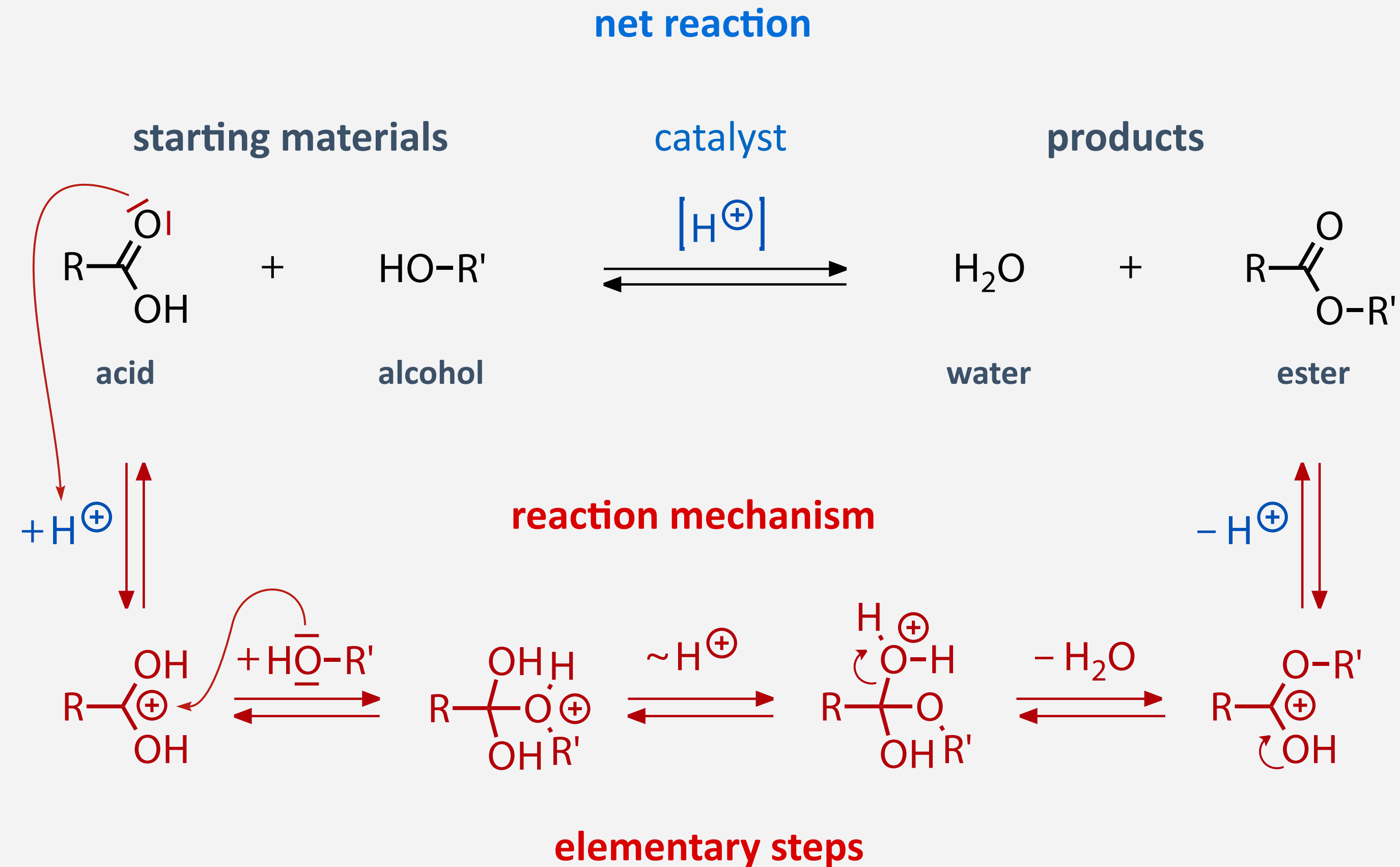


4.2 Reaction Types and Reactive Intermediates

Net Reaction versus Reaction Mechanism



- **net reaction** describes the starting materials and the products of a reaction
- **reaction mechanisms** describes the individual **elementary steps** of the reaction
- **catalyst** takes part in the reaction mechanism but is retained unchanged

