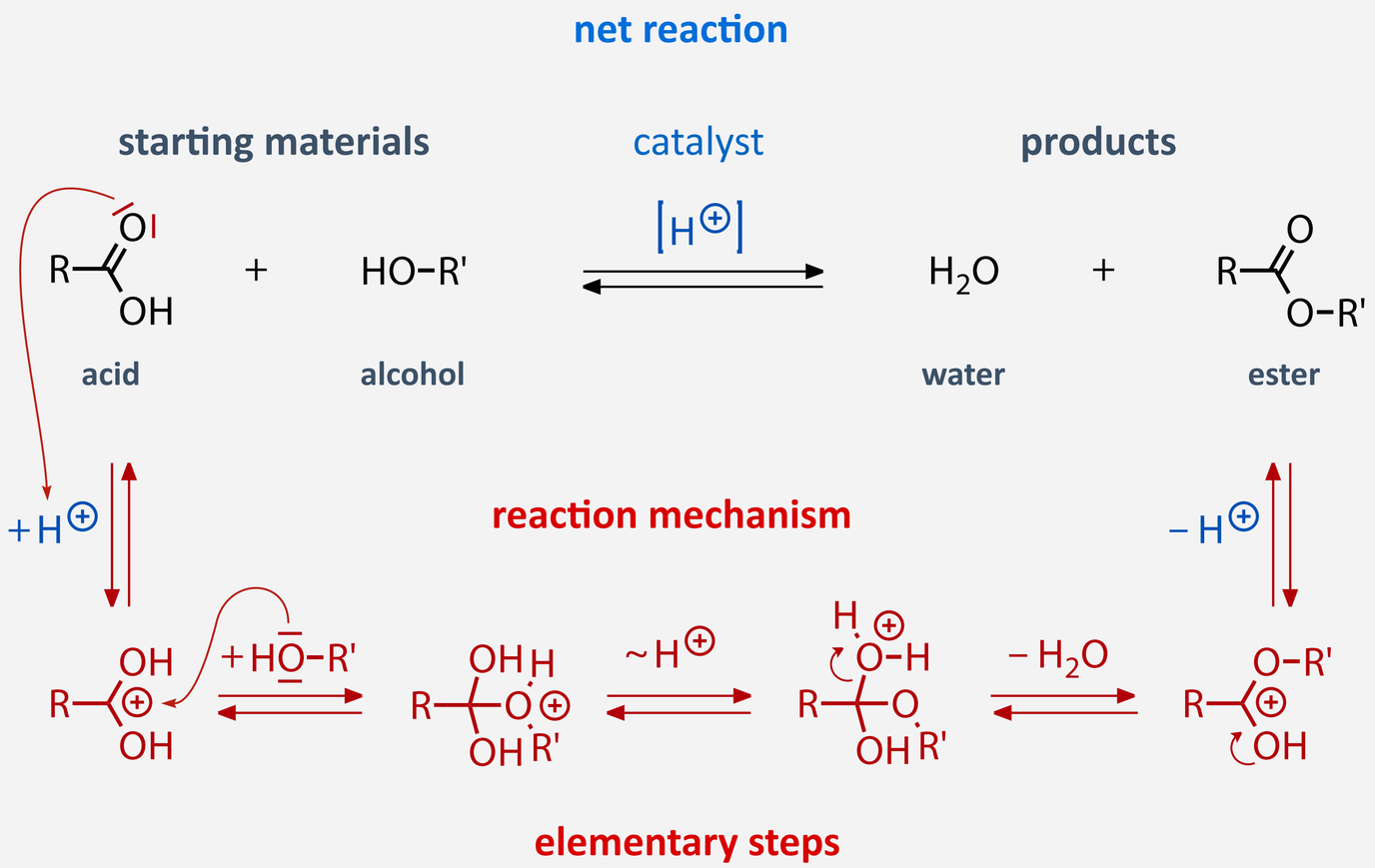
4.2 Reaction Types and Reactive Intermediates

Net Reaction versus Reaction Mechanism

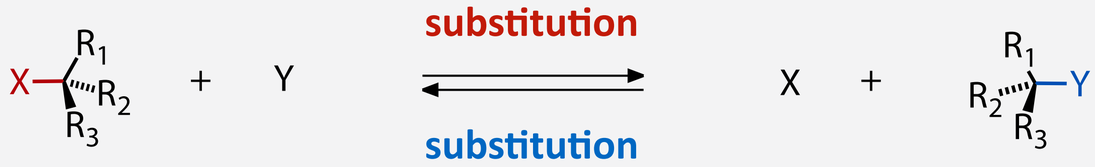


- **net reaction** describes the starting materials and the products of a reaction
- **reaction mechanisms** describes the individual elementary steps of the reaction
- **catalyst** takes part in the reaction mechanism but is retained unchanged

