The structure and bonding of a cobalt–cyclopentadiene complex

A single-crystal X-ray structural analysis of π-cyclopentadienyl (1-benzoylcyclopentadiene) cobalt has been performed, using conventional Patterson, Fourier and least-squares refinement techniques. The present discrepancy index, R_1, for 844 independent three-dimensional reflexions is 8.5 %; estimated standard deviations are 0.025 Å for cobalt–carbon, 0.03 Å for carbon–oxygen, and 0.04 Å for carbon–carbon vectors. The compound crystallizes as air-stable purple needles[1] in spacegroup $P2_1$ (C_2^2; no. 4) with $a = 10.608 \pm .008$, $b = 10.545 \pm .006$, $c = 6.048 \pm .005$ Å, $\beta = 101.1 \pm .1°$, $Z = 2$. Fig. 1 shows the molecule viewed down c. The benzoyl group occupies the expected *exo*-position and the cyclopentadiene ligand is bent across the terminal carbon atoms of the "butadiene" system in exactly the same way as in the analogous 1-phenylcyclopentadiene complex[2]. However, a detailed examination of the carbon–carbon bondlengths within the cyclopentadiene ligand indicates that the bond-order around the "butadiene" portion is more-or-less constant. This is in contrast to the 1-phenyl derivative and may, possibly, reflect the different inductive

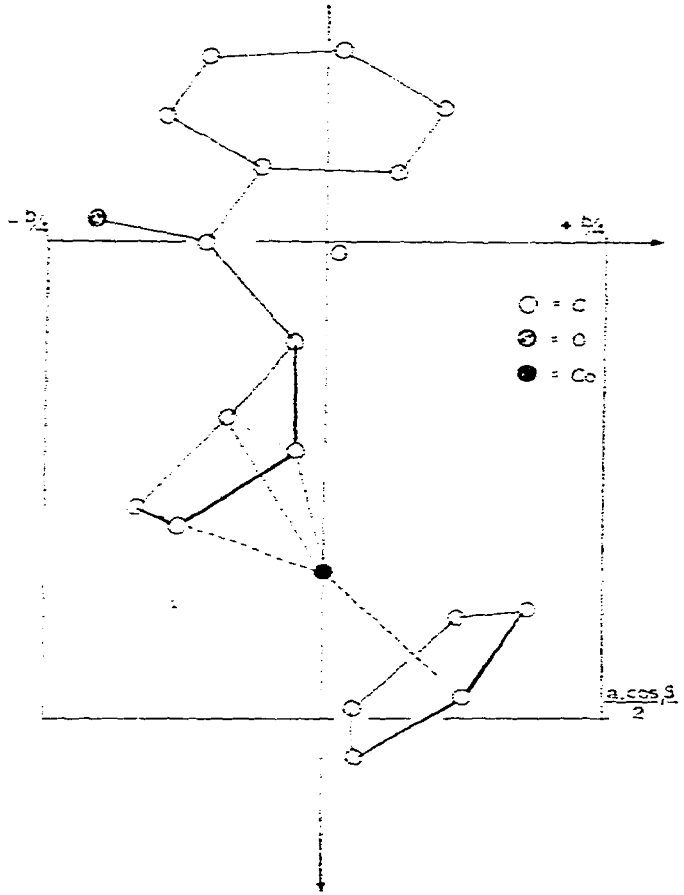

Fig. 1. π-cyclopentadienyl (1-benzoylcyclopentadiene)cobalt, viewed down c.

effects of phenyl and benzoyl substituents. The terminal carbon atoms of the "butadiene" system are 2.03 (± .02) Å, the central carbon atoms are 1.97 ± 0.02. Å, and the non-bonded carbon atom of the cyclopentadiene ligand 2.57 (± .03) Å distant from the cobalt atom. The mean distance of the cyclopentadienyl carbon atoms from the metal is 2.05 (± .03) Å.