Reaction Types

Substitution Reactions

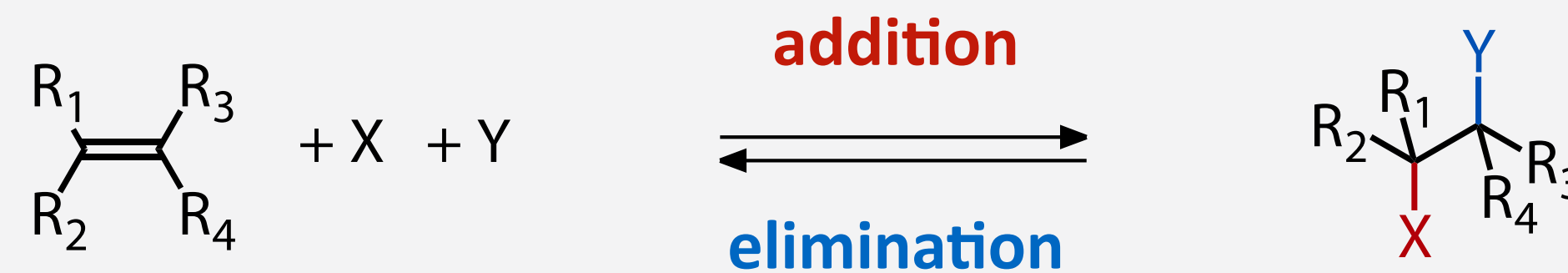
- classification by reaction type describes changes in molecular topology (atom connectivity)



- substitution reactions are displacement of a fragment X by a fragment Y
- coordination number and geometry (i.e., hybridization) do not change
- the reverse reaction of a substitution reaction is also a substitution reaction

Addition and Elimination Reactions

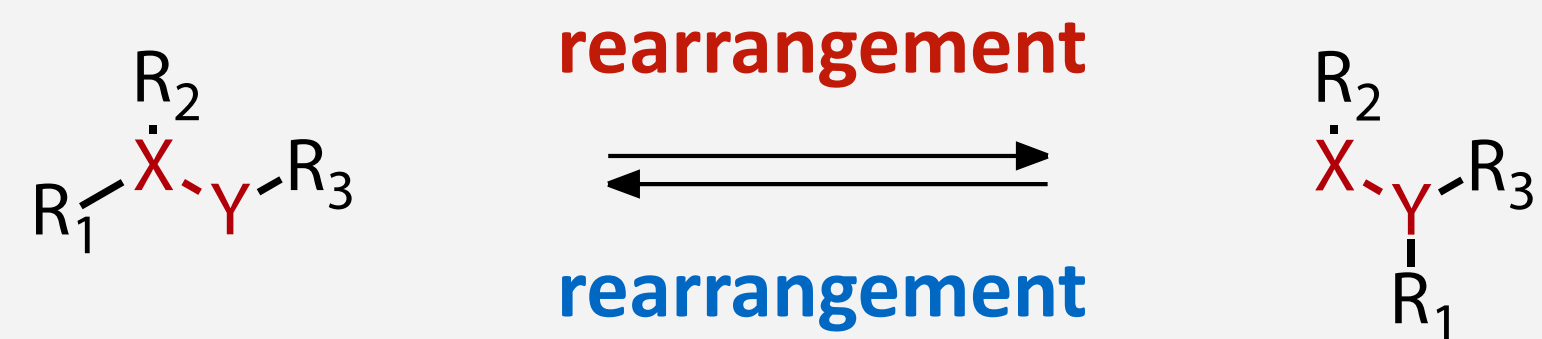
- classification by reaction type describes changes in molecular topology (atom connectivity)



- addition reactions are additions of molecular fragments X and Y to a molecule
- in addition reactions, coordination numbers increase, and geometry (hybridization) changes
- in addition reactions, starting material must be coordinatively unsaturated !
- the reverse reaction of an addition reaction is an elimination reaction
- in elimination reactions, coordination numbers decrease, and geometry (hybridization) changes
- in elimination reactions, product must be coordinatively unsaturated !