Reaction Types

Substitution Reactions

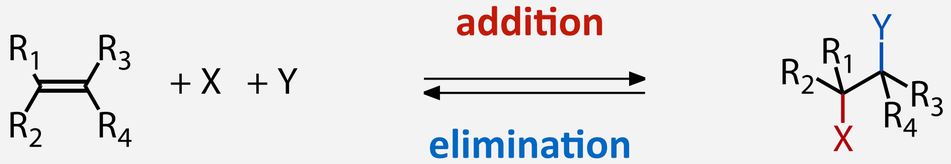
- classification by reaction type describes changes in molecular topology (atom connectivity)



- **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

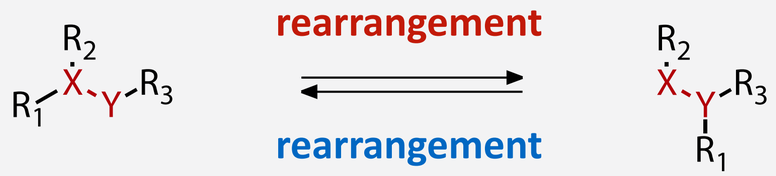
- classification by reaction type describes changes in molecular topology (atom connectivity)



- **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

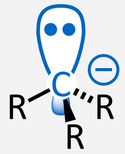
- classification by reaction type describes changes in molecular topology (atom connectivity)



- **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



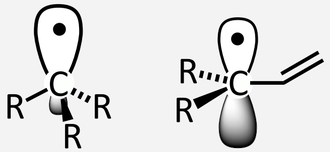
carbanion

5 electrons
negative formal charge

teatrahedral

sp^3

3 bonds, 1 electron pair
octet rule fulfilled



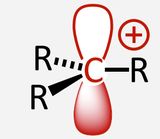
radical

4 electrons
neutral

in between

sp^3 or sp^2 or mixed

open shell



carbenium cation

3 electrons
positive formal charge

trigonal planar

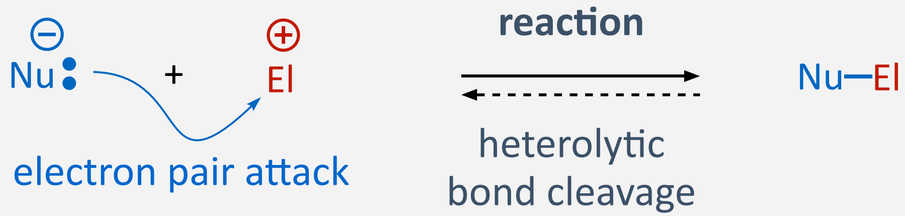
sp^2

3 bonds
electron sextet (deficient)

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

Polar Reaction Mechanisms

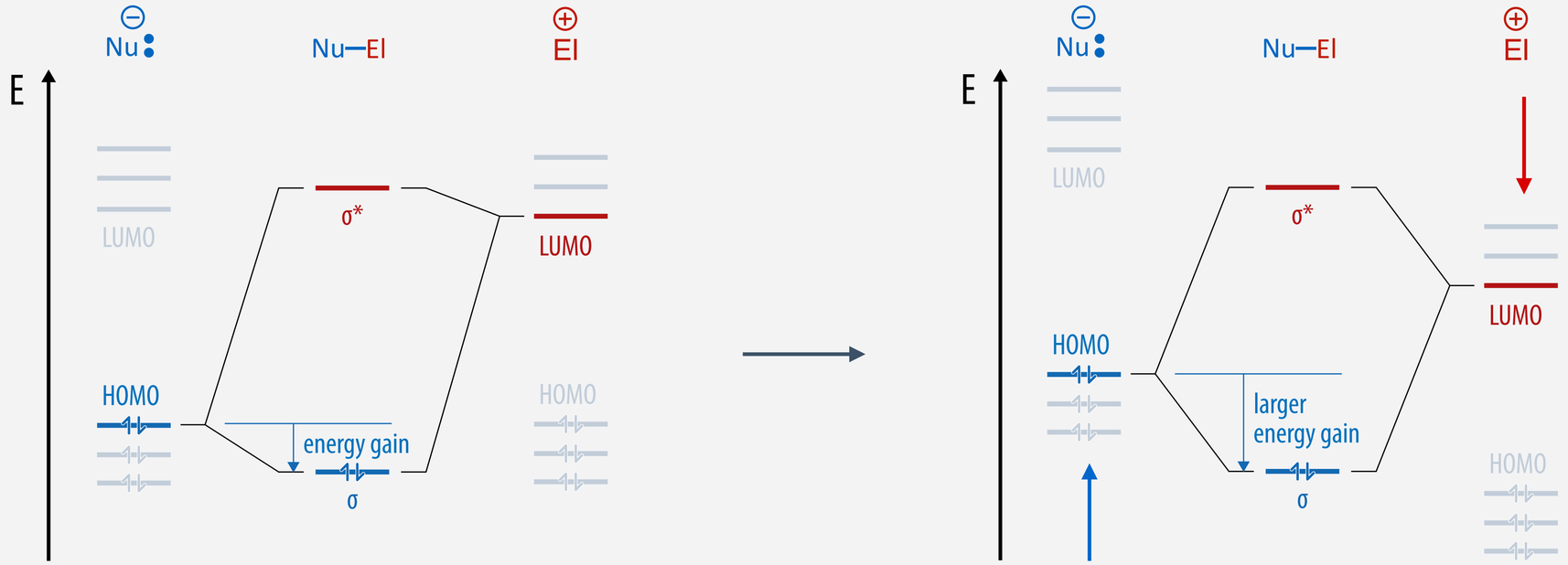
- **polar reaction mechanisms involve reactive intermediates that carry formal (or partial) charges**
- polar reactive intermediates carrying formal charges are typically obtained from stable molecular precursors by heterolytic bond cleavage (electron pair stays with more electronegative partner)



