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Molecular Orbital Calculations on Transition Metal Complexes. Part XVIII. π-Cyclopentadienyl-π-cyclobutadiene-cobalt

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INDO SCF molecular orbital calculations have been carried out for the title compound and indicate a diamagnetic ground state, in accordance with the results of nmr studies. The molecule is found to be a formally d^6 system, in which the mainly d-orbitals follow the sequence $d_{z^2} < d_{x^2-y^2} < d_{xy} < d_{xz}, d_{yz}$. Calculations of the ionisation energies show that electron loss should take place first from the occupied dominantly d-orbitals d_{xy}, $d_{x^2-y^2}$, and d_{z^2}, and then from a mainly π-cyclobutadiene orbital, which constitutes the highest occupied ligand level. The principal bonding interaction involves this level and the metal d_{xz}, d_{yz} orbitals, and results in a substantial ligand → metal charge donation. The behaviour and classification of the cyclobutadiene ligand as a π-donor is discussed in terms of the calculated charge distribution.

Introduction

The mixed sandwich compound, π-cyclopentadienyl-π-cyclobutadiene-cobalt, CpCoCb, which is the only authenticated example containing a π-cyclobutadiene ring, was first obtained by Amiet and Pettit [1], although tetramethyl- and tetraphenyl-π-cyclobutadiene derivatives had previously [2, 3] been prepared. The nmr spectra of all these systems showed two sharp singlets, with the expected area ratios, thus showing almost conclusively that each was diamagnetic. However, the early authors [1, 2] classified their products as derivatives of Co^I, which would correspond to a d^8 configuration, although for all known mixed sandwich species a two-fold degenerate e type level constitutes the highest lying dominantly d-orbital, so that formally d^8 systems would be expected to be paramagnetic. Moreover, the very recent crystal structure determination by Riley and Davis [4] confirmed that CpCoCb was indeed a genuine mixed sandwich complex, with planar four- and five-membered carbocyclic rings, unique in the involvement of a π-cyclobutadiene ligand, and showed the metal–carbon distances to be appreciably shorter than those encountered for the metallocenes, with the Co–C (Cb) length some 0.07 Å shorter than the Co–C (Cp) distance. We have therefore carried out INDO SCF MO calculations on this unusual molecule, so as to investigate the nature of the bonding therein, and in order to find a basis for its observed diamagnetism and the shortness of the Co–C (Cb) bond. In the course of this study we have also been led to reconsider the nature of the cyclobutadiene ligand as a π-electron donor.

Method

The all valence electron INDO SCF MO method previously described [5] was used for the calculations. The resulting molecular orbitals are linear combinations derived from the metal 3d, 4s, and 4p, the carbon 2s and 2p, and the hydrogen 1s orbitals, and the molecular geometry used was that given by Riley and Davis [4]. The molecular x- and y-axes were alligned parallel to carbons C1 and C3 and carbons C2 and C4 of the cyclobutadiene ring.

Results and Discussion

Although the X-ray diffraction measurements showed the CpCoCb molecule to have a symmetry no higher than C_s, they did reveal the presence of a crystallographic mirror plane passing through one carbon atom of the Cp ring and through two carbon atoms of the Cb ring. Moreover, the system could be regarded as being formed by the union of two fragments, CpCo and CbCo, of C_{5v} and C_{4v} symmetry respectively, fused together at the metal atom.

In the calculations both the σ- and the π-framework of the ligand rings were considered, but it transpires that the main interaction giving rise to the splitting of the metal d-orbitals is that involving the π-orbitals of the ligand rings, which we illustrate in Figure 1, wherein are shown the appropriate H^{core} energy levels. The π-orbitals of the Cp and Cb rings give rise respectively to the symmetry combinations $a_1 + e_1 + e_2$ and $a_1 + e + b_2$, but because of the Cb

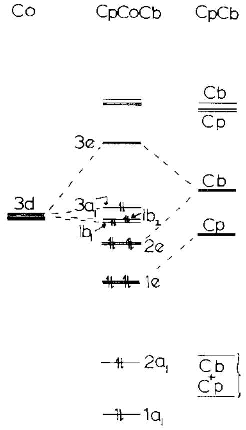

Figure 1. H^{core} energy level diagram for π-Cyclopentadienyl-π-cyclobutadiene-cobalt.

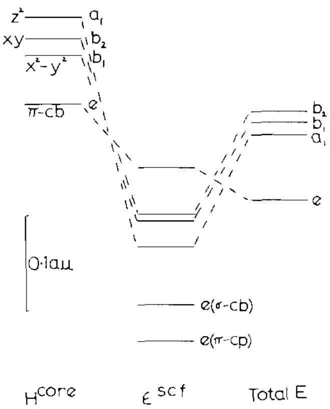

Figure 2. Energy levels for π-Cyclopentadienyl-π-cyclobutadienecobalt from H^{core}, ϵ^{SCF}, and total energy calculations.

ligand, with a lower than five-fold rotational axis, the d-levels no longer behave as in pseudo-axial symmetry, but are more conveniently labelled by the C_{4v} designations. Thus the d_{xz}, d_{yz} pair, formerly e_1, transform as e, the hitherto degenerate e_2 orbitals, $d_{x^2-y^2}$ and d_{xy}, become b_1 and b_2 respectively, whilst the designation of the d_{z^2} level remains unchanged as a_1.