Rearrangement Reactions

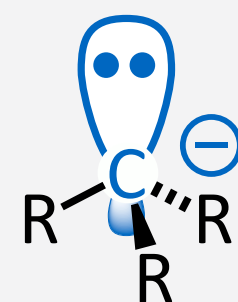
- classification by reaction type describes changes in molecular topology (atom connectivity)



- rearrangement reactions are intramolecular changes to molecular topology (atom connectivity)
- coordination numbers and geometries (hybridizations) on the connecting atoms X and Y change
- the reverse reaction of a rearrangement reaction is also a rearrangement reaction

Reactive Intermediates

Carbon-Centered Reactive Intermediates



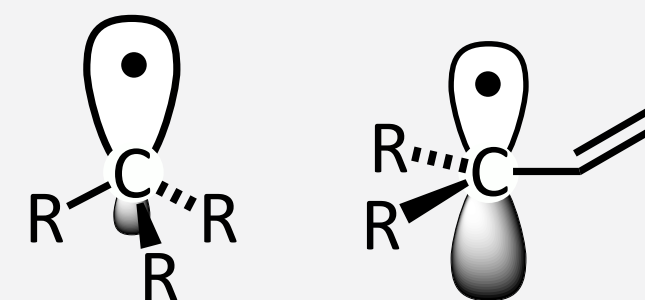
carbanion

5 electrons
negative formal charge

tetrahedral

sp^3

3 bonds, 1 electron pair
octet rule fulfilled



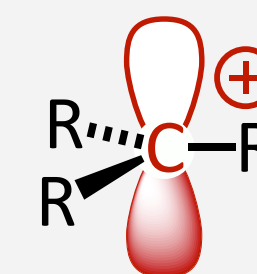
radical

4 electrons
neutral

in between

sp^3 or sp^2 or mixed

open shell



carbenium cation

3 electrons
positive formal charge

trigonal planar

sp^2

3 bonds
electron sextet (deficient)

- **formal charges** are determined by **homolytic bond cleavage** and counting electrons

Polar Reaction Mechanisms

- **polar reaction mechanisms** involve **reactive intermediates** that carry **formal (or partial) charges**
- formed by **heterolytic bond cleavage** (electron pair stays with more electronegative partner)



