Aromatic Stabilization of the Dewar-Chatt-Duncanson Bonding Model

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Synopsis. Metal-olefin complexes can be considered as aromatics if their conjugated systems are described well by the Dewar-Chatt-Duncanson bonding model.

Stable complexes between transition metal salts and olefins have long been known,[1] but not understood until comparatively recently.[2-5] Zeise's salt is a typical example of such complexes. Ethylene in this salt occupies the fourth coordination site of the square-planar platinate ion with the C–C axis perpendicular to the platinum-ligand plane.[6] In this note, the author would like to point out that many such metal–olefin complexes are essentially aromatic, being stabilized by cyclic conjugation.

The useful bonding model for the metal–olefin complexes was presented by Dewar[7] and by Chatt and Duncanson.[8] They proposed that the bonding consists of a two-way donor-acceptor mechanism: σ donation of the π-bonding electrons of the olefin to vacant orbitals on the metal and π back donation of metal valence electrons to the π^* orbital of the olefin. The extent of back bonding varies depending upon the substituents on ethylene and other ligands on the metal. This bonding model has been referred to as a Dewar-Chatt-Duncanson model. It is noteworthy that few qualitative pictures have served us as beautifully as the Dewar-Chatt-Duncason model.[3]

This bonding model is shown graphically in Fig. 1. The basis-set orbitals for the Hückel calculation are two valence orbitals of the metal (**1** and **2**) and two carbon $2p_z$ orbitals of ethylene (**3** and **4**). In many complexes, **1** is a metal d_{xz} orbital while **2** is a metal d_{z^2} orbital or one of the dp^2- or d^2p^2-hybrid orbitals.[2-8] These two metal orbitals are represented by unconnected vertices because they are orthogonal to each other.

Such a conjugated system is depicted in terms of five resonance integrals and four Coulomb integrals. Coulomb integral parameters for **1** and **2** are denoted by h_1 and h_2, respectively. Four of the resonance integrals have a negative sign and one has a positive sign, reflecting the phase change which results from the nodal characteristic and the position of the metal d_{xz} orbital relative to the carbon $2p_z$ orbitals. Resonance integral parameters between metal and carbon valence orbitals are denoted by $\pm k_a$ and k_b, where k_a and k_b are positive in sign. The resonance integral parameter for the ethylene π bond is equal to unity. The Hückel calculation then demonstrates that the four basis-set orbitals combine to form two bonding and two antibonding molecular orbitals. Four electrons fill the two bonding molecular orbitals.

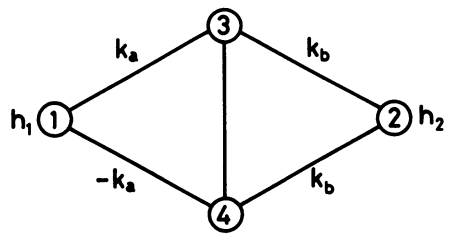

Fig. 1. Graphic representation of the Dewar-Chatt-Duncanson bondng model (k_a, k_b>0).

We then apply our graph theory of aromaticity[9] to this Dewar-Chatt-Duncanson bonding model. A characteristic polynomial for this conjugated system is obtainable by expansion of the Hückel secular determinant.[9] It is written as

$$P(X) = X^4 - (h_1+h_2)X^3 - (1+2k_a^2+2k_b^2-h_1h_2)X^2 + (h_1+h_2+2h_1k_b^2+2h_2k_a^2+2k_a^2-2k_b^2)X + (4k_a^2k_b^2-h_1h_2+2h_1k_b^2-2h_2k_a^2). \quad (1)$$

Zeros of this polynomial represent the energies of molecular orbitals for the conjugated system. The corresponding reference polynomial is derived graph-theoretically from the characteristic polynomial.[9] It is written as

$$R(X) = X^4 - (h_1+h_2)X^3 - (1+2k_a^2+2k_b^2-h_1h_2)X^2 + (h_1+h_2+2h_1k_b^2+2h_2k_a^2)X + (2k_a^2k_b^2-h_1h_2). \quad (2)$$

Zeros of this polynomial represent the energies of hypothetical molecular orbitals which the system would possess if it were totally deprived of aromaticity.[9] A conjugated system defined by this polynomial is named an olefinic reference structure.[9] Total energy for each system is given by summing energies of four electrons in the two bonding molecular orbitals.

The difference in total energy between a real conjugated system and its olefinic reference system is defined as resonance energy due to cyclic conjugation.[9] Resonance energy of the system in question is a function of h_1, h_2, k_a, and k_b. Here, h_1 must not be smaller than h_2 since **1** and **2** are electron-donating and accepting orbitals, respectively. For symplicity, h_2 is set equal to $-h_1$, and k_a equal to k_b. Here, h_1 takes a positive value. This way of choosing the parameter set satisfies the empirical fact that the metal-ethylene bond is essentially electroneutral, with donation and back-acceptance approximately balanced.[3,4] A couple of realistic values were chosen independently for h_1 and k_a. The resonance energy values thus determined for the metal–ethylene bonding system are listed in Table 1. It is worth noting that the resonance energy stays positive in sign for all parameter values. It varies in the range 0.173—0.775 β, where β is an absolute value of β. This value is comparable to the resonance energy of benzene, 0.273 β.

The nodal property of the metal d orbitals is known to aromatize the olefin–tricarbonyliron complexes.[10,11] It is now true for the present Dewar-Chatt-Duncanson

Table 1. Resonance energies of the Dewar-Chatt-Duncanson bonding model in units of β.

k_a	h_1		
	0.00	0.50	1.00
0.50	0.173	0.395	0.373
1.00	0.404	0.659	0.775

model. The presence of one phase change in the metal-olefin conjugated system makes it a Möbius system with four bonding electrons. Möbius systems are characterized by the $4n$ rule for aromaticity,[12] in contrast to the common $4n+2$ Hückel rule. The Möbius ring found along the periphery of the bonding network (Fig. 1) can, therefore, be considered to be aromatic in nature. This is the primary reason why an entire metal-ethylene conjugated system can be regarded as an aromatic species. Furthermore, it is quite likely that many other metal-olefin complexes are totally or partly stabilized by such a bonding pattern.

Bicyclo[1.1.0]butadiene has a similar bonding network, but has no phase change along the periphery. In fact, it has a large negative resonance energy of $-0.473\ \beta$. Thus, bicyclo[1.1.0]butadiene must differ in stability from the Dewar-Chatt-Duncanson bonding model. This suggests that any metal-olefin complexes whose conjugated system is analogous to bicyclo[1.1.0]-butadiene, if any, must be very unstable.

Now, several stabilizing mechanisms have been clarified for organometallic conjugated systems and polyhedral molecules. Multicenter bonds and/or a network of three-center bonds stabilize polyhedral cluster compounds.[13,14] Metallocenes and olefin-tricarbonyliron complexes are stabilized by the bonds formed between metal atoms and carbocyclic rings.[11,15] Formation of all these bonds is obviously associated with aromatization. The binding of olefins to transition metals has also occupied a central position in organometallic chemistry.[1-8] As has been seen above, the Dewar-Chatt-Duncanson model is stabilized by aromatization.

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