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THE ROLE OF COORDINATE BONDING IN METAL-CATALYZED SYMMETRY-FORBIDDEN VALENCE ISOMERIZATIONS

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Symmetry-forbidden reactions (1) can presumably be catalyzed in a variety of ways including a special case in which a transition metal totally removes the symmetry restrictions to reaction through metal-ligand orbital interactions (2). In this process ("forbidden-to-allowed"), the ligand transformation exactly mirrors the metal-free, symmetry-forbidden organic reaction. This proposal has recently received critical attention questioning the relevance of symmetry factors to the catalysis of concerted forbidden reactions (3). In this treatment, certain assumptions were made which may not have been valid.[a] Moreover, formally symmetry-forbidden ligand transformations were addressed to support the central theme when alternative, symmetry-allowed paths existed which, if considered, would have altered basic conclusions. We wish to discuss these points here placing them in broader perspective. We shall show that orbital symmetry conservation is tightly associated with metal-ligand coordinate bonding, that coordinate bonding is preserved along the forbidden-to-allowed path and that the coordinate bond creates in the ligand system a propensity to transform along this route.

To illustrate these points, we shall consider the [2 + 2] valence isomerization generally, simply as two localized bonds coordinated to a metal, in a bidentate manner, transforming to a new valence bond configuration, specifically A ⇄ B in Figure 1.

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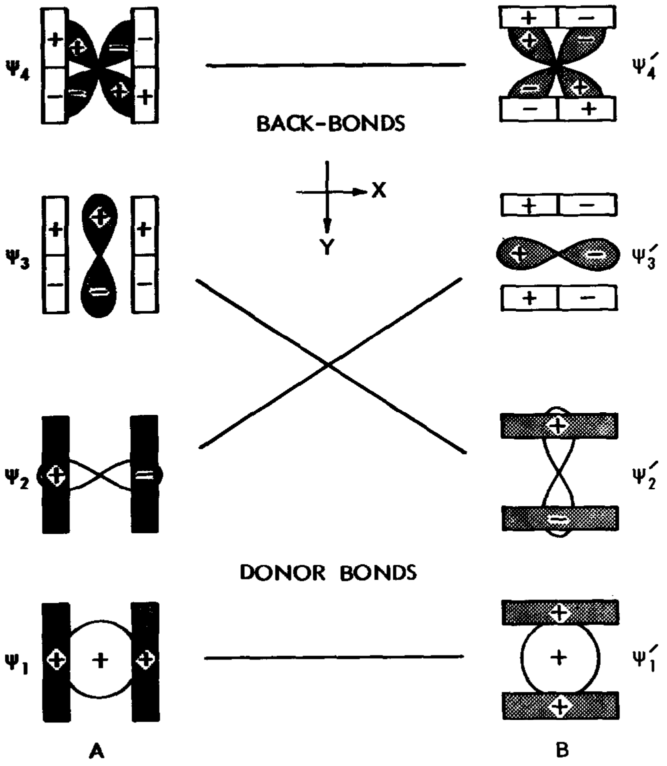
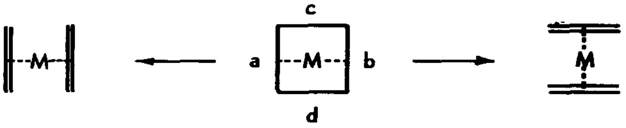
[a] The catalysis of forbidden reactions by Ag^+ (4) was compared to similar processes by other transition metals assuming a common mode of catalysis. The d^{10} electronic configuration of Ag^+ was cited as being unable to support concerted ligand transformations in an allowed manner and configuration interaction was offered to explain the metal's role. The importance of orbital symmetry factors was thus questioned generally for other metals since it did not seem to be a critical factor with Ag^+. But Ag^+ may operate catalytically in a distinctly different way from other elements. The novel Ag^+ catalyzed $[{}_{\sigma}2_a + {}_{\sigma}2_a]$ process recently reported (4b) appears unique to silver, suggesting a special mode of catalysis. The deposition of metallic silver in some cases (4c) indicates that electron transfer occurs in some systems suggesting that it may be an important feature to silver's role, perhaps involving intermediate ion radicals. Whatever the case, Ag^+ would seem to be sufficiently different from most transition elements (5) to make the assumption of common mechanisms questionable.

Figure 1. Correlation diagram for a $[2_s + 2_s]$ pericyclic ligand transformation. In this perspective, the ligand orbitals (represented by rectangles) rest in a plane above and parallel to the XY plane which contains the metal center (thus only the upper lobes of the d_{zx} and d_{zy} orbitals are projected). Shaded areas represent centers of maximum electron density within the respective molecular orbitals. Pure d orbitals can be assumed for simplicity; the exclusion of metal s and p mixing is not implied.



