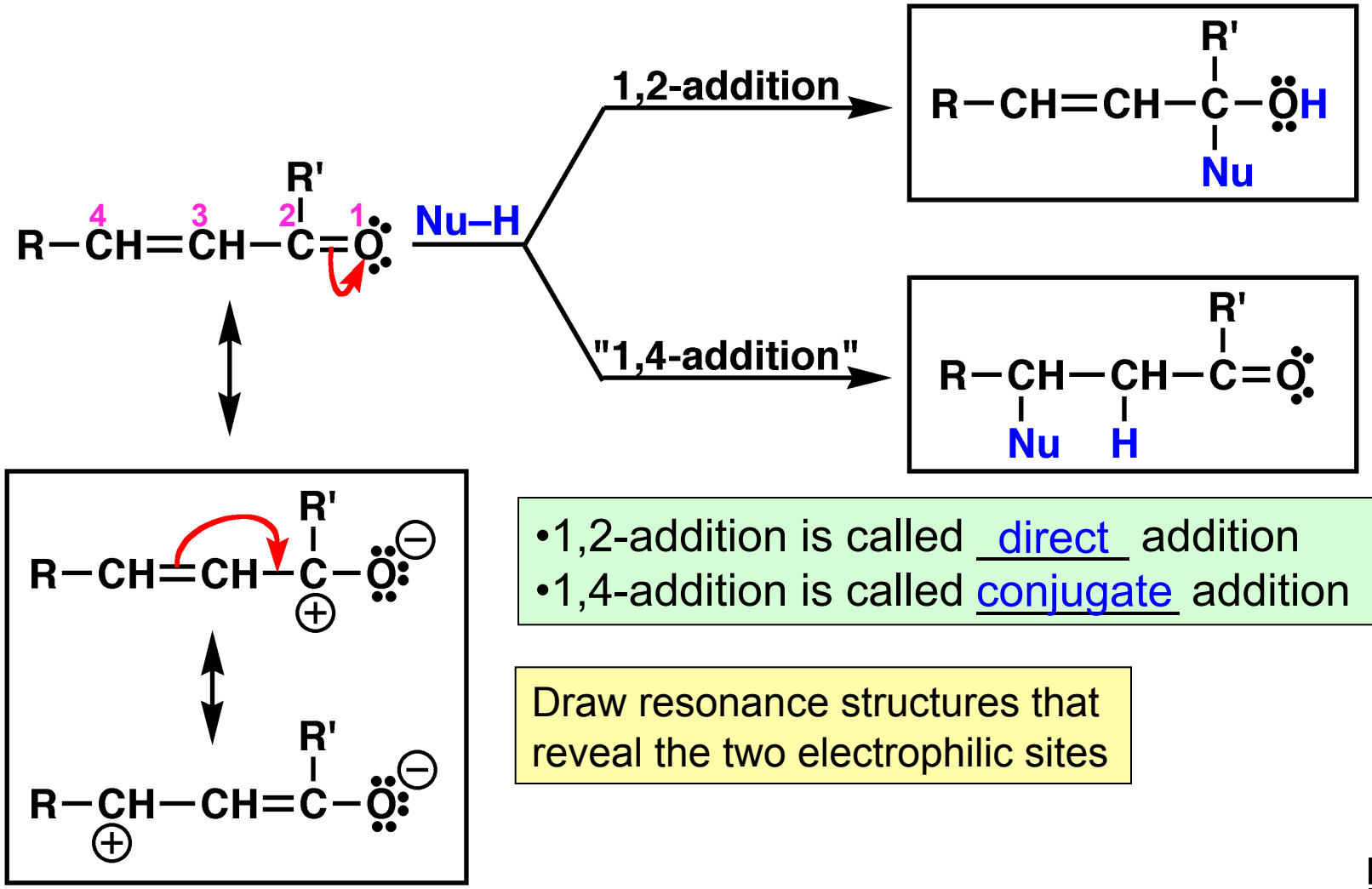
Nucleophilic Addition to α,β−Unsaturated Carbonyl Compounds



