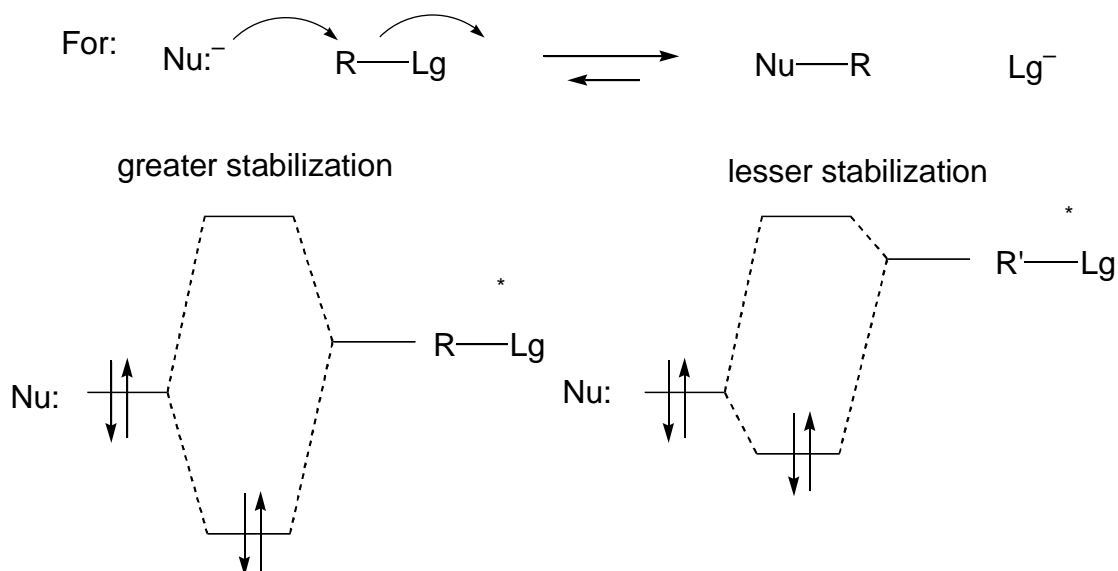


There are many factors that contribute to making a good nucleophile. Here are a few words and pictures about one of the most important of these. The subject is not an easy one because there are no (no!) absolutes here. For example, If I were to ask you, "Is iodide a good nucleophile?" the only possible answer is "With respect to WHAT Lewis acid?"

That is, something may be a good nucleophile in one reaction and a not-so-good one, or even a bad one, in another reaction. Here's why:

The phrase, "Lewis bases (nucleophiles) react with Lewis acids" can also be expressed: "The interaction of filled and empty orbitals is stabilizing." This is no trivial point, as we have just summarized most of chemistry in those few words. A nucleophile contains, by definition, a reactive pair of electrons. Those electrons must interact with a Lewis acid, an empty orbital. As we know, the closer two orbitals are in energy the more they interact and the greater the resulting stabilization. The further apart they are in energy, the smaller the interaction and the smaller the resulting stabilization. So, in general, for a good nucleophile you want a high energy HOMO, and for a good electrophile, you want a low-lying LUMO. Under those circumstances orbital energy matching is likely to be good and the reaction fast.



Nu:^- is a better nucleophile in the left diagram (lower energy LUMO) than it is in the right diagram (higher energy LUMO) because the orbital containing the reactive pair of electrons is closer in energy to σ^* of the substrate, R-Lg than it is to σ^* of R'-Lg .

So an answer to "What makes a good nucleophile?" might be, "A Lewis base in which the energy of the orbital containing the reactive electrons is close in energy to σ^* of the substrate, R-Lg ."

Be sure to read the book on this complex subject!