Hypervalent Molecules and Peripheral Orbitals

San-Yan Chu and Shyi-Long Lee
National Tsing Hua University, Hsinchu, Taiwan, Republic of China

Several discussions in the literature concerning the hypervalent systems (1-5) have appeared recently. Such systems are cited as examples in which the carbon atom violates the octet rule. In fact, those systems are hypervalent in a superfical sense, since a peripheral orbital not participating in bonding to the central atom is usually used for storing the extra electron(s). We feel that an introduction to these topics is quite educational since those special examples provide insight into the physical basis of the octet rule.

Schleyer et al. (1, 2) have discussed recently the bonding nature in hypervalent ClLi₃ and ClLi₂. They indicated that the octet rule still holds since the formal charges on the carbon are -0.81 in ClLi₃ and -0.93 in ClLi₂, not appreciably more negative than -0.81 in ClLi. The "extra" electron(s) actually contribute to the Li-Li bonding and help to start building a metallic "cage" around the central C atom.

In this article, we would like to point out a similar situation in some other hypervalent systems such as (C₅H₅)₃W⁺ and XeF₂ (where C₅H₅ = cyclopentane), of which each extra electron pair beyond the 18 electrons or 8 electrons is stored in the peripheral region of the molecule. Our discussion is designed to explore this general feature as well as some differences among these hypervalent systems including ClLi₃ and ClLi₂. We will also discuss the existence of such bonding patterns in certain reaction intermediates such as the penta-coordinated C atom in Sn₂2 reactions.

Ligand Nonbonding Orbitals

A brief introduction on the basis of the octet rule and the 18-electron rule will help us to appreciate their exceptions. In a common situation, all the bonding orbitals and nonbonding orbitals involving the central atom are populated, giving a formal total of 8 or 18 electrons around this atom. By bonding and nonbonding orbitals here we mean that the central atomic orbitals match and mismatch, respectively, in symmetry with the symmetry-adopted functions from the ligands. Therefore, any excess electron density beyond 8 electrons or 18 electrons is expected to occupy some antibonding orbital(s). The high nucleophilicity of such high-energy electron(s) would make the system quite unstable. However, the unfavorable antibonding situation can be avoided by localizing extra electron(s) in the peripheral region of the system. For instance, some symmetry-adopted ligand orbital may fail to find any low-lying metal orbital of the right symmetry to interact with. We should term the orbitals of this type as the ligand nonbonding orbitals. They can also be viewed as a counterpart of the more familiar nonbonding orbitals on the central atom. The existence of such ligand nonbonding orbitals allows the central atom to tolerate more electrons than the number permitted by the octet rule or the 18-electron rule (6).

Examples

One hypervalent system that can demonstrate this point clearly is (C₅H₅)₃W⁺ (7). By usual practice of electron count, W⁺⁺ atom is a d² ion with a nonbonding d² electron pair along the C₅H₅ main axis. Each Cp⁻ contributes 6 electrons to the central W⁺⁺ ion. The corresponding 18 electrons from Cp rings therefore occupy three sets of nearly degenerate levels (Fig. 1). Each set consists of three levels. The lowest a₁ + e set is the result of combining the three nodeless π orbitals on the Cp rings with suitable counterparts from the metal atomic orbitals. The second a₁ + e arises from the three Cp π orbitals with the nodal planes perpendicular to the C₅ axis, plus proper participation of metal atomic orbitals. The third set, a₁ + e set is a similar combination the three Cp π orbitals and metal atomic orbitals. In the last set, each Cp π orbital has a nodal plane passing through the C₅ axis. However, the a₁ orbital is a pure ligand-based orbital and is weakly antibonding among three Cp rings since there is no mixing of the metal (s, p, d) set in the C₅ₙ point group. Therefore, this is a peripheral ligand nonbonding orbital, oppositely comparable with the nonbonding orbital d₄² localized on the central metal. The rest of the 8 orbitals are active in metal-ligand bonding with various degrees. Thus the central atoms actually are associated only with 18 electrons out of 20, i.e., 2 from metal d₄² plus 16 from metal-Cp bonding orbitals.

It is interesting to examine an example of a simpler system, the expanded octet of Xe in XeF₂ with D₄h geometry in terms of the concept of ligand nonbonding orbital just presented. The electron configuration of XeF₂ is (1sₓ)²(1sᵧ)²(2sₓ)²(2sᵧ)²(1π)⁴ (8). Here 1sₓ is essentially of the atomic 5s (Xe) character and the 1π orbitals are largely of the atomic (5pₓ, 5pᵧ) character (2 axis is the molecular axis). Both can be called, in an approximate sense, the nonbonding orbitals on the central Xe atom. The bonding between Xe and F can arise only from the remaining 1sᵧ and 2sₓ orbitals. Note that for 2sₓ only negligible contributions from any atomic Xe orbital can be expected, since the vacant 5d(Xe) orbital is about 13 eV above, while the 5s(Xe) is about 8 eV above.
The antibonding interaction which may exist in some less symmetric geometries. A simple analogy is that the highest occupied MO, (1s₁ - 1s₃) in linear H₂, the intermediate in the H + H₂ reaction, is a "peripheral" nonbonding orbital localized on the two end atoms (11). It becomes an antibonding orbital in the triangular H₃ (12).

Finally let us return to the CLi₅ systems. Instead of being localized on the axial Li atoms, excess electron density tends to spread over all the Li atoms (1, 2). The α HOMO (4α₄ orbital) describes favorable bonding interactions between 12 neighboring Li-Li pairs against six C-Li small antibonding contributions. One may interpret that the octet of carbon is expanded by including a carbon 3s orbital as assisted by a set of electropositive Li atoms. This is different from the expansion in XeF₂ or CH₃X₂⁻ along one axis. Furthermore, in CLi₅ and CLi₆, the "extra" electron(s) are ligand-bonding rather than nonbonding, as in XeF₂ and CH₃X₂⁻ cases. However, they fit into a general pattern that hypervalent systems utilize the peripheral region in a molecule for storing the extra electron(s). Finally, there is nothing magic about peripheral nonbonding orbitals on the ligands. They can be simply referred to as a counterpart of the nonbonding orbitals on the central atom.

Acknowledgment

This work was supported by the National Science Council, Taiwan, Republic of China. Many helpful suggestions and corrections from the referee and T. S. Lee are greatly appreciated.

Literature Cited


Dexter Award Nominations Sought

The History Division of the American Chemical Society and the Dexter Chemical Corporation are soliciting nominations for the 1986 Dexter Award. The Award, which honors outstanding accomplishment in the History of Chemistry, consists of $1000 and an engraved plaque to be presented at the fall meeting of the American Chemical Society.

The nomination should consist of a cover letter containing an assessment of the contributions of the nominee to the field, a vita, and a bibliography of publications. Copies of no more than three select publications may also be included if available. The documents should be forwarded to: Robert H. Goldsmith, Secretary-Treasurer of the History Division, Division of National Science, Anne Arundel Hall 201A, St. Mary's College of Maryland, St. Mary's City, MD 20686. Please submit nominations no later than January 1, 1986.