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AN ORBITAL SYMMETRY DESCRIPTION OF TRANSITION METAL CATALYZED BUTADIENE CYCLOBUTANATION

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The concerted, suprafacial fusion of two olefins to a cyclobutane ring is symmetry-forbidden (1). This transformation can, in theory, proceed on the coordination sphere of certain transition metals (2). The metal in this process ("forbidden-to-allowed" catalysis) performs a special function involving an exchange of electron pairs with the transforming olefin ligands. The metal-catalyzed fusion of adjacent olefin ligands proceeds with a relocalization of d electron density (2) which can introduce transformation restraints depending on the nature of the fusing olefin ligands (3) and the ligand field.[a)] The role of the transition metal in the cyclobutanation of coordinated butadiene ligands differs from that in the cyclobutanation of simple, nonconjugated olefins or acetylenes. This Note discusses some differences and their implications to catalysis.

Consider the concerted interconversion of the bis(cis-butadiene)metal complex I (C_{2v}) and the cis-1,2-divinylcyclobutane metal complex II (C_s) (cf. figure). In this transformation, the ZY plane is the element of symmetry maintained by the composite molecular orbitals. The ligand orbitals in I and II are assigned to the symmetric (S) or antisymmetric (A) set according to their symmetries about the ZY plane. These assignments are indicated in the correlation diagram in the figure; the subscripts in the symmetry symbols refer to the particular ligand orbitals used in the indicated combinations, e.g., A_{ψ_2} refers to the antisymmetric combination of butadiene ψ_2 orbitals in I and S_{π^*} to the symmetric combination of olefin ligand π^* orbitals in II. The metal atomic orbitals similarly fall into S and A sets. The metal d_{xy}, d_{xz} and p_x are A and the remaining six are S. S_m in the figure refers to the two remaining metal symmetric

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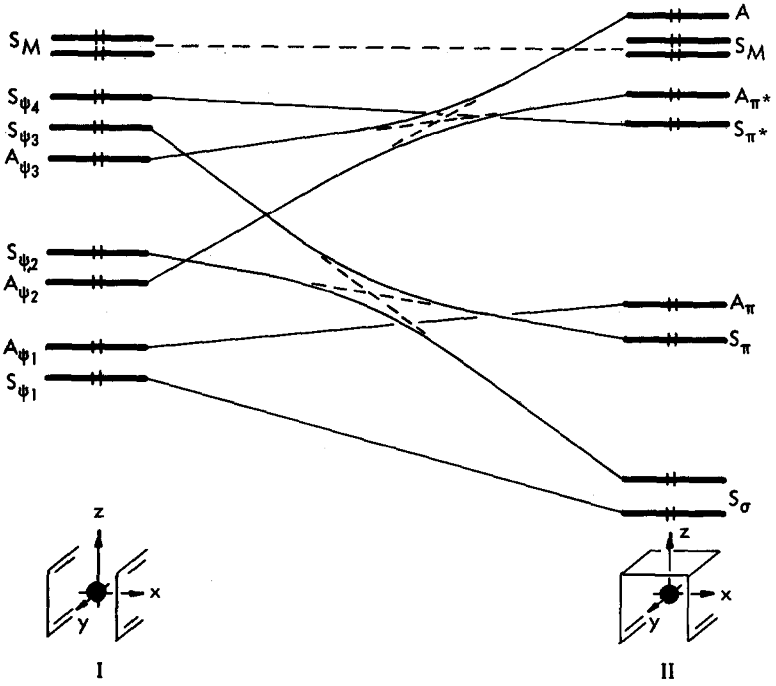
[a)] Three possibilities exist for the ligand field splitting of the two critical metal d orbitals (i.e., the ligand field exclusive of the transforming olefins), 1) the orbitals are left degenerate in which case no restraints are imposed, 2) the AS (2) orbital is of higher energy introducing the possibility of generating a metal complex in an excited state, and 3) the SA orbital is of higher energy which can, conceivably, provide ligand field driving force for the ground-state transformation.

Figure. Correlation diagram for the interconversion of bis(cis-butadiene)metal (d^{10}) and cis-1,2-divinylcyclobutane metal (d^{10}).



atomic orbitals; the orbital designated A (in II), left unassigned, refers to the next highest orbital of A symmetry. This orbital should possess some antibonding properties with respect to the divinyl ligand system.

