The fragment molecular orbital approach in organometallic reactivity. Reactions of the binuclear complexes

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Abstract. The fragment molecular orbital approach has emerged as a framework model in theoretical organometallic chemistry. This provides an understanding of the electronic structure and bonding in polynuclear complexes in terms of their constituent fragments that are well understood. Symmetry properties of the frontier molecular orbitals of organometallic complexes help in explaining their reactivity towards various reagents.

Keywords. Fragment molecular orbitals; reactivity in organometallics.

1. Introduction

Modern transition metal organometallic chemistry defies most attempts at prediction. With the experimental facilities at his disposal the organometallic chemist generates a bewildering array of complexes (Wilkinson *et al* 1982; Yamamoto 1986). Whether these are products of planned syntheses or fall-outs from totally unexpected conditions, nature has taken its course. It is left to the chemist to develop a model based on the available information for understanding the structure and bonding of these complexes and the reactions leading to them. After a measure of success is achieved in explaining the observations, predictions can be attempted based on the same model. Here we present a brief introduction to the fragment molecular orbital approach, which is a reasonably successful model for understanding the structural preferences of transition metal organometallic complexes (Hoffmann 1981). Reactivity presents a more formidable problem. Examples of the theoretical studies of the reactivity of binuclear complexes leading to new C–C bonds will be discussed based on the fragment molecular orbital approach.

2. The fragment molecular orbital approach

In this approach the molecule is divided into smaller fragments that can be understood easily. The variations in the energy levels and wavefunctions of the fragments as a result of the reconstruction of the molecule provide valuable insights. Such a method has been used frequently in organic chemistry (Jorgensen and Salem 1973). It is ideal in organometallic chemistry where the fragmentation only separates the organic and metal parts. An ever-expanding library of the
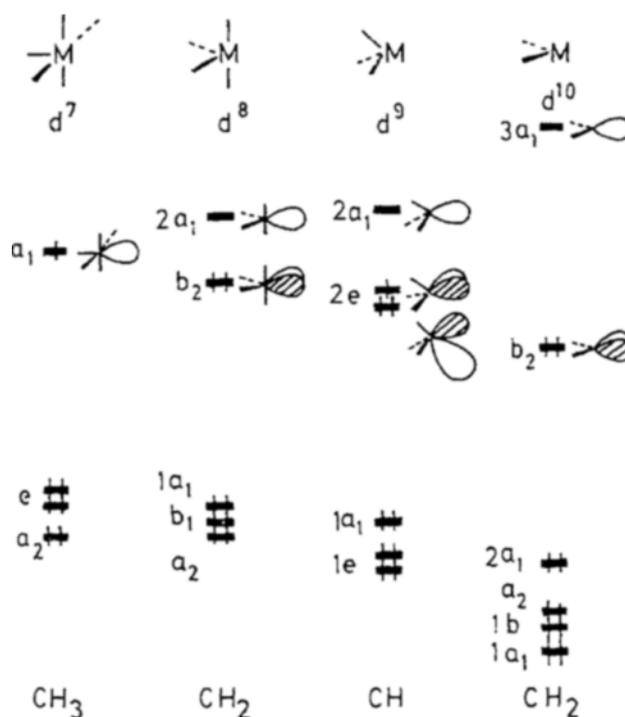
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Figure 1. The frontier orbitals of ML_5, ML_4, ML_3, and ML_2 fragments and their isolobal organic equivalents.

molecular orbitals of such fragments are available (Albright *et al* 1985). These can be constructed logically starting from the molecular orbitals of a transition metal complex. Figure 1 shows the frontier orbitals of a general octahedral complex and the fragments ML_5, ML_4, ML_3, and ML_2 (Jemmis and Hoffmann 1980). The variation of the energy levels as a function of the structure of these fragments is studied in detail. The basic splitting of the d orbitals in an octahedral field and the decrease in energy of metal based orbitals on removing each ligand justify these orbital patterns. From a valence bond point of view the removal of a ligand leaves a directed orbital at the metal. When there are more than one such orbital the appropriate symmetry-adapted linear combinations are shown. Even though the details vary with the ligand, the general pattern of orbitals is independent of them. The use of the fragment approach is not restricted to these small fragments. If a fragment, however large it may be, appears as a common part in many complexes it is profitable to analyse the electronic structure in terms of the fragment molecular orbitals of the larger fragment (Hoffmann 1981).