The interaction between the metal and the π-framework of the ligands, shown in Figure 1, involves a total of eighteen electrons, and the resulting molecular orbitals are filled up to and including the $3a_1$ level. Since the H^{core} terms follow the sequence $e_1(\pi\text{-Cp}) < 3d < e(\pi\text{-Cb})$ it might be anticipated that the highest filled degenerate levels, 2e, would be predominantly metal in character so that the system would formally constitute a d^{10} configuration, but even at the H^{core} stage of the calculation the 2e level is mostly ligand in composition, and becomes more so in the SCF result. Thus the orbital occupation corresponds to a diamagnetic d^6 arrangement, rather than the paramagnetic d^8 configuration expected for a Co^I system; furthermore, the simulation of a d^8 system by the promotion of two electrons from the 2e to the 3e level (yielding a $^5A_1$ state) resulted in a system less stable than the $^1A_1$ d^6 ground state by some 6 eV, but as will be seen later the actual d-orbital occupancy is rather greater than six electrons, largely by virtue of the appreciable metal admixture in the 2e level.

However, the ordering of the mainly d-orbitals at the H^{core} stage of the calculation, $x^2 - y^2 < xy < z^2$, is not maintained in the SCF result, where these levels follow the sequence $z^2 < x^2 - y^2 < xy$. Moreover, the SCF eigenvalues would purport to show that these mainly metal d-levels actually lie lower than an e level of mainly ligand π-Cb character, but it is of course well known that Koopmans' theorem cannot safely be applied to metal sandwich systems because of the extensive reorganisation effects which follow electron loss. We therefore determined the energetic ordering of the highest lying levels by calculating the ionisation energies from the differences in total energy between the neutral molecule ground state and those of the various ionised systems, and in this way found the three highest occupied levels to be those of dominantly metal 3d character with the mainly ligand π-Cb e level lying appreciably deeper. However, the ionisation energies for electron loss from these mainly d orbitals do follow the SCF eigenvalue sequence, the respective values for the d_{xy} (b_2), $d_{x^2-y^2}$ (b_1), and d_{z^2} (a_1) levels being 7.84, 8.16, and 8.52 eV, whilst ionisation from the mainly ligand π-Cb e level requires 10.42 eV.

The SCF eigenvalue sequence is however normally reliable in deciding the energy ordering of the dominantly ligand levels since these usually show only small reorganisation effects upon ionisation; thus, below the mainly ligand π-Cb e level lie two further e levels, the higher being of chiefly σ-Cb composition and the lower deriving mainly from π-Cp contributions. Treating these in order of ascending energy the lowest e level contains some 66.0% of π-Cp character, with smaller amounts of σ-Cb, σ-Cp, and π-Cb, but contributes relatively little to the overall bonding since the metal contribution is actually less than 1%. On the other hand the mainly ligand σ-Cb e level shows some 5.8% metal character whilst the major contributions are from the σ-framework of the Cb ring (57.8%) and from the Cb ring hydrogen atoms (27.4%). However, the principal bonding interaction arises from the highest mainly ligand e level, which shows 21.3% metal character by virtue of its strong mixing with the vacant formally metal 3d e (d_{xz}, d_{yz}) level; the major ligand component is due to the π-Cb ring orbitals (60.6%), but there are also smaller con-

TABLE I. Charge Distribution in CpCoCb and CpCb.

	Cp^-Cb^{2-}	Cp^-Cb^0	CpCoCb
σ-Cb (C, 2s, $2p_x$, $2p_y$)	2.83	2.97	2.81
π-Cb (C, $2p_z$)	1.50	1.00	1.15
Cb (H, 1s)	1.19	1.00	1.01
σ-Cp (C, 2s, $2p_x$, $2p_y$)	2.90	2.92	2.86
π-Cp (C, $2p_z$)	1.20	1.20	1.03
Cp (H, 1s)	1.10	1.08	1.00
Co (3d)	–	–	7.17
Co (4s)	–	–	0.56
Co (4p)	–	–	1.84

tributions from the π-Cp and σ-Cb levels. The occupied formally metal 3d levels are nevertheless only slightly contaminated by ligand admixtures; thus the b_2, b_1, and a_1 levels show respective metal coefficients of presence of 0.970, 0.970, and 0.963 (*i.e.* some 93 to 94% metal 3d), but the vacant mainly metal 3d e level is in fact only about 65.6% metal 3d, with 18.8% π-Cb, 6.0% π-Cp, and other smaller σ-contributions. Largely by virtue of this e interaction the actual SCF d-orbital population amounts to 7.17 electrons ($d_{z^2}^{1.97} d_{x^2-y^2}^{1.92} d_{xy}^{1.96} d_{xz}^{0.66} d_{yz}^{0.66}$), appreciably greater than the formal d^6 configuration implied by the orbital occupations, and with the various σ-interactions yielding 4s and 4p populations of 0.56 and 1.84 electrons respectively, the final charge on the cobalt atom amounts to –0.60. The d-orbital occupancy is thus not very far below the d^8 required by the formulation $Cp^-Co^ICb^0$, and we discuss now the implications of the results as regards the nature of the Cb ligand as a π-donor.

