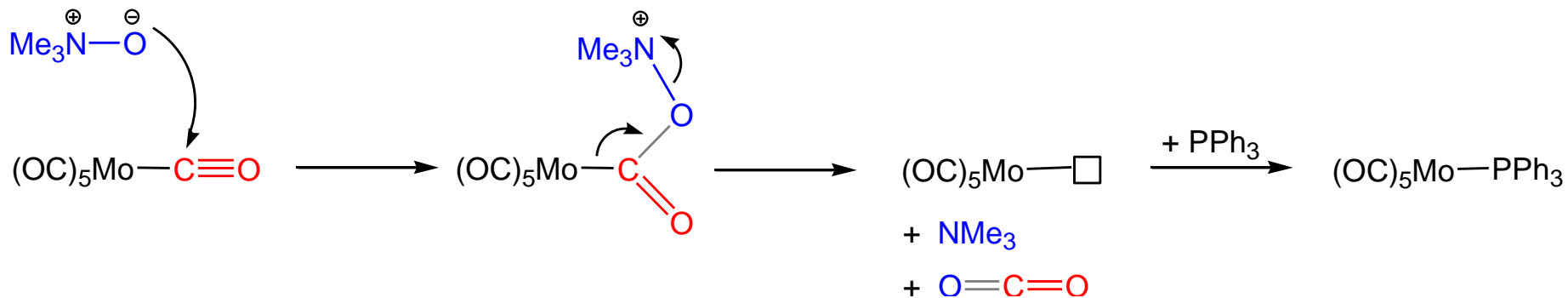
- Since we have already examined the different types of reactivity which can occur from nucleophilic attack at the metal (substitution reactions, coordination in a vacant site, insertion reactions), herein we are mainly concerned with reactions involving *direct nucleophilic attack on unsaturated ligands*.



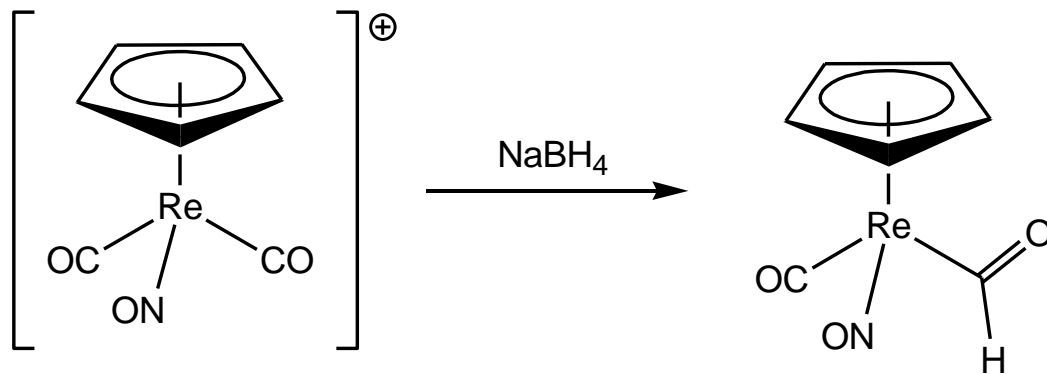
## REACTIONS WITH NUCLEOPHILES – DIRECT ATTACK AT CO

- Because they are electron rich, molecules such as CO, alkenes, polyenes and arenes generally do not react with nucleophiles.
- Once attached to a metal, these ligands give up some of their electron density and become susceptible to direct nucleophilic attack.
- Unsaturated ligands are more susceptible to direct nucleophilic attack when:
  - there is less electron density on the metal (e.g.  $\pi$ -acceptor co-ligands, overall positive charge).
  - the metal is coordinatively saturated – this avoids nucleophilic attack at the metal centre.