Just like the building-up of complicated organic molecules from smaller fragments such as CH_3, CH_2, CH and C, that of larger stable organometallic complexes may be envisaged by putting together the ML_n fragments with appropriate organic groups. The advantage of such a treatment has been amply demonstrated. Thus the interaction of a d^7 ML_5 fragment, say $Mn(CO)_5$ with CH_3 gives $Mn(CO)_5CH_3$ with an Mn–C σ bond. Two of these fragments could give $(OC)_5Mn–Mn(CO)_5$ with an M–M σ bond.

A somewhat more complex example is shown in some detail. Derivatives of $(OC)_2Ni(\mu-C_3H_3)$ $Ni(CO)_2^+$, 1 are shown to possess a C_{2v} structure where the C_3H_3 group straddles the M–M bond (Jeffery *et al* 1981; Jemmis and Prasad
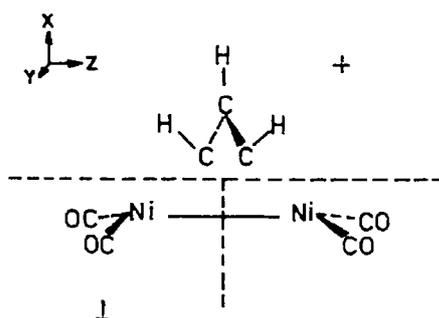
1987b). Let us see how the fragment molecular orbital approach helps in understanding the factors that hold this molecule together. The obvious way of dissecting this molecule is into $(CO)_4Ni_2$ and $C_3H_3^+$ groups. The $(CO)_4Ni_2$ can be further divided into the two $Ni(CO)_2$ groups. The d^{10} ML_2 fragment has a LUMO a_1 (mostly a $4s$, $4p$ hybrid) and a HOMO b_2 (mostly d_{xy} in the coordinate system shown in 1). The remaining metal orbitals lie much lower in energy. When two $Ni(CO)_2$-groups are brought together the frontier orbitals obtained are the bonding combinations of the sp hybrid and the two π type orbitals arising from the $b_2(d_{xy}$ orbital) (figure 2). The lower-lying occupied orbitals do not play much of a role in binding the C_3H_3 unit. The frontier orbitals of the C_3H_3 group can be obtained starting from the well-known allyl cation. Removing two hydrogens from the allyl cation leaves the bonding and anti-bonding combination of the hybrid orbitals. The non-bonding π MO is also within the bonding range in relation to the metal fragment. Since there are three orbitals of matching symmetry in $Ni_2(CO)_4$ and the number of electrons involved, six, is sufficient to occupy the three bonding combinations the structure is stable (Jemmis and Hoffmann 1980; Jemmis and Prasad 1987b).
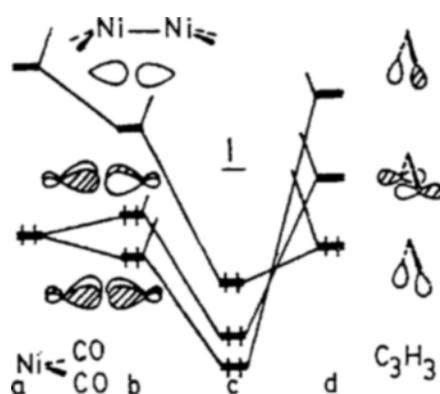

Figure 2. The construction of frontier orbitals of $(CO)_2Ni(\mu\text{-}C_3H_3)Ni(CO)_2^+$, 1. (a) The frontier molecular orbitals of $Ni(CO)_2$ (cf. figure 1). (b) Only three frontier orbitals result from the interaction of two $Ni(CO)_2$ fragments. (c) This represents the 3 pairs of 2e-2 orbital interactions leading to the stable structure 1. (d) The nonbonding π and the σ and σ^* combinations of the didehydroallyl cation.