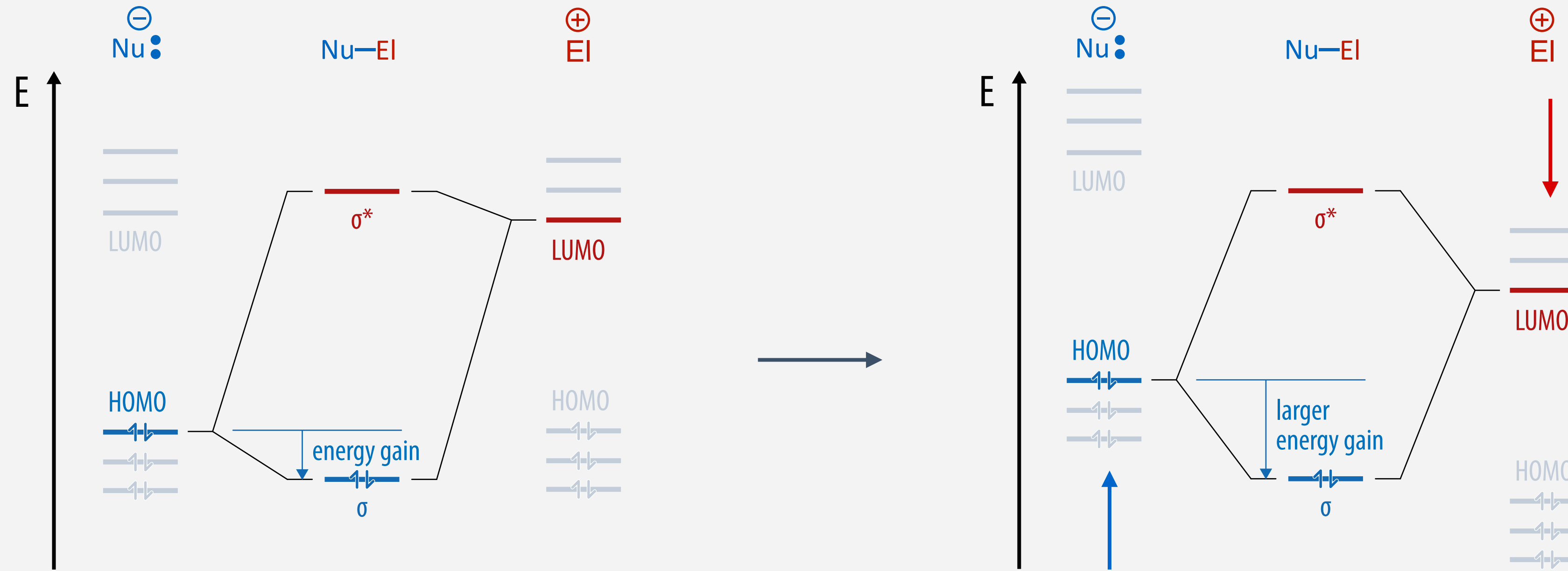
- vast majority of chemical reactions occurs between **“nucleophiles”** and **“electrophiles”**



- **nucleophiles** are **electron-pair donors** and **electrophiles** are **electron-pair acceptors**
 - reaction involves “attack” of the nucleophile free electron pair on **electrophile** (full curvy arrow)
 - new nucleophile–**electrophile** bond is formed using the electron pair of the nucleophile