## REACTIONS WITH NUCLEOPHILES – DIRECT ATTACK AT CO



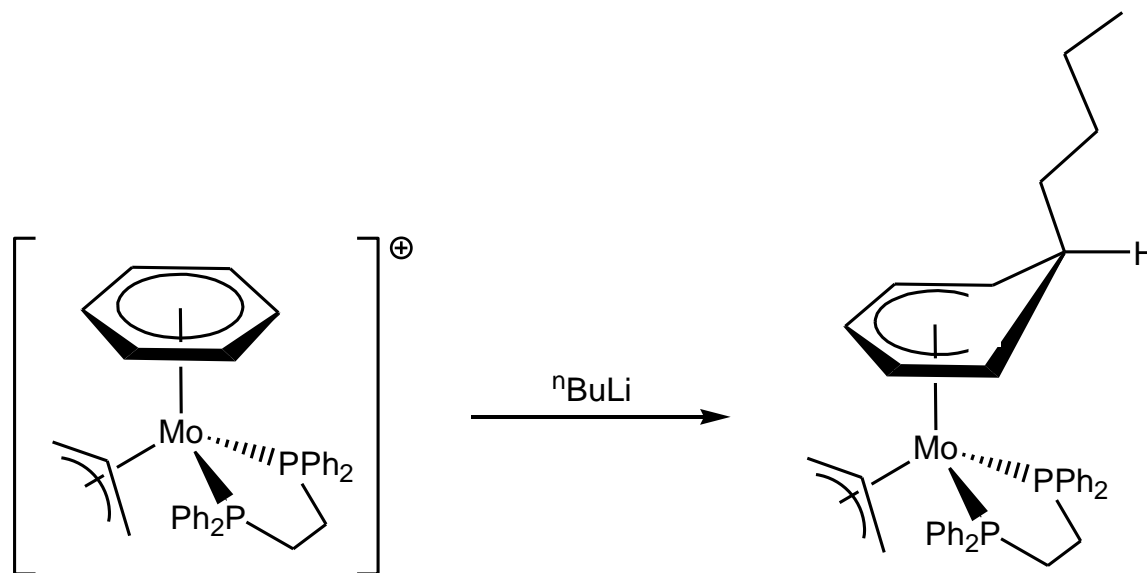
- **R<sub>3</sub>NO** (a trialkylamine oxide; R = Me or Et) is commonly used instead of heat or UV-irradiation to remove CO ligands in order to speed up dissociative substitution reactions.



- The above reaction involves direct nucleophilic attack of H<sup>-</sup> on a CO ligand. Note: It is possible to get similar reactions with CNR or carbenes.

## REACTIONS WITH NUCLEOPHILES – ATTACK AT $\pi$ -LIGANDS

- There are many examples of direct nucleophilic attack on coordinated  $\pi$ -ligands, and these transformations can be very useful in synthesis. For example (nucleophilic attack at least hindered face):