3. Isolobal analogy

Often the concept of isolobal analogy is employed for comparison of the organometallic complexes with the familiar organic compounds. Two groups are termed as isolobal if the number, symmetry properties, approximate energy and shape of the frontier orbitals and the number of electrons in them are similar (Hoffmann 1982). The various ML_n fragments in figure 1 are then isolobal to CH_3, CH_2, CH. This enables us to predict the organometallic equivalents of cyclobutane, tetrahedrane and the like. All these enable us to look at the electronic structure and bonding in organometallic complexes in comparison to those of the organic counterparts. With a series of replacements the $Ni_2(CO)_4(\mu - C_3H_3)^+$, 1, discussed above can be shown to be the organometallic equivalent of cyclopentenyl cation (Jemmis and Prasad 1987b). What can be said about reactions involving organometallic compounds?

## 4. The fragment molecular orbital approach to reactivity

In principle the potential energy hypersurface for a given assembly of atoms can be studied theoretically. In practice however, only the smallest of these can be done currently with the desired accuracy. Theoretical methods at various levels of approximation have been applied to study reactions of organometallic compounds. A survey of the theoretical study of the various reactions involving C–C bond formation at mononuclear complexes shows that just about all theoretical methods available for calculation of the electronic structure of molecules have been employed. These include the Extended Hückel method, various modifications of the semiempirical SCF methods, the non-empirical Fenske-Hall, ab initio SCFMO with CI, and the Generalized Valence Bond method. The reactions studied are methyl migration or carbonyl insertion (Koga and Morokuma 1986), olefin metathesis (Rappe and Goddard 1982), ethylene coupling (Steigerwald and Goddard 1985), Ziegler-Natta catalysis (McKinney 1980), oxidative addition and reductive elimination (Low and Goddard 1986), and double carbonylation (Tatsumi et al 1986).

A common observation in all of them is that at the end of even the most sophisticated study, numerical predictions cannot be made with a high degree of accuracy, and hence, the results are analysed in terms of qualitative concepts. This may remain so for some time to come.

There are a few studies of the reactions of binuclear and polynuclear complexes (Hoffmann et al 1978). The concept based on perturbation theory and symmetry developed for organic reactions (Woodward and Hoffmann 1971; Fukui 1975; Fleming 1976; Klopman 1974) can be profitably extended to the transition metal complexes. Such extensions are not very straightforward due to the increased number of variables present. Each set of reactants has to be analysed as a separate problem for some time to come. With the experience gained from a series of such studies, generalizations that are widely applicable should emerge. We shall now present an example where a fragment molecular orbital approach based on a qualitative wavefunction provided useful insight into an organometallic reaction (1) (Jemmis and Prasad 1987a). The substituents on the carbons are shown as

