

Molecular Orbital Calculations on Transition Metal Complexes. Part XVI. The Mixed Sandwich Complex π -Cyclopentadienyl- π -cyclooctatetraenyl- titanium

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INDO SCF molecular orbital calculations have been carried out for the title complex. The results confirm the 2A_1 ground state indicated by esr measurements, showing the unpaired electron to reside in a dominantly metal d_{z^2} orbital, whilst the next filled level is derived mainly from a π -ligand e_2 orbital, to which the eight-membered ring makes the major contribution. The mainly metal d levels are found to follow the ordering $a_1 < e_2 < e_1$, and the implications of this sequence are discussed, the absence of any appreciable metal to ligand back-bonding being especially significant. Calculations concerning g values, hyperfine coupling constants, ionisation potentials, effective metal charge, and substitutional reactivity show good agreement with experimental results.

Introduction

π -Cyclopentadienyl- π -cyclooctatetraenyltitanium, CpTiCot, was first obtained by Van Oven and De Liefde Meijer [1] by the action of $K_2C_8H_8$ on CpTiCl₂, and shown by Kroon and Helmholdt [2] to contain both a η^5 -C₅H₅ and a η^8 -C₈H₈ ring, each bound symmetrically to the titanium atom. It thereby constitutes the only genuine sandwich compound of the 3d series yet known which possesses a η^8 -C₈H₈ ring, and as such has already attracted considerable experimental interest. Thus esr measurements by Thomas and Hayes [3] indicated that the unpaired spin was located in a mainly d_{z^2} metal orbital, and this may be rationalised on a simple molecular orbital scheme, considering for the moment only the metal 3d and ligand π -orbitals. Thus the η^5 -C₅H₅ ring yields the ligand combinations a_1 , e_1 , and e_2 , and the η^8 -C₈H₈ ring the levels a_1 , e_1 , e_2 , e_3 , and b_2 , the expected energetic order being [4] $a_1(\text{Cp}) \sim a_1(\text{Cot}) < e_1(\text{Cot}) < e_1(\text{Cp}) < e_2(\text{Cot}) < e_2(\text{Cp}) < e_3(\text{Cot}) < b_2(\text{Cot})$. Since, on this basis, 17 electrons are to be accommodated, the observed ground state is consistent with the ligand e_2 -

(Cot) level lying below the metal 3d level, thus leading to the filling of dominantly ligand orbitals up to and including $e_2(\text{Cot})$; fairly strong interactions between the 3d e_1 and e_2 levels and the $e_1(\text{Cp})$ and $e_2(\text{Cot})$ levels thus impart substantial anti-bonding character to these mainly metal orbitals, leaving the weakly interacting a_1 (d_{z^2}) orbital to contain the odd electron.

Nevertheless, in all other sandwich complexes of the 3d series the metal levels have been found [5] to show the one-electron sequence $e_2 < a_1 < e_1$, and in interpreting their photoelectron spectrum Evans *et al.* [6] preferred to treat CpTiCot as a d^5 system (with $e_2(\text{Cot}) > 3d(\text{Ti})$), rather than as the d^1 configuration suggested by this molecular orbital model and by the ligand field formulation [5, 7] of the system as $\text{Cp}^- \text{Ti}^{3+} \text{Cot}^{2-}$. Consequently it was concluded [6] that the highest occupied a_1 and e_2 levels were both of dominantly metal character, despite the failure to detect exchange splitting for ionisation from the e_2 level.

However, the simple molecular orbital calculations of Fischer [4] show that the energies of the π -ligand e_1 and e_2 combinations should decrease progressively with increasing ring size, and it has therefore been suggested [3, 5, 8] that the