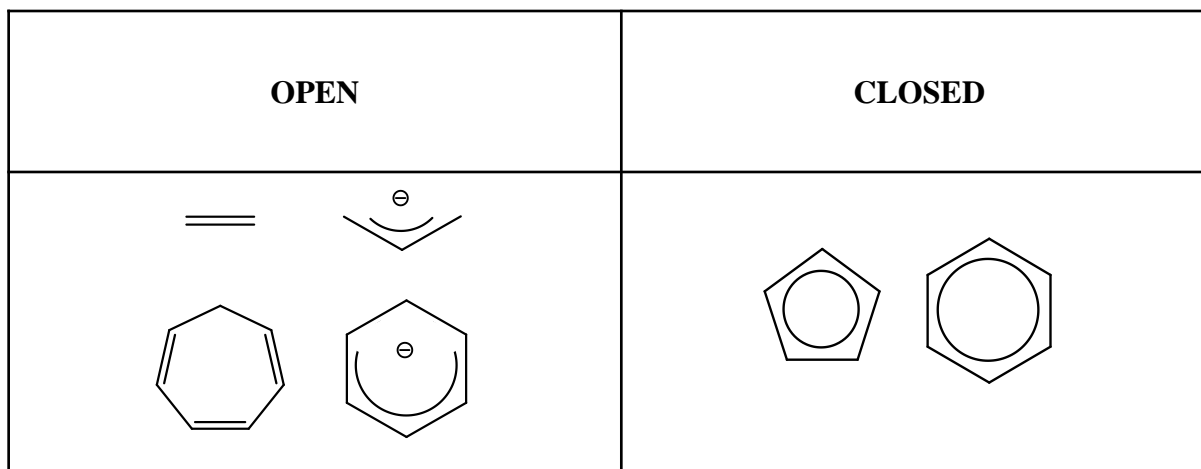


- For nucleophilic attack at  $\pi$ -ligands, use the DGM (Davies-Green-Mingos) Rules (*cationic or dicationic complexes only*).

# DGM RULES (MUST BE FOLLOWED IN ORDER)

**Rule 1 – Even before Odd:** Nucleophilic attack occurs preferentially at even polyenes

**Rule 2 – Open before Closed:** Nucleophilic addition occurs preferentially at open polyenes (not closed).



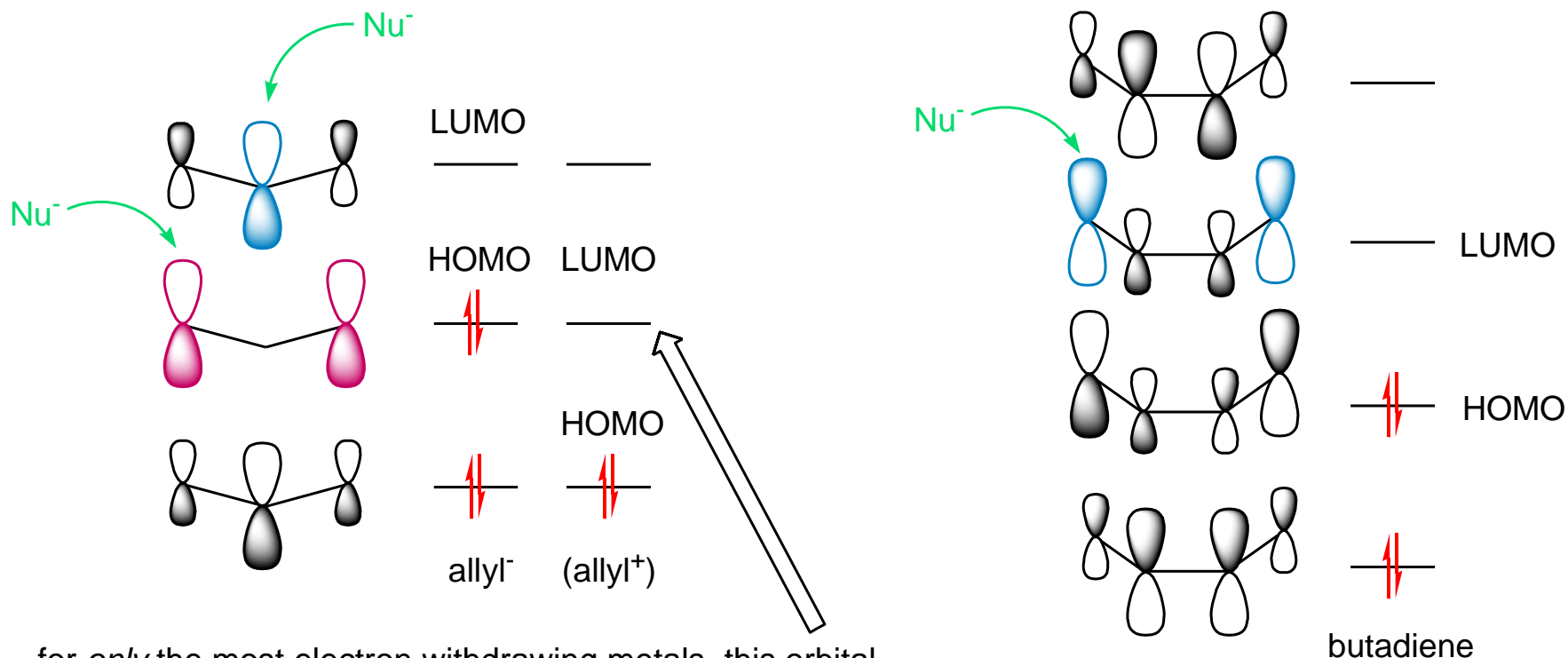
**Rule 3 – For open polyenes:**

If Even → attack occurs at a terminal position.