R = CH$_3$

+ HC $\equiv$ CH $\longrightarrow$

(1)
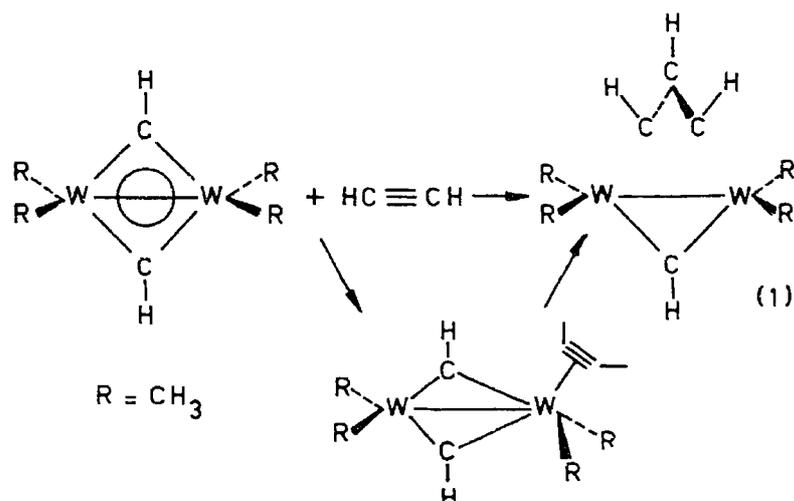
hydrogens for simplicity. The following points may be noted about this reaction. Among the two μ-CH groups only one group reacts even if an excess of acetylene is used. Reaction is facile with acetylene or allene but does not proceed with ethylene or butadiene. Isostructural Ta and Nb complexes which have two electrons less do not react with alkynes under the same condition. An intermediate acetylene π complex has been isolated and characterized during this reaction. A fragment molecular orbital analysis showed that the HOMO is a metal-metal σ bond and LUMO is δ^* in character. Distortion of this compound to a geometry appropriate to those found in the intermediate acetylene complex localizes the HOMO and LUMO to the pyramidalized metal. This facilitates the donor acceptor interactions shown in $\underline{2}$.

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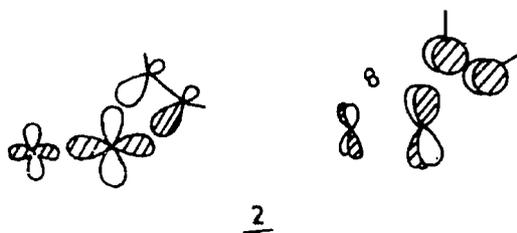
Since these involve a μ donor orbital in one plane and a μ acceptor orbital in a perpendicular plane of the organic group, only molecules with μ orbitals in perpendicular planes will react. Thus alkynes, allene, CO, HCN, HNC etc. but not butadiene and ethylene are expected to react. The reaction may not proceed if two electrons that form the M–M bond are not available for donation. This happens in Nb and Ta complexes. There is already an incipient bonding between the intermediate acetylene complex which proceeds to form the product with a bridging C$_3$H$_3$ group. A comparison of the LUMO of (CH$_3$)$_2$W(μ-CH)$_2$W(CH$_3$)$_2$ and the final complex explains the absence of reactivity of the μ-CH group of the final complex with excess acetylene. The replacement of the CH group by C$_3$H$_3$ brings in the nonbonding π orbital of a_2 symmetry. This orbital, occupied in the current electron count, has the right symmetry for interaction with the δ^* orbital pushing it from the bonding range. Hence acceptance of electrons from the acetylene is not possible, thus preventing the reaction (Prasad *et al* 1986).

The fragment molecular orbital approach has recently been applied to study the reactivity of $[C_pFe(CO)]_2(\mu\text{-}CO)(\mu\text{-}L)(L = CO, CH_2, C = CH_2, CH^+)$ (Bursten and Cayton 1986). Here two CpFe(CO) units are brought together. This is interacted with one bridging carbonyl. The resultant $[C_pFe(CO)]_2$ ($\mu-CO$) group has been combined with various second-bridging substituents. The photochemical reactions of the doubly-bridged complexes are shown to be LUMO-controlled. Protonation of the complex is shown to be controlled by the nature of the bridging ligands. It is charge controlled when $L = CH_2$ but orbital controlled when $L = CO$. We feel that there is a lot to be gained by such studies of polynuclear systems.

5. Conclusions

A fragment molecular orbital approach where a molecule is schematically dissected into small fragments which are well-understood helps in understanding the electronic structure and bonding of transition metal organometallic complexes. This is demonstrated for $(OC)_2Ni(\mu - C_3H_3)Ni(CO)^+$. Theoretical studies of the reactions of transition metal complexes are more difficult and less common. Symmetry and overlap-based arguments may be applied for explaining and predicting reactivity in specific cases. The reaction of $L_2W(\mu - CR)_2WL_2$ with acetylene is given as an example.

Acknowledgements

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