The ordering of the molecular orbitals in I and II illustrated in the figure is only approximate; further, the metal atomic orbital assignments have been deliberately omitted since they would in fact be complex mixtures dictated by energy and overlap factors differing with each metal system. These factors, however, should not significantly alter the arguments to be presented.

In the forbidden-to-allowed process, the critical orbitals are the crossing S_{ψ_3} and A_{ψ_2}. Conceivably, a number of metal systems can provide the appropriate number of valence electrons and orbital ordering to allow a ground-state interconversion of the ligands. In the hypothetical system in the figure, for example, d^4 metal systems would provide the ground-state[a] metal complex ordering for ground-state ligand interconversion. These metal systems need not be

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[a] We are not considering here low energy excited states. Excited states of metals with fewer d electrons could have the proper symmetry for smooth interconversion.

the most energetically favorable, however. If one considers the change in ligand-to-metal bonding character that accompanies ligand transformation a somewhat different picture emerges. The bonding between the metal and ligand systems stems from donor interactions (ligand bonding orbitals-to-metal) and backbonding interactions (metal-to-ligand antibonding orbitals). In I, there are three backbonds, the $S\psi_4$, $S\psi_3$, and $A\psi_3$, in II there are two, $A\pi^*$ and $S\pi^*$. Maximum bonding between the transforming ligands and the metal should be achieved when the entire core of bonding orbitals in the product complex correlates with occupied orbitals of the starting complex. Assuming the orbital ordering in the figure, maximum bonding should be maintained in I → II with metal systems containing six or more valence electrons. For the reverse transformation (i.e., II → I) ten valence electrons would be required, i.e., to occupy all three A orbitals in II and maintain full bonding across the reaction coordinate with incipient formation of $A\psi_1$, $A\psi_2$ and $A\psi_3$. This description does not restrict transformation II → I to d^{10} transition metal systems, however. Additional donor ligands on the metal could play a contributing role in this catalytic transformation by reordering metal valence electrons through coordination with the metal. Metal systems with fewer valence electrons could thus populate the third A orbital in II thereby providing a full bonding core of populated orbitals across the reaction coordinate. Metal systems rich in valence electrons should nevertheless be catalytically more active than other systems which can less readily provide the indicated ordering, other considerations being equal.

It is important to separate the role of the metal in its forbidden-to-allowed capacity from its other catalytic functions. The metal-free concerted interconversion of *bis*-butadiene and *cis*-1,2-divinylcyclobutane requires an intersystem flow of electron pairs between the bonding cores of I ($S\psi_2$, $A\psi_2$, $A\psi_1$ and $S\psi_1$) and II ($S\sigma$, $S\sigma$, $S\pi$, $A\pi$). The metal can achieve this by populating $S\psi_3$ in I and $A\pi^*$ in II and by providing two empty orbitals of the same symmetries (2). To the extent that these operations are not achieved, the ligand transformations remain "forbidden" in the Woodward-Hoffmann sense (1). The second function of the transition metal is to maximize ligand-to-metal bonding across the reaction coordinate by providing a sufficient number of valence electrons and the required ordering of metal complex orbitals. Deficiencies here need not preclude reaction. This area reflects more the energetics of the process, and not necessarily "forbiddenness" in the previous sense.

Butadiene is converted smoothly to *cis*-1,2-divinylcyclobutane with various zero-valent nickel complexes (4). This reaction produces, in addition, cyclooctadiene and vinyl cyclohexene. It has also been demonstrated that the divinylcyclobutane is formed reversibly; thus butadiene and the spectrum of other products formed can be obtained from the divinylcyclobutane. All products from this reaction are believed to be formed from π-allyl intermediates generated from the condensation of nickel-coordinated butadiene ligands.

The symmetry arguments presented here do not allow a definitive statement on the actual role of zero-valent nickel in these reactions. This simple molecular orbital treatment indicates only that a ground-state reaction path exists (I $\rightleftarrows$ II), and, further, that it is particularly favorable for d^{10} transition metal systems (e.g., zero-valent nickel). This does not imply, however, an obligation in any reaction system for a single step reaction along the thermally-allowed reaction coordinate. Similarly, the observation that some products in a reaction arise through π-allyl intermediates (5) does not preclude contributions from the concerted reaction path, even significant ones. These results, we feel, do introduce the concerted interconversion I $\rightleftarrows$ II as a viable candidate in nickel(0)-butadiene chemistry.

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