If Odd → attack is usually NOT at a terminal position  
→ attack is only at a terminal position if the metal is very strongly electron withdrawing.

# REASONS FOR DGM RULES

- Rule 1: Even polyenes are formally neutral (alkene, benzene vs  $\text{Cp}^-$ ,  $\text{allyl}^-$ ,  $\text{C}_7\text{H}_7^-$ ).
- Rule 2: Largely an empirical observation. The reasons behind it are not well understood.
- Rule 3: This has to do with the relative size of the lobes in the LUMO (see below):

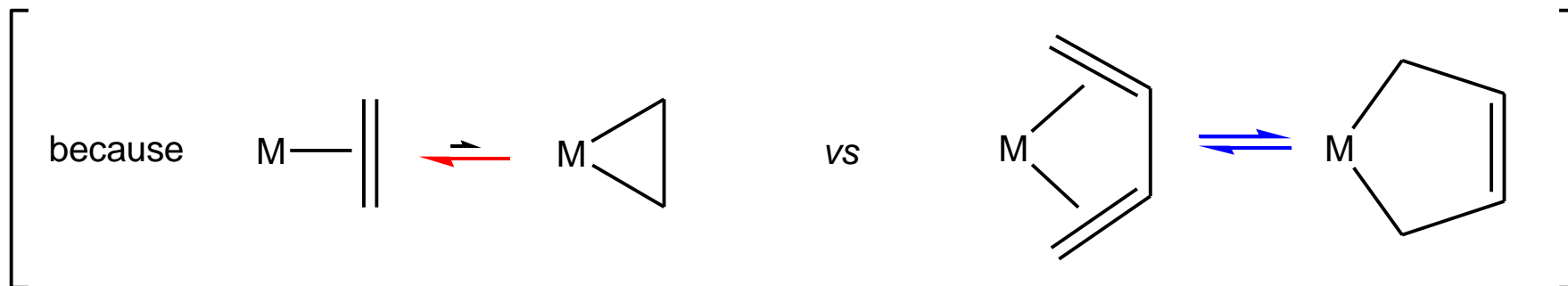
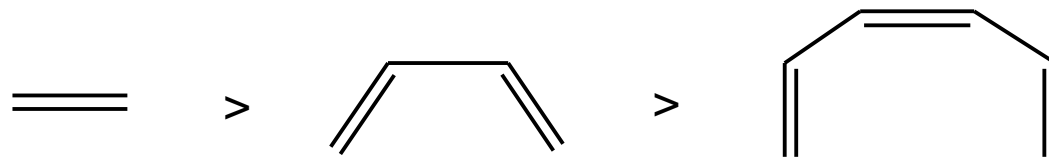


for *only* the most electron withdrawing metals, this orbital becomes sufficiently depleted of electron density that it becomes the preferred site for nucleophilic attack.

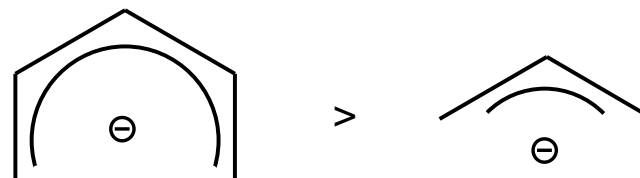
# REASONS FOR DGM RULES

## Rule 3b:

For neutral open polyenes:



For monoanionic open polyenes:



[ because the negative charge is delocalized over more carbons in pentadienyl than allyl ]

- **Secret rule zero!** – nucleophiles generally add once to a monocation, twice to a dication *etc.*