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

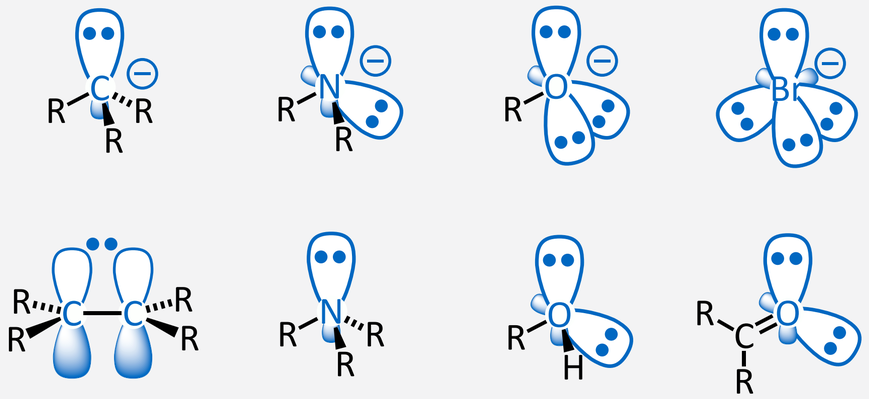
Polar Reaction Mechanisms

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



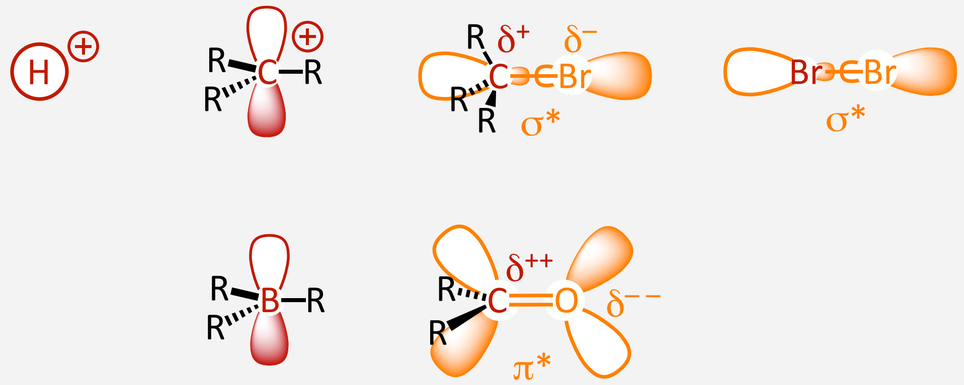
- both electrons are donated by nucleophile, energy gain larger if contributing MO closer in energy
  - high-energy nucleophile HOMO: high electron density, anionic charge, higher valency shell
  - low-energy electrophile LUMO: low electron density, positive charge, lower valency shell

