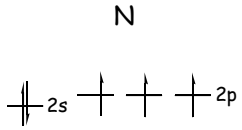
Appendix 1

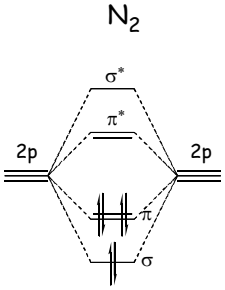
Theoretical basis for nitrogen scission

The chemistry of dinitrogen scission by $Mo[N(t\text{-}Bu)Ar]_3$ can be understood in terms of molecular orbital (MO) theory. In MO theory, the electrons of a molecule are viewed as residing in orbitals that may exist over the entire molecule and are not localized in bonds between atoms (valence bond or VB theory). Different levels of sophistication can be applied to MO theory, from high level quantum calculations, to simple "back of the envelope" treatments of the orbitals in a molecule. Nevertheless, each level of theory can provide very useful information about the electronic structure and chemical reactivity of a molecule.

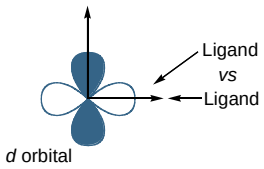
To begin, let us consider the MO picture of the dinitrogen molecule. In the free gaseous state, the nitrogen atom is a ground-state quartet ($2s^2 2p^3$), and prefers to form three bonds to complete its octet (e.g. HC≡N, NH_3, and PhN=NPh).



In the nitrogen molecule, these three unpaired electrons combine to form three bonds (one σ and two π). The result of this bonding is a very stable and unreactive molecule (ΔH_{dis} = 225 kcal/mol).

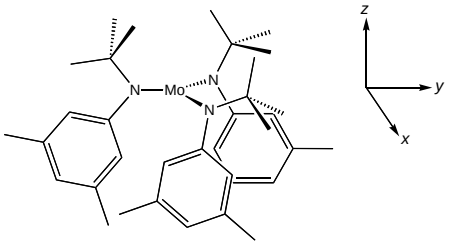


In the simple case of the N_2 molecule, the MOs can be thought of as the bonds between the nitrogen atoms (σ and two π) because there are only two atoms in the molecule. As molecules become more complex (larger numbers of atoms), however, it becomes more difficult to derive the MOs. Inorganic chemists have developed simplified ways of treating complex molecules so that information concerning the electronic structure and reactivity of metal compounds can be understood. One of the simplest methods for examining transition metal complexes is *crystal field theory* (CFT). In CFT, the ligands surrounding the metal are viewed as point charges. These charges interact with the familiar *d* orbitals (d_{z^2}, $d_{x^2-y^2}$, d_{xy}, d_{xz}, d_{yz}) with differing degrees of magnitude based on the directionality of the overlap with the orbitals. This interaction results in a Coulombic repulsion leading to an orbital on the metal (*d* orbital) of higher energy. For instance, a ligand which approaches the metal directly along an axis on which one of the *d* orbitals lies will give rise to a higher energy orbital then one which approaches at an angle.

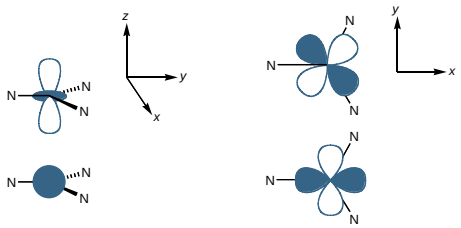


Since the *d* orbitals on metal atoms are typically those involved in the reaction chemistry (frontier orbitals), these are of greatest interest to the inorganic chemist. It is important to remember, however, that though these orbitals are considered to "belong" to the metal atom, they are still molecular orbitals. A more rigorous treatment known as *ligand field theory* (LFT) takes into account the covalent nature of metal ligand bonding, and derives MOs from linear combinations of atomic orbitals, instead of interaction of point charges and electron clouds.

Using CFT, we can begin to develop the MO picture of the Mo[N(t-Bu)Ar]$_3$ molecule. We will first consider the σ-bonding picture:

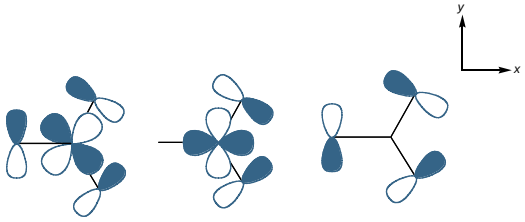


The three nitrogen atoms lie in a plane and are directed at 120º towards Mo.