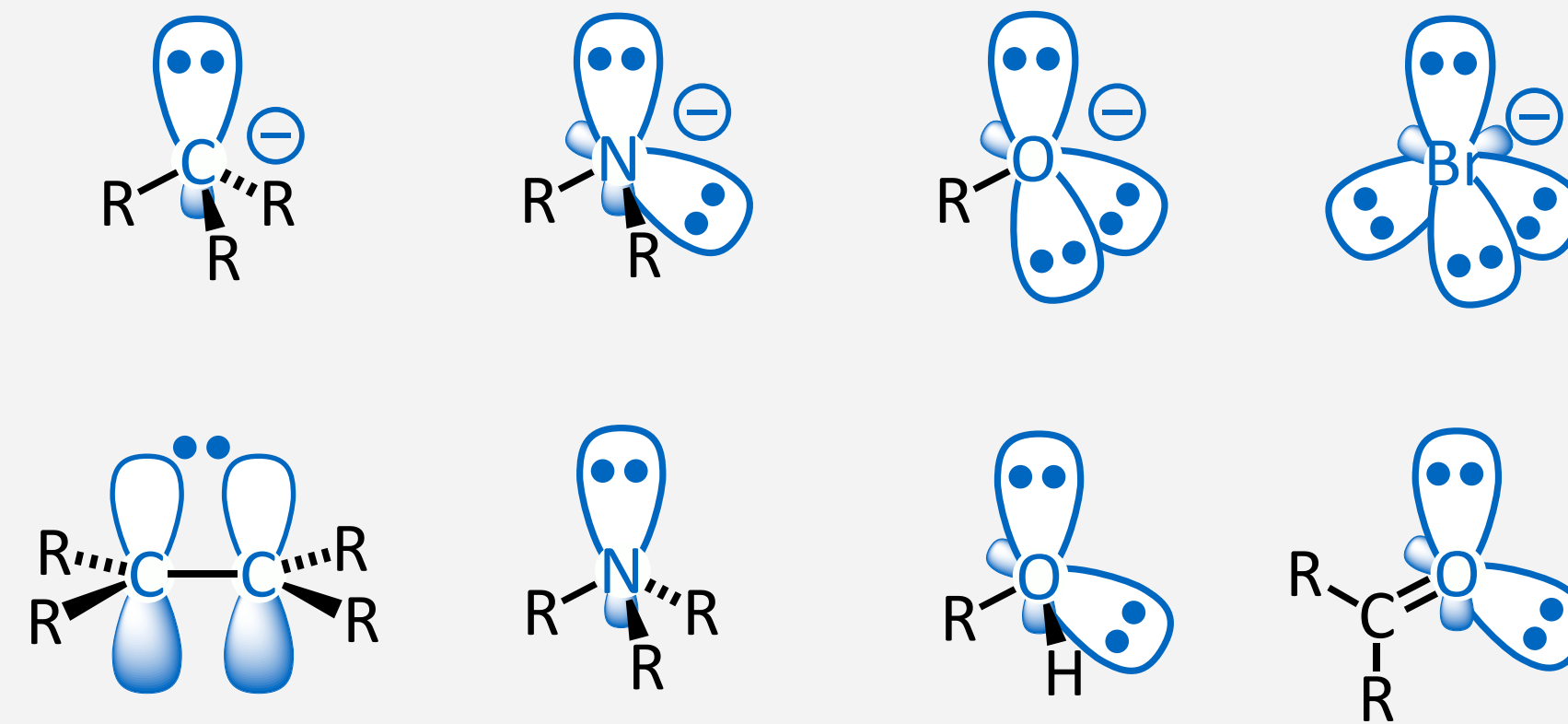
Polar Reaction Mechanisms

- reaction can be described as bond formation between **nucleophile HOMO** and **electrophile LUMO**



- both electrons are donated by nucleophile, energy gain larger if contributing MO closer in energy
 - high-energy nucleophile HOMO: high electron density, anionic charge, higher valency shell
 - low-energy electrophile LUMO: low electron density, positive charge, lower valency shell