There have recently been a large number of crystallographic studies on complexes containing conjugated organic ligands with a formal "butadiene" residue bonded to a transition metal. These include complexes of butadiene[3], cyclopentadiene[2,3a], cyclopentadienone[4,5,6], cyclohexadiene[7], hexakis(trifluoromethyl)benzene[8], cycloheptatrienone[9,10] and cyclo-octatetraene[11]. In each case (save possibly that of the butadiene complex itself) the large angle by which the non-bonded portion of the ligand is bent from the plane of the bonded ("butadiene") part of the ligand, coupled with the decrease in distance between the terminal carbon atoms of the "butadiene" from the value expected in the free ligand, indicates that some form of localized bonding occurs between the metal and the 1- and 4-positions of the "butadiene" system and that these carbon atoms are probably in something approaching an sp^3 hybridized state. However, a survey of the carbon–carbon bondlengths in these complexes[12] often fails to substantiate this, and, as in the present case, tends to indicate that all four carbon atoms in the "butadiene" system may be more appropriately described as sp^2 hybridized. This sp^2 character is further evidenced by some observations concerning the organic chemistry of some derivatives of butadiene iron tricarbonyl[13], which indicates that the butadiene system is still conjugated when complexed to the tricarbonyl–iron group. It is thus apparent that the valence-bond approach has, in these complexes, reached the limits of its applicability.

In setting up a general molecular-orbital scheme for these complexes, the conjugated ligand is treated as having the molecular orbitals of *cis*-butadiene. Fig. 2

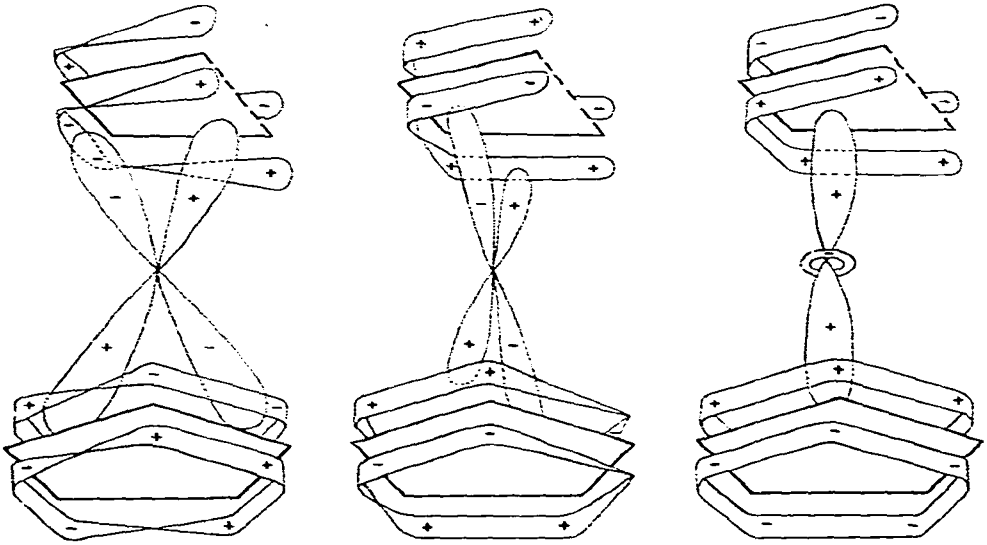

Fig. 2. Overlap scheme for a π-cyclopentadienyl–metal–diene system. (i) π-cyclopentadienyl A_{1u}, metal d_{z^2}, butadiene B_2 (1) orbitals; (ii) π-cyclopentadienyl E_1 (a), metal d_{xz}, butadiene A_2 (1) orbitals; (iii) π-cyclopentadienyl E_1 (b), metal d_{yz}, butadiene B_2 (2) orbitals.

shows the possible overlap for orbitals of different symmetries in the case of the π-cyclopentadienyl-diene complex investigated. The molecular orbitals produced will be similar to those established[14] for ferrocene. The "butadiene" system must be regarded as donating four electrons to, and back-accepting two electrons from, the metal *or* may be regarded formally as a (butadiene)$^{2-}$ anion (*i.e.* a six-electron donor). The first two parts of Fig. 2 show the overlap involving the two π-orbitals normally occupied in *cis*-1,3-buta-diene; the third set of orbitals involves the first antibonding molecular orbital of butadiene ($\psi = 0.60\,\Phi_1 - 0.37\,\Phi_2 - 0.37\,\Phi_3 + 0.60\,\Phi_4$ from Hückel theory), and it is the incorporation of this orbital into the bonding-scheme which will give the terminal carbon atoms their pseudo-sp^3 character. In order for the positive lobes of the butadiene B_2 (2) orbital to maximize their overlap with the metal d_{yz} orbital, they will be pulled, or twisted inwards. This is consistent with the decreased distance between the terminal carbon atoms, and the distortion of all complexes of cyclic dienes from planarity.

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