The Structure of Perfluorocyclopentadienedicobalt Heptacarbonyl

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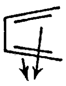
THE reactions of perfluorocyclopentadiene with transition-metal carbonyls and π-cyclopentadienyl metal carbonyls have been reported by Banks *et al.*[1] A structural analysis of one of the perfluorocyclopentadienecobalt carbonyl adducts has now been completed to a point where the discrepancy index for 1495 independent reflexions is 0·11, the solution being achieved by Fourier and least-squares methods. The molecular stereochemistry is shown in the Figure, the average e.s.d.'s of the bond lengths being Co–C 0·025, C–C, C–O, and C–F 0·03 Å.

The two cobalt ions are bridged by a single perfluorocyclopentadiene ligand. The bonding of the fluorinated diene is quite different from that which has been observed, for example, in π-cyclopentadienyl-1-phenylcyclopentadienecobalt[2] and in related molecules.[3] The cobalt tricarbonyl moiety is bonded to a fluoro-allyl fragment of the perfluorocyclopentadiene, the cobalt tetracarbonyl grouping being σ-bonded to the cyclic ligand. The electron localisation pattern in the perfluorocyclopentadiene parallels the structure suggested for an intermediate in the reaction of perfluorocyclopentadiene with cyclopentadiene.[4]

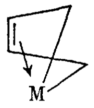
Both cobalt ions have a formal d^8-configuration (+1 oxidation state) and distorted trigonal bipyramidal stereochemistries. The observed paramagnetism of the complex is due to impurities since the metal ions have a pseudo-inert-gas configuration.

The bonding of butadiene to a transition-metal ion has, as yet, been represented as one of the structures (I) and (II).

These π- and σ–π-bonded structures have a conceptual value only, a molecular-orbital description[5] of the bonding in substituted butadiene complexes of cobalt emphasising their complementary nature. The metal–carbon and carbon–carbon bond lengths in the $C_5F_6Co_2(CO)_7$ complex prove that the metal–ligand bonds are to be formally represented as (III).



(I)



(II)

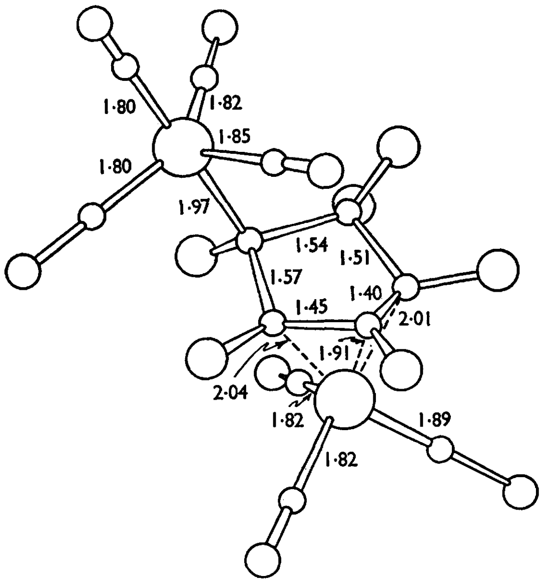
(III)

The molecular-orbital description of this bonding scheme can be seen from an inspection of the butadiene, allyl radical, and σ-bonded carbon orbitals.

						Energy
C_4H_6	$\psi_1 = 0{\cdot}37\ \chi_1$	$+0{\cdot}60\ \chi_2$	$+0{\cdot}60\ \chi_3$	$+0{\cdot}37\ \chi_4$	$\alpha + 1{\cdot}6\ \beta$
	$\psi_2 = 0{\cdot}60\ \chi_1$	$+0{\cdot}37\ \chi_2$	$-0{\cdot}37\ \chi_3$	$-0{\cdot}60\ \chi_4$	$\alpha + 0{\cdot}6\ \beta$
	$\psi_3 = 0{\cdot}60\ \chi_1$	$-0{\cdot}37\ \chi_2$	$-0{\cdot}37\ \chi_3$	$+0{\cdot}60\ \chi_4$	$\alpha - 0{\cdot}6\ \beta$
	$\psi_4 = 0{\cdot}37\ \chi_1$	$-0{\cdot}60\ \chi_2$	$+0{\cdot}60\ \chi_3$	$-0{\cdot}37\ \chi_4$	$\alpha - 1{\cdot}6\ \beta$
C_3H_5	$\phi_1 = 0{\cdot}50\ \chi_1$	$+0{\cdot}71\ \chi_2$	$+0{\cdot}50\ \chi_3$		$\alpha + 1{\cdot}4\ \beta$
	$\phi_2 = 0{\cdot}71\ \chi_1$		$-0{\cdot}71\ \chi_3$		α
	$\phi_3 = 0{\cdot}50\ \chi_1$	$-0{\cdot}71\ \chi_2$	$+0{\cdot}50\ \chi_3$		$\alpha - 1{\cdot}4\ \beta$
C	$\phi_4 =$			χ_4	α

The allyl molecular orbitals can be rewritten as linear combinations of butadiene orbitals,

$$\begin{aligned}
\phi_1 &= 0{\cdot}91\ \psi_1 \quad +0{\cdot}38\ \psi_2 \quad -0{\cdot}15\ \psi_3 \quad +0{\cdot}06\ \psi_4\\
\phi_2 &= -0{\cdot}16\ \psi_1 \quad +0{\cdot}69\ \psi_2 \quad +0{\cdot}69\ \psi_3 \quad -0{\cdot}16\ \psi_4\\
\phi_3 &= 0{\cdot}06\ \psi_1 \quad -0{\cdot}15\ \psi_2 \quad +0{\cdot}38\ \psi_3 \quad +0{\cdot}91\ \psi_4
\end{aligned}$$

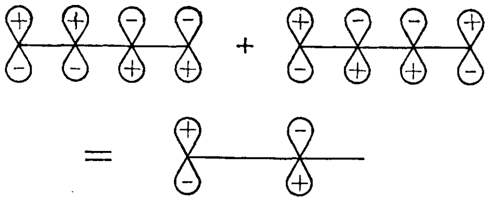


FIGURE

while the carbon orbital ϕ_4 is given by

$$\phi_4 = 0{\cdot}37\ \psi_1 \quad -0{\cdot}60\ \psi_2 \quad +0{\cdot}60\ \psi_3 \quad -0{\cdot}37\ \psi_4$$

ϕ_1 is very largely made up, as is intuitively obvious, from the totally symmetric ψ_1 orbital. That ϕ_2, the non-bonding allyl molecular orbital, is largely made up of ψ_2 and ψ_3, the highest filled and lowest unfilled orbitals of butadiene, can be seen *qualitatively* as follows,



The effects of fluoro-substitution in the cyclopentadiene ligand and of metal–ligand bonding is to induce substantial mixing of the various butadiene molecular orbitals.

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[4] R. E. Banks, A. C. Harrison, and R. N. Haszeldine, *Chem. Comm.*, 1966, 338.
[5] S. F. A. Kettle and R. Mason, *J. Organometallic Chem.*, 1966, **5**, 97.