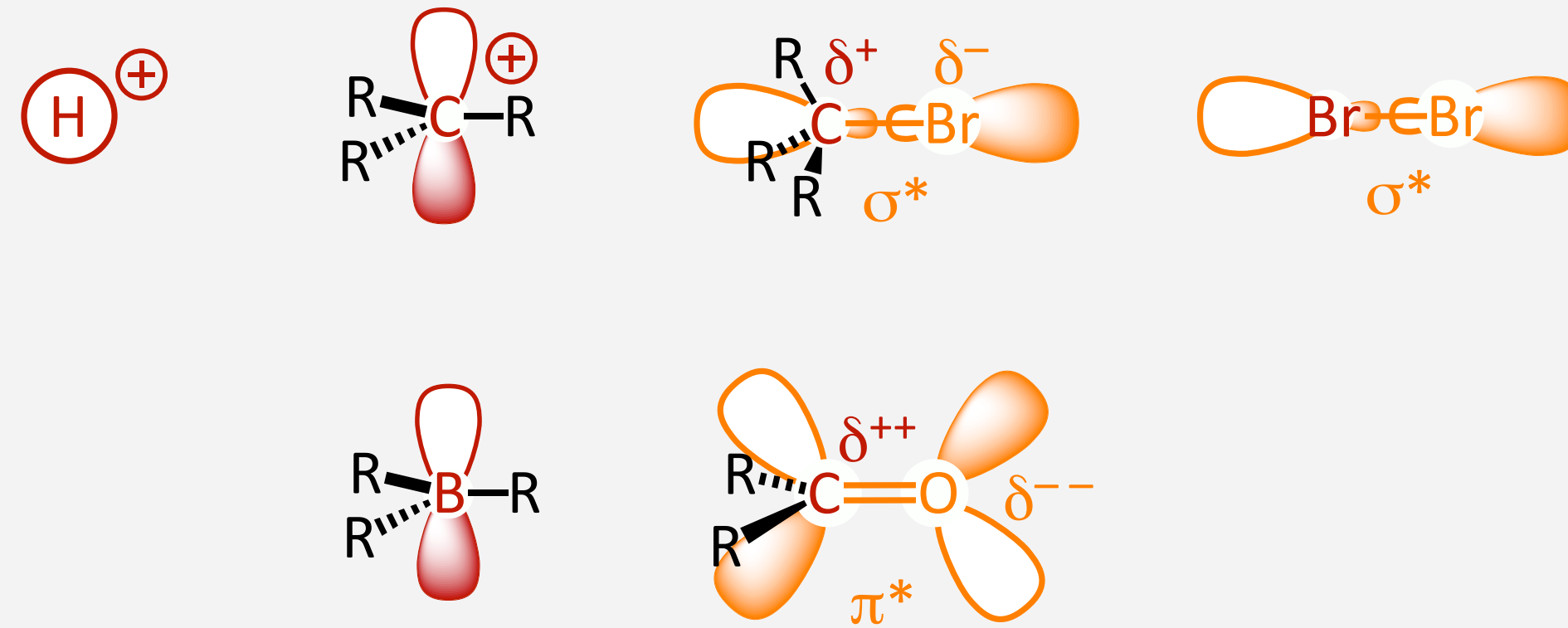
Examples of Nucleophiles



- **nucleophiles are electron pair donors**

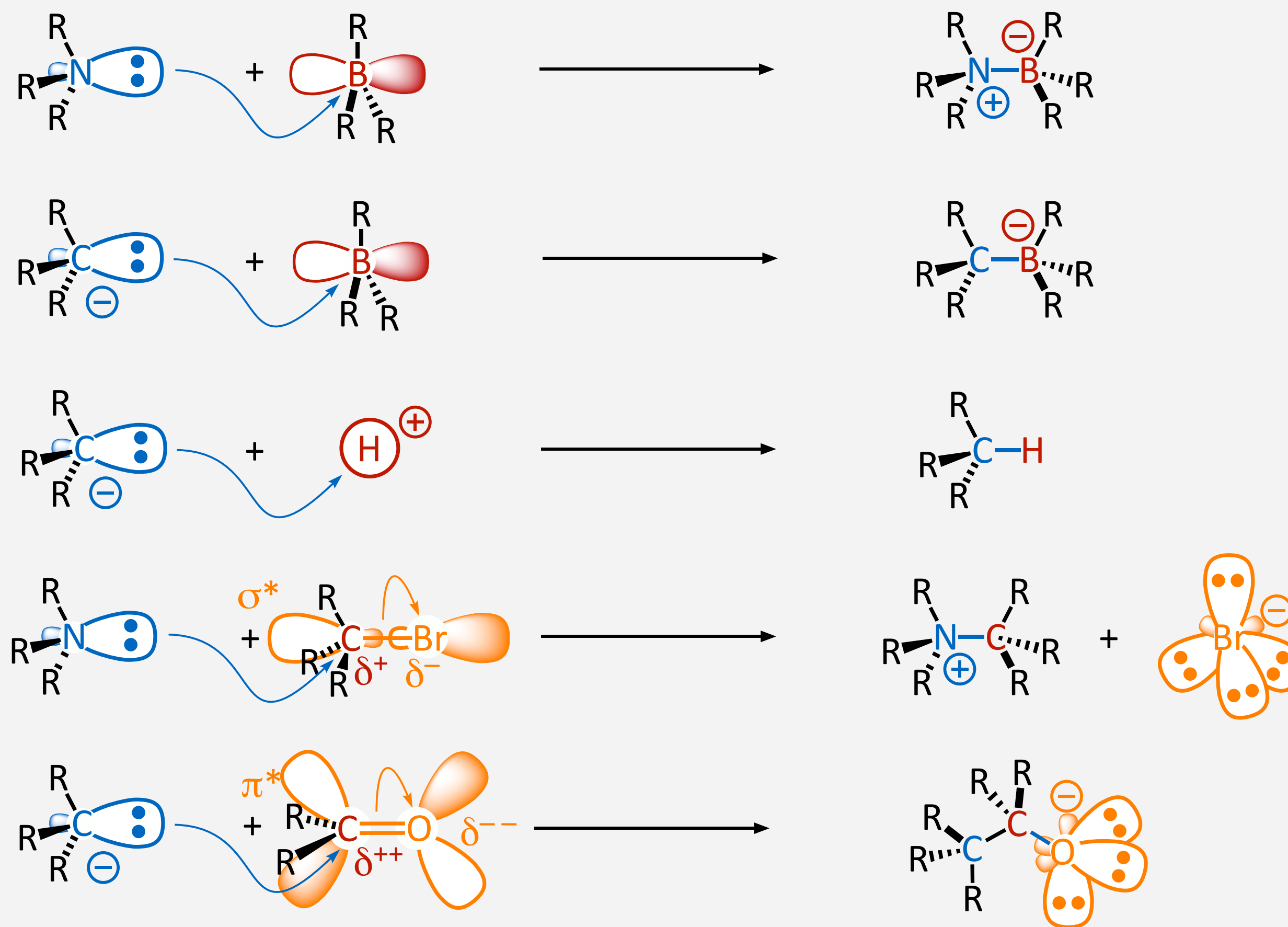
- nucleophiles must have a high energy electron pair available for bonding
- nucleophiles can be negatively charged or neutral but must be electron-rich, polarizable species
- typically a non-bonding electron lone pair (carbanion or a neutral / anionic heteroatom)
- alternatively, a high-energy and polarizable bonding, such as a π bond