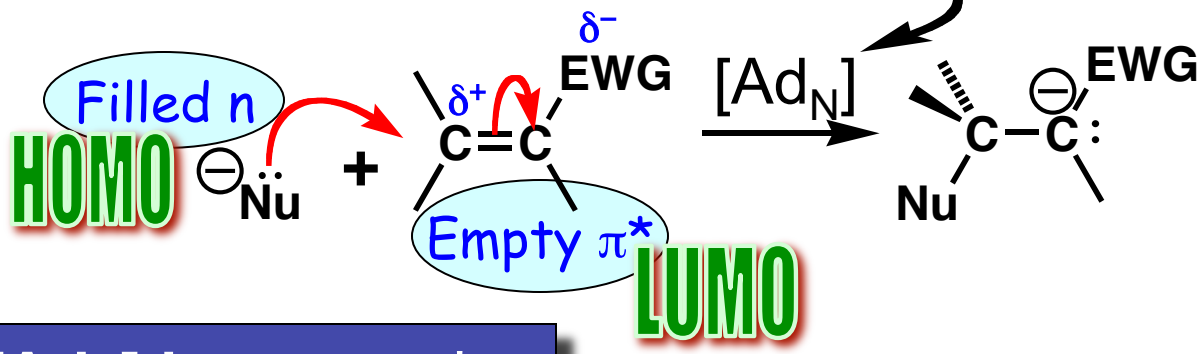
- 1,2-addition is called direct addition
- 1,4-addition is called conjugate addition

Draw resonance structures that reveal the two electrophilic sites

[Ad_N] Also Applies to Polarized C=C π-Bonds

EWG is an **electron withdrawing group** that polarizes the π-bond and lowers the LUMO energy

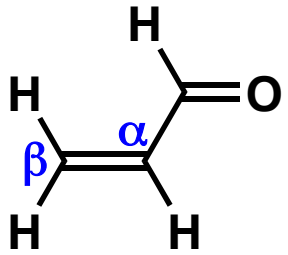
This symbol means nucleophile addition to a π-bond

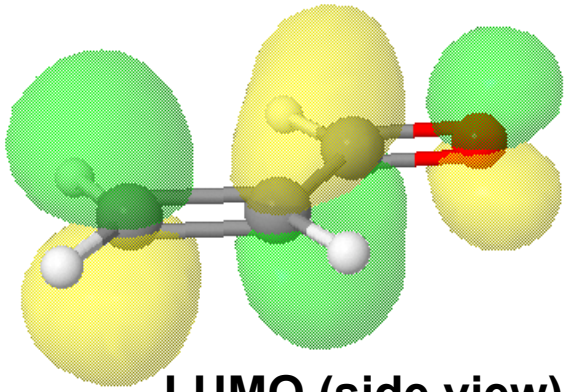


[Ad_N] involves σ-bond making and π-bond breaking

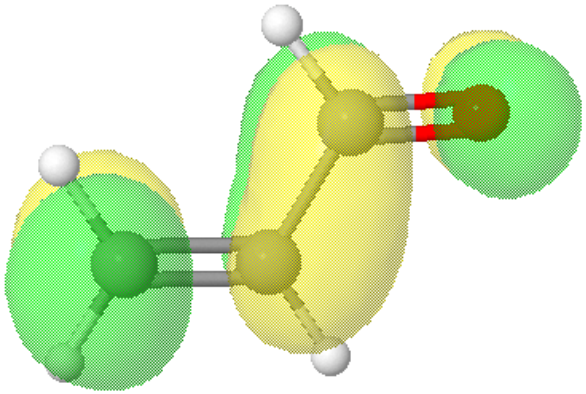
[Ad_N] is a *n* → π* σ-type interaction

Orbital calculations (see below) show that C_β makes a significant contribution to π*



