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The Verification of Three-Dimensional Aromaticity: Tricarbonyliron Complexes of Olefins

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Synopsis. Using Mingos's Hückel molecular-orbital model, polyolefins were found to be markedly aromatized by the coordination of tricarbonyliron. The Dewar-type resonance energies calculated for the title compounds are consistent with their chemistry.

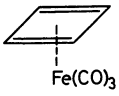
In 1956, Longuet-Higgins and Orgel pointed out the possibility that quite an unstable cyclobutadiene molecule can be stabilized by combination with a suitable transition-metal compound.[1] In 1965, Pettit *et al.* first achieved such a stabilization of cyclobutadiene by adding tricarbonyliron to it.[2] The chemistry of transition-metal complexes of olefins has since been rapidly developed.[3,4] In parallel with this, two important concepts have been employed to elucidate the stability of these complexes; one is a symmetry-based molecular-orbital approach derived from perturbation-theory arguments,[5,6] and the other is the eighteen-electron (or inert-gas) rule.[4,7]

On the other hand, the present author has been developing a graph-theoretical theory of aromaticity within the framework of the Hückel molecular-orbital (HMO) theory.[8-10] The aromaticity theory is characterized by its ability to determine the Dewar-type resonance energy[11] of any conjugated compound without parametrization. Recently, Mingos reported his attempt to frame tricarbonyliron complexes of typical olefins by means of the HMO theory.[7] Accordingly, it can now be shown that the theory of aromaticity can be extended to verify the aromaticities of three-dimensional conjugated systems in these complexes.

In applying the graph-theoretical theory of aromaticity[8-10] to the tricarbonyliron complexes, Mingos's HMO model[7] was adopted in its original form. The signs of the iron-carbon resonance integrals were chosen in a way which reflects the phase changes in the set of basis orbitals. The absolute values of all the resonance integrals were taken to be equal to that of the carbon-carbon resonance integral (β_{C-C}). The Coulomb integral of iron was taken to be equal to $\alpha_C-\beta_{C-C}$, where α_C signifies the Coulomb integral of carbon. The resonance energies of typical tricarbonyliron complexes were calculated according to a procedure previously described;[8] they are presented in Table 1.

TABLE 1. RESONANCE ENERGIES OF TRICARBONYLIRON COMPLEXES OF TYPICAL OLEFINS

Complex	Resonance energy (β)
1[2,13]	0.894
2[15]	0.646
3[16]	0.671
4[17]	0.373
5[18]	0.593



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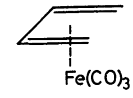

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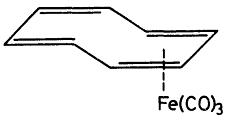

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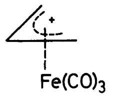

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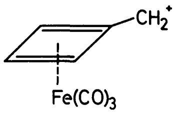

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Alone, the olefins investigated here are not aromatic, because they do not have positive resonance energies. The resonance energies are −1.226 for cyclobutadiene, 0.000 for butadienene, −0.594 for cyclooctatetraene, 0.000 for an allyl cation, and −0.401 for a methylenecyclobutadiene cation, all in units of β. Accordingly, it should be noted that the resonance energies of these olefins dramatically increase when they form complexes with tricarbonyliron.[12]

Since it has been fully proved that the resonance energy of this type excellently correlates with the experimental stability for a wide variety of conjugated compounds,[8,9,11] we might safely say that these olefins are markedly aromatized by the coordination of tricarbonyliron. The positive resonance energy is a distinct indication of aromaticity. This fact clearly supports the view of Pettit *et al.*,[13] who first insisted that the tricarbonyliron complex of cyclobutadiene is aromatic because of its tendency toward electrophilic substitution reactions.[14] An analogous trend in the reactivity is also found among the other tricarbonyliron complexes listed in Table 1.[15-18] The results of the present approach are, of course, consistent with Mingos's conclusion, based on the eighteen-electron rule, leading to the stabilization of these complexes.[7] The decrease in the degree of bond alternation gives further support to the aromaticities of the complexes.[7,19]

In contrast to the aromatic compounds so far identified, each of the tricarbonyliron complexes has a three-dimensional conjugated system. They can, hence, be considered to be the first examples of three-dimensional aromatic compounds ascertained in terms of the Dewar concept of aromaticity.[8,9,11] The application of the HMO theory to the other organometallic compounds[3,4] and also to such hydrocarbons as a square-pyramidal $C_5H_5^+$ species[20] would help to extend the concept of three-dimensional aromaticity.

This work was motivated by Dr. Shigeo Yoneda's article on three-dimensional aromaticity [Kagaku Sôsetsu, **15**, 36 (1977)]. The use of the facilities of the Hokkaido University Computing Center is gratefully acknowledged.

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10) A definition of resonance energy presented in a recent paper [J. Aihara, *Bull. Chem. Soc. Jpn.*, **50**, 2010 (1977)] is not used here because the original definition proposed in Ref. 8 appears most suitable for describing the stability of any conjugated system. Note that the reference energy in Ref. 8 defines the lowest energy of the reference structure relative to which aromatic stabilization is considered. For all the conjugated systems investigated here, however, both definitions of resonance energy give the same results.

11) M. J. S. Dewar and G. J. Gleicher, *J. Am. Chem. Soc.*, **87**, 685, 692 (1965); M. J. S. Dewar and C. de Llano, *ibid.*, **91**, 789 (1969); J. Aihara, *Kagaku No Ryoiki*, **30**, 269 (1976).

12) Note that, in each of these tricarbonyliron complexes, one of the iron d orbitals and any three carbon p_π orbitals which are arranged in sequence and coordinated to the iron atom form a singly twisted conjugated ring (*i.e.*, a Möbius ring) because of the nodal characteristics of d orbitals. Such four-membered Möbius rings make a significant contribution to the aromaticity of the entire conjugated system.[9] In this context, the hypothetical Möbius cyclobutadiene can be considered to be highly aromatic. See, *e.g.*, J. Aihara, *Bull. Chem. Soc. Jpn.*, **48**, 517 (1975).

As a general rule, polyolefins do not tend to form very stable compounds in which only one double bond is coordinated to a transition metal atom. See, *e.g.*, F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 3rd ed, Wiley-Interscience, New York, N. Y. (1972), Chap. 23. This fact is consistent with the above structural consideration of conjugated systems.

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