

The metal-ligand bonding in substituted butadiene complexes of cobalt

In a recent communication, Schrauzer¹ has reported the electronic spectra of the two complexes, (tetramethylcyclopentadienone)cyclopentadienylcobalt and its tetrakis(trifluoromethyl) analogue. The *ground state* geometries of these molecules have been discussed by Dahl and Smith², Bailey, Gerloch and Mason³ and Gerloch and Mason³. The conformation of the dienone ligand indicates that there is no question that a structure such as (I) (in Fig. 1) makes an important contribution to a simple

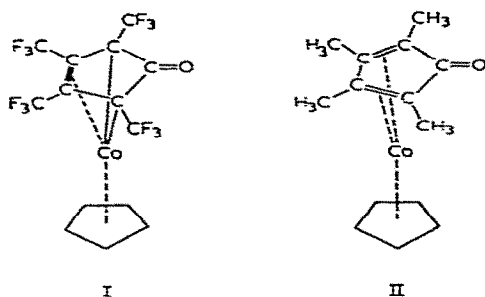


Fig. 1. The metal-ligand bonding in substituted butadiene complexes of cobalt.

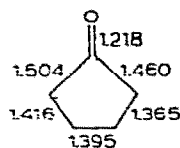


Fig. 2. Bond lengths (Å) in the cyclopentadienone ring in $(\text{CF}_3)_4\text{C}_5\text{OFe}(\text{CO})_3$.

TABLE I

THEORETICAL DATA FOR CYCLOPENTADIENONE AND CYCLOPENTADIENE


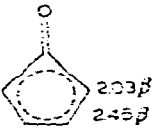
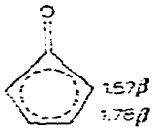
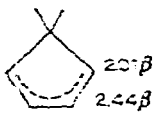
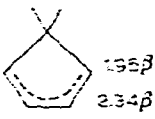
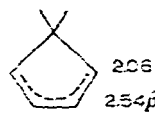
Atomic orbital coefficients	Energy	Comments
	$\alpha + 1.4 \beta$	Doubly filled
	$\alpha + 0.6 \beta$	Doubly filled
	$\alpha - 0.03 \beta$	Unfilled
	$\alpha - 1.7 \beta$	Unfilled

valence bond description of the bonding in this molecule; there is equally no question that this contribution is not sufficient to completely destroy conjugation in the dienone ring as may be seen from the bond lengths (Fig. 2) in the cyclopentadienone ligand in [tetrakis(trifluoromethyl)cyclopentadienone]iron tricarbonyl^{3,5}, (the average e.s.d.'s of these values are 0.027 Å so that there is no significant distortion of the ligand from C_5 symmetry).

The qualitative interpretation¹ of the bonding in $(\text{CH}_3)_4\text{C}_5\text{OCo}(\pi\text{-C}_5\text{H}_5)$ and $(\text{CF}_3)_4\text{C}_5\text{OCo}(\pi\text{-C}_5\text{H}_5)$ needs to be commented upon however. In Table 1, theoretical data, provided by Hückel molecular orbital calculations, for the cyclopentadienone ligand are listed for the higher lying filled and lower lying unfilled molecular orbitals.

TABLE 2

ATOM LOCALISATION ENERGIES IN (i) CYCLOPENTADIENONE AND (ii) CYCLOPENTADIENE

	(a) Radical attack	(b) Electrophilic attack	(c) Nucleophilic attack
(i)	 1.70β 2.11β	 2.03β 2.45β	 1.57β 1.76β
(ii)	 2.01β 2.44β	 1.95β 2.34β	 2.06β 2.54β

In valence bond terms, the possible contributions of such structures as (I) can be measured by the atom localisation energies (more specifically by the *para*-localisation energies). In keeping with intuition, atom localisation energies are a minimum at those centres where Diels-Alder addition by the metal may take place. Moreover, the localisation energies for electrophilic attack are much smaller for cyclopentadiene than for cyclopentadienone; the distortion from planarity of the diene ligands in π -cyclopentadienyl(1-phenylcyclopentadiene)cobalt⁶ is 36.5° rather than the 21° found in tetrakis(trifluoromethyl)cyclopentadienone complexes^{3,4,5}. Intra-ring bond lengths and bond angles⁶ in the diene complex also demonstrate the increased charge localisation and rehybridisation at what are *formally* described as the σ -bonding centres.

While this model has a good deal of conceptual value, it is also worthwhile examining a description of the structure according to molecular orbital theory. In a molecular orbital discussion of the relationship between the two extreme valence bond structures (I) and (II) (Fig. 1) it is convenient to consider the four $2p_\pi$ orbitals of the carbon atoms of the butadiene fragment of the ligand. If these are labelled *A* to *D*, then they form the basis for molecular orbitals of symmetries $2A_2$ and $2B_1$, which are of the form

$$a_2(1) = \frac{1}{\sqrt{1+\lambda^2}} \{A + D + \lambda(B + C)\} \quad \alpha + 1.6\beta$$

$$a_2(2) = \frac{1}{\sqrt{1 + \lambda^2}} \{ \lambda(A + D) - (B + C) \} \quad \alpha - 0.6 \beta$$

$$b_1(1) = \frac{1}{\sqrt{1 + \mu^2}} \{ (A - D) + \mu(B - C) \} \quad \alpha + 0.6 \beta$$

$$b_1(2) = \frac{1}{\sqrt{1 + \mu^2}} \{ \mu(A - D) - (B - C) \} \quad \alpha - 1.6 \beta$$

where we have neglected overlap. The bonding molecular orbitals of (II) span A_2 and B_1 and the ligand contribution to these molecular orbitals arises from $a_2(1)$ and $b_1(1)$ [Formula (II) does not allow explicitly for a back-donation process]. In contrast, the " σ - π -bonded" structure (I) has bonding molecular orbitals which span $2A_2 + B_1$, where, besides $a_2(1)$ and $b_1(1)$, the ligand combination $a_2(2)$ is involved. The molecular orbitals of the cyclopentadienone molecule listed in Table 1 are related to those of the butadiene fragment; we identify $a_2(1)$ with γ , $a_2(2)$ with ε , $b_1(1)$ with δ , and $b_1(2)$ with ν . The formulations (I) and (II), it must be stressed, do not imply a "fundamental difference in the electronic structures"¹; rather there is a smooth transition between the two schemes as $a_2(2)$ contributes increasingly to the bonding. The essential difference between the two bonding schemes is therefore the contribution which the unfilled ligand orbital lying at $(\alpha - 0.03 \beta)$ makes to the metal-ligand bond. Two points should be stressed in this connection. The first is that the theoretically derived energy implies that this lowest unfilled molecular orbital is virtually *bonding*, even so far as the ligand itself is concerned. Tetrakis(trifluoromethyl)cyclopentadienone has indeed virtually the same electron acceptor properties as tetracyanoethylene, as judged by the frequencies of the charge transfer spectra of these two separate Lewis acids with aromatic donors⁷. As far as the cobalt cyclopentadienone complex is concerned, this low-lying ligand level implies an increase in the metal to ligand "back-donation" process compared, say, with π -cyclopentadienyl complexes. As a result of the node in the ketonic group in this unfilled M.O., metal-ligand overlap will clearly be increased if the oxygen were pushed away from the plane of the remaining five carbon atoms⁸. But it must be emphasized that the major part of the ring distortions in the fluoromethyl-substituted dienone complexes originate from the bending of the ketonic group as a whole and this is due to the interaction of orbital γ of Table 1 with the metal d_{z^2} or d_{z^2}/s hybrid.

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