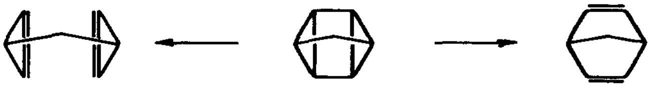
In the Figure the distribution of metal valence electrons in A and B describes full bidentate coordinate bonds to the respective ligand systems, i.e., $[d_{z^2}, d_{zx}, d_{zy}(2), d_{xy}(2)]$ for A and $[d_{z^2}, d_{zy}, d_{zx}(2), d_{xy}(2)]$ for B. Since the occupied orbitals in A correlate with occupied orbitals in B, the transformation A → B is symmetry-allowed. There is in this process an exchange of electron pairs between the metal and the ligand system (2) which proceeds through $\psi_2 \rightarrow \psi_3'$ and $\psi_3 \rightarrow \psi_2'$. It is this process which redistributes the metal electrons in such a way (i.e., $[d_{zx}, d_{zy}(2)] \rightarrow [d_{zx}(2), d_{zy}]$) to refocus the metal's bidentate bonding centers 90°, thus preserving full bidentate coordination with the $[2_s + 2_s]$ pericyclic process. Moreover, the population of ψ_3 in A alters the bonding configuration of A in the direction of B, creating a propensity to transform along that reaction path. The metal, through back-bonding, mixes into the ground state configuration of ligand system A a portion of its excited state, the composite reflecting bonding configuration B. A bidentate ligand system such as A with full coordinate bonding to a metal should experience molecular distortion in the direction of B (i.e., bond orders between bonded nuclei in A will diminish while increasing between bonded nuclei in B), and, given thermodynamic driving force, should possess a propensity to transform to B with preservation of full coordinate bonding.

A coordinated cyclobutane ring can open to a bis-olefin system in two directions (eq. 1) (2b).



C A B 1)

The ordering of the metal's valence electrons will focus bidentate coordinate bonding at centers ab (A, Figure 1) or cd (B, Figure 1). When the coordinate bonds are focused at centers ab, path A → B is symmetry-allowed (neglecting restrictive ligand fields (2b)) and path A → C remains formally symmetry-forbidden. In the example used by van der Lugt (3), only path A → C was considered and reaction along this path was described through configuration interaction. Path A → B, however, was available, and it would have been symmetry-allowed, receiving assistance of the kind noted in Figure 1. For [2 + 2] pericyclic transformations in which system A has clearly preferred bidentate sites of coordination, the forbidden-to-allowed path (A → B, Figure 1) would be the clear choice. Consider the metal-catalyzed isomerization of quadricyclene (I) to norbornadiene (II) (6). I has a second valence isomer, the dicyclopropenyl



III I II

derivative III. The relative stability of III is not known, but reasonable approximations place it below I and II (7). Quadricyclene can assume bidentate bonding with a metal center using either one of its two sets of σ bonds (i.e., ab or cd). If bonds ab are the centers of bidentate coordination, quadricyclene undergoes a molecular distortion in the direction of its excited state configuration, namely, norbornadiene (II). This would be an energetically favorable distortion since II possesses significantly less strain energy than I (ca. 65 Kcal/mole (7)). If, on the other hand, bonds cd are the centers of coordinate bonding, I should experience ring distortion in the direction of III, the least preferred of the three valence isomers. For I to transform to II along the symmetry-forbidden reaction path, with configuration interaction (3), quadricyclene must direct bonds cd towards the metal's centers of coordination. Considering the strong propensity for I to transform to II, it is doubtful that this would be the case. Quadricyclene should be a strong ab bidentate ligand, ordering metal electrons as indicated in Figure 1, thereby releasing the maximum amount of ring strain with coordinate bonding. Indeed, the coordination of ab seems to virtually unlock the energy-rich configuration I, allowing the smooth, energetically favorable and ground state expansion to II. This process, moreover, proceeds with preservation of metal-ligand bidentate coordinate bonding.

It has been suggested that orbital symmetry conservation is not relevant to the transition metal catalysis of symmetry-forbidden transformations (3). Orbital symmetry conservation and coordinate bonding, however, are closely related. Orbital symmetry factors would only seem to be irrelevant to concerted ligand transformations along otherwise restricted paths if coordinate bonding was irrelevant to the metal's role. If coordinate bonding is important in the catalytic chemistry of these systems, then orbital symmetry conservation becomes equally so, the two factors being inseparably related.

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