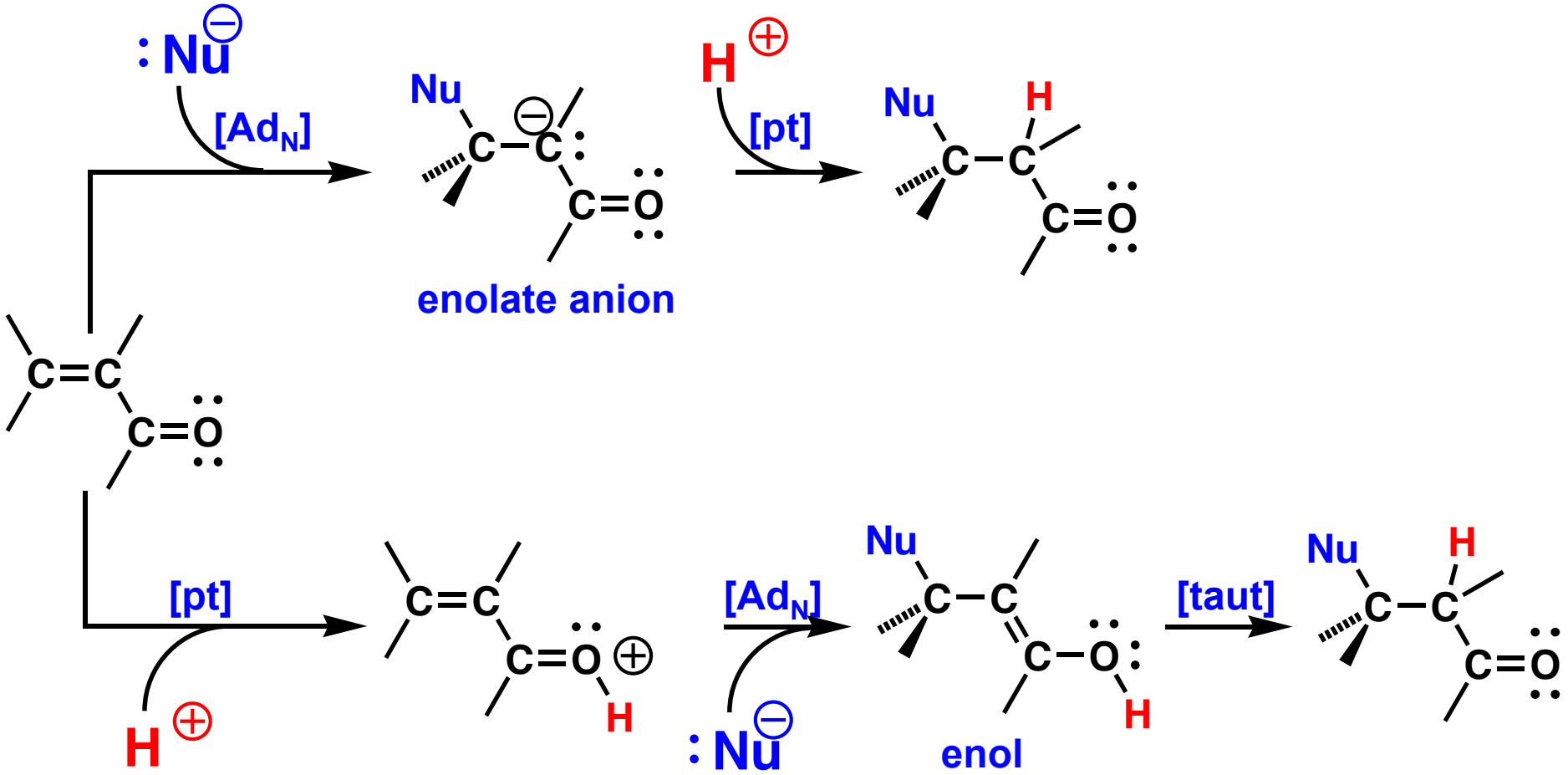


LUMO (side view)



LUMO (top view)

Analogous Pathways for Nu Addition to Polarized C=C



Nucleophilic addition to a polarized carbon-carbon π-bond takes place by analogous pathways. The top case is just like carbonyl addition except that [Ad$_N$] occurs at the C$_\beta$ site. The initially formed **enolate anion** is resonance stabilized (via electron donation into the withdrawing group (e.g., C=O)). For the bottom case, the proton first adds to the carbonyl oxygen. Then, [Ad$_N$] occurs at the C$_\beta$ site giving rise to an **enol**. The enol is usually unstable and undergoes spontaneous **tautomerization** to produce the addition product.