To examine more closely the mode of bonding of the Cb ring, calculations were also made for the combined ring systems (CpCb) in the absence of the metal but at the same inter-ring separation as in the neutral cobalt complex. Two sets of results were obtained, one with 48 electrons, thereby corresponding to the formal ring charges Cp^-Cb^{2-}, whilst the other computation considered two fewer electrons, which should therefore be appropriate for a neutral 4-electron type Cb ring.

The electronic populations for these systems are given in Table I alongside those for the metal complex. The major difference in the results for the uncomplexed ring systems (48 and 46 electrons) lies as expected in the placement of two additional π-electrons on the Cb ring for the Cp^-Cb^{2-} case, but σ-electrons move from the Cb ring carbon orbitals to the hydrogen atoms to compensate for this increased carbon π-density. However, addition of these two electrons to the Cp^-Cb moiety causes no significant change in the Cp ring electron densities.

Since the molecular energy levels for the cobalt complex imply a picture of formal bonding of a Cb^{2-} moiety to $[Co^{III}Cp^-]$ (d^6) and not of a neutral Cb ring to $[Co^ICp^-]$ (d^8), comparison is first made of the charge difference between Cp^-Cb^{2-} and CpCoCb. The results show that both rings lose σ-electronic charge on complexation by virtue of the relatively strong bonding between the ring σ-orbitals and the metal 4s and 4p orbitals, although each ring releases considerably more electrons from its π-system through bonding to the metal e (d_{xz}, d_{yz}) orbitals. Thus these latter metal orbitals each acquire 0.66 electrons, the greater portion of which derives from the Cb ring. The SCF charges thus show that the π-electron occupation in the complex does in fact resemble more closely the π-electron charge in the 4-electron donor Cb ring than in the 6-electron system, Cb^{2-}; however, it should be remembered that generally it is found that in complexes of this type electronic charge is invariably *lost* from the ligand rings on formation of the metal complex, so that the calculated π-electron occupation of 4 X 1.15 (*cf.* 4 X 1.00 for the uncomplexed neutral Cb) is not consistent with the model of a neutral 4-electron donor Cb ring.

The photoelectron spectrum of CpCoCb has not as yet been determined experimentally but our results suggest that it could be of some interest. Thus the calculated differences between the ionisation energies for the mainly d-orbital a_1, b_1, and b_2 levels amount to some 0.30 to 0.35 eV, which is just about within the resolution of the pes experiment, so that it might be possible to observe three essentially d-electron ionisations, all of comparable intensity. Of the ligand ionisations the lowest energy band predicted (from the e mainly π-Cb level) would be expected to be rather weaker and somewhat more diffuse than the next two bands (due to e σ-Cb and e π-Cp ionisations respectively), by virtue of the substantially greater metal d-admixture contained therein. It is also noteworthy that if the small splitting of the $d_{x^2-y^2}$, d_{xy} pair of orbitals (e_2 in pseudo-axial symmetry) is disregarded, the ionisation energy sequence, $d_{xy} < d_{x^2-y^2} < d_{z^2}$, is the same as that observed in the familiar d^6 system, ferrocene, ($e_2 < a_1$), *i.e.* d_{z^2} lies lowest in both cases; moreover both CpCoCb and $FeCp_2$ give an orbital ordering at the H^{core} stage in which the d_{z^2} level lies highest of the occupied d-orbitals ($d_{x^2-y^2} < d_{xy} < d_{z^2}$ and $d_{x^2-y^2}$, $d_{xy} < d_{z^2}$ respectively), and in each case the d_{z^2} level eventually proves to lie deepest, thereby underlining the analogy between the two species and reinforcing the description of CpCoCb as a d^6 complex. Finally, as in $FeCp_2$, the occupied mainly d-levels are all essentially non-bonding in CpCoCb and electron loss from any of them actually *increases* the occupation of the formally vacant (but strongly admixed) metal e level (d_{xz}, d_{yz}) from 0.66 to 1.00 electron.

In conclusion our calculations also shed some light on the metal–carbon bond lengths observed [4] for CpCoCb. Thus, although the Co–C (Cp) distance of 2.036 Å is unusually short – some 0.06–0.08 Å less than the lengths found [6, 7] for $CoCp_2$ – it is at first sight somewhat surprising that the Co–Cb(Cb) length is even shorter at 1.964 Å. However, our results are fully consistent with the observed distances since it is clear that the dominant bonding interaction in CpCoCb is that between the metal d_{xz}, d_{yz} (e) orbitals and the ligand e π-Cb level, the π-Cp orbitals being much less strongly involved.

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