The orbitals on Mo that participate in the σ bonding will be $d_{x^2-y^2}$, d_{xy}, and to a smaller extent d_{z^2}.

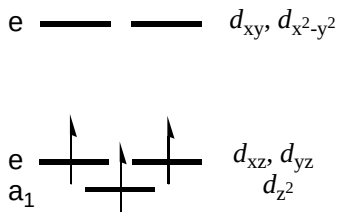
Next, let us consider how the p orbitals on nitrogen of π symmetry interact with the Mo atom:



The d_{xy} and $d_{x^2-y^2}$ also participate in π bonding with the p orbitals of the nitrogen atoms.

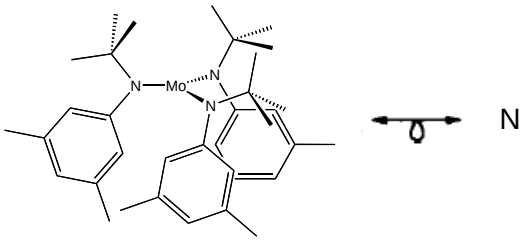
There is one combination of p orbitals for which there is no match on Mo. This set gives rise to a non-bonding MO (similar to lone pairs in VB theory).

When this information is put together, it becomes apparent that the d_{xy} and $d_{x^2-y^2}$ orbitals interact strongly with the *d* orbitals in Mo[N(t-Bu)Ar]$_3$, whereas the d_{z^2}, d_{xz}, and d_{yz} orbitals remain somewhat unperturbed from their original state in the Mo(III) ion. We fill in the electrons keeping in mind that Mo(III) has three electrons, and remembering to obey Hund's rule.

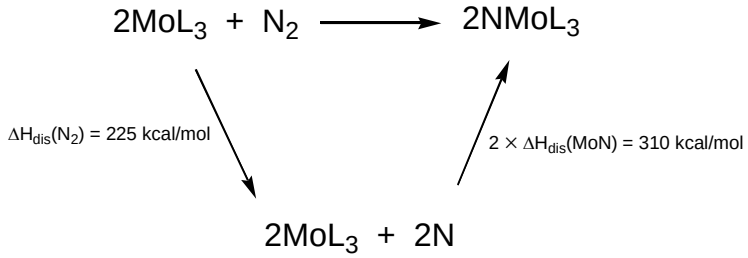


Note that we could have also arrived at this picture using LFT by considering how the ligand orbitals transform in C_{3v} symmetry, then considering the symmetry allowed interactions (combinations) with the orbitals on Mo (*s*, *p*, and *d*). The orbital labels above are symmetry designations derived from LFT, more familiar examples are the e_g and t_{2g} labels commonly encountered with octahedral complexes.

From the ordering of the *d* orbitals we see that the Mo[N(t-Bu)Ar]$_3$ molecule contains three unpaired electrons. This picture very much resembles that of the free nitrogen atom. This fact may even lead us to predict that Mo[N(t-Bu)Ar]$_3$ may react with nitrogen to form a very stable molecule. In fact, this idea is the basis of the *isolobal analogy*. Fragments are referred to as isolobal if the symmetry properties, approximate energy and shape of the frontier orbitals and the number of electrons in them are similar. The isolobal analogy is a very good guide in predicting the likelihood and magnitude of an interaction between two molecules or molecular fragments.



The result of the interaction between Mo[N(t-Bu)Ar]$_3$ and N is the nitride complex, which is the end product of the scission reaction. The very strong bonding interaction in the nitride complex provides the thermodynamic driving force for the splitting of the very strong N≡N bond.



Through MO theory we have just explained in large part why the scission takes place. We have not, however, addressed how this occurs. MO theory may once again be used to explain the mechanism of N_2 binding and scission at Mo[N(t-Bu)Ar]$_3$, but this treatment requires a slightly more sophisticated discussion. The aspects of MO theory concerning the mechanism of N_2 scission can be found in Prof. Cummins' paper, "Reductive cleavage and related reactions leading to molybdenum-element multiple bonds: New pathways offered by three-coordinate molybdenum (III)", *Chem. Communications*, 1998, 1777 – 1786, included as a supplement to

this writeup. The paper is also available on-line at
http://www.rsc.org/is/journals/current/chemcomm/cc998017.htm .