Examples of Electrophiles



- **electrophiles are electron pair acceptors**
 - electrophiles must have free valency to accept electron pair
 - electrophiles can be positively charged or neutral but must be electron-deficient
 - proton H^+ with empty 1s orbital is the strongest electrophile
 - often an electron sextet, such as a carbenium cation or a neutral borane
 - alternatively, **low-energy antibonding orbital** (such as a σ^* MO of a weak bond, or π^* MO in $\text{C}=\text{O}$)

Writing Polar Reaction Mechanisms



- formal charges reflect the formal count of electrons on each atom
- total formal charge status must be maintained between starting materials and products
- if antibonding (σ^* or π^*) orbitals are involved in nucleophile attack, (σ or π) bonds are broken !

Radical Reaction Mechanisms

- **radical reaction mechanisms** involve **molecules with unpaired electrons (•)** as reactive intermediates
- “radicals” are obtained by **homolytic bond cleavage** (electron pair is equally split between atoms)



- simple **radical reactions** occur between **two (same or different) radicals**



- reaction sequence ends finally by “**combination**” of the unpaired electrons (•) to form new bond
- bond formation hence requires electrons to have **opposite spin** (represented by half arrows)
- however, many steps can happen in between

Bond Energies

	$\Delta G / \text{kJ mol}^{-1}$		$\Delta G / \text{kJ mol}^{-1}$		$\Delta G / \text{kJ mol}^{-1}$
H–OH	498	H ₃ C–OH	383	HO–OH	213
H–CH ₃	435	H ₃ C–CH ₃	368	MeO–OMe	151
H–Cl	431	H ₃ C–Cl	349	Cl–Cl	243
H–Br	366	H ₃ C–Br	293	Br–Br	192
H–I	298	H ₃ C–I	234	I–I	151

- **homolytic bond cleavage can be achieved by thermal activation or light as an energy source**
 - all bonds can undergo homolytic cleavage at elevated temperatures (typically ≥ 200 °C)
 - just a matter of kinetics because molecules show a Boltzmann distribution of thermal energies
 - light can serve as an energy source (e.g. blue of UV, ≤ 400 nm, ≥ 300 kJ/mol)