Examples of Nucleophiles



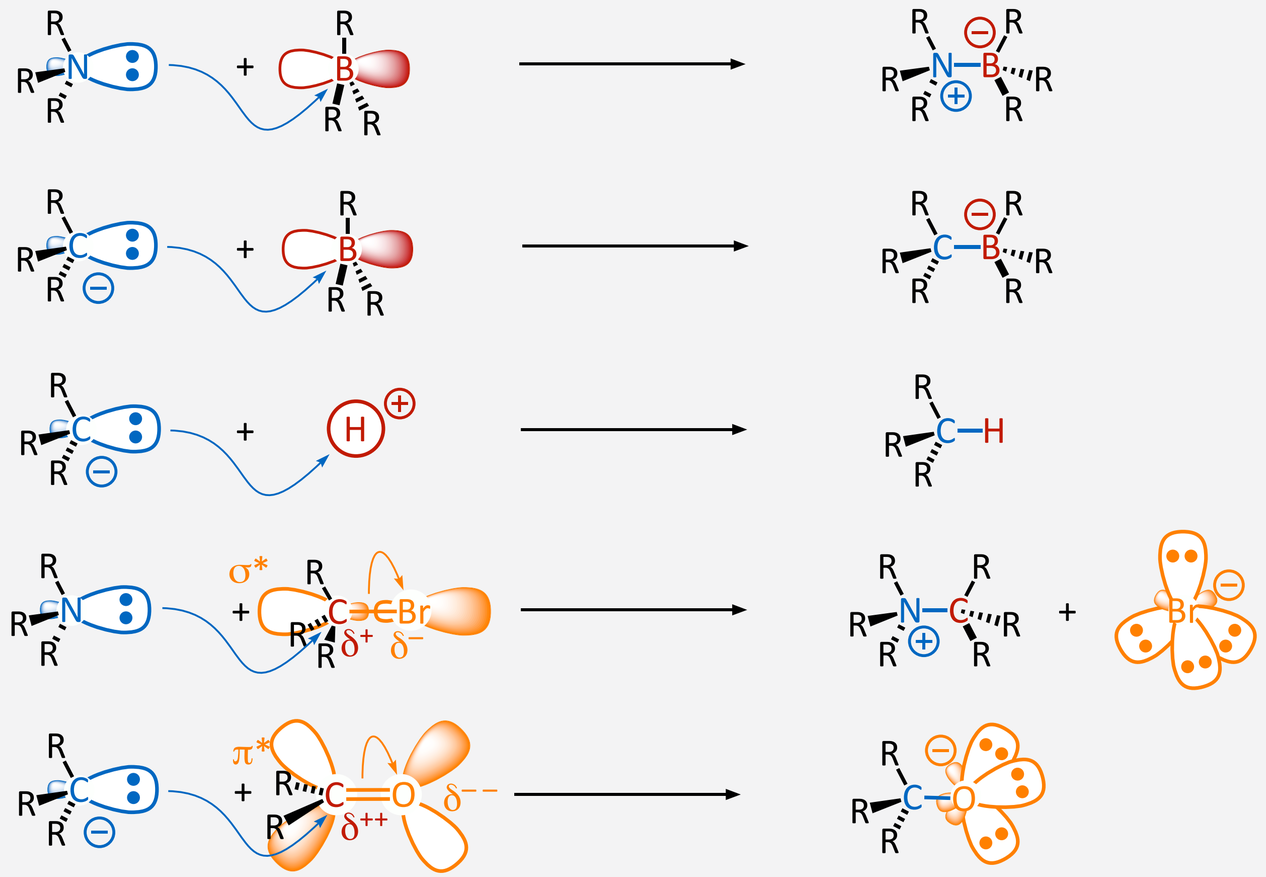
- **nucleophiles are electron pair donors**
  - nucleophiles must have a high energy electron pair available for bonding
  - nucleophiles can be negatively charged or neutral but must be electron-rich, polarizable species
  - typically a non-bonding electron lone pair (carbanion or a neutral / anionic 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, a low-energy antibonding orbital (such as a σ* MO of a weak bond, or π* MO in C=O)

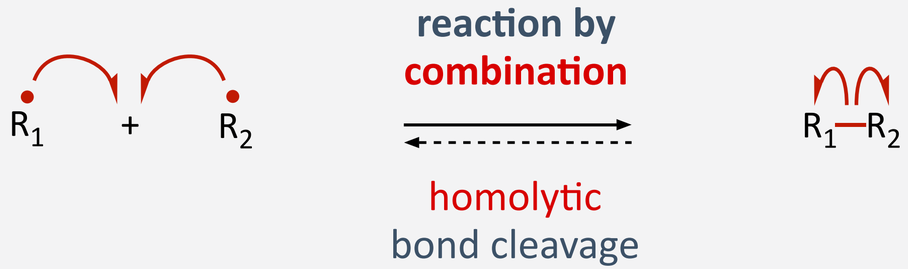
Writing Polar Reaction Mechanisms



- 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 from stable molecular precursors by homolytic bond cleavage of weak σ bonds (bonding electron pair is equally separated between the bonded atoms)



- **simple radical reactions occur between two (same or different) radicals**
  - formation of a new bonding electron pair by "combination" of the unpaired electrons (•)
  - bond formation hence requires electrons to have opposite spin (represented by half arrows)

Bond Energies

	ΔG / kJ mol^{-1}		ΔG / kJ mol^{-1}		ΔG / kJ mol^{-1}
H–OH	498	H_3C–OH	383	HO–OH	213
H–CH_3	435	H_3C–CH_3	368	MeO–OMe	151
H–Cl	431	H_3C–Cl	349	Cl–Cl	243
H–Br	366	H_3C–Br	293	Br–Br	192
H–I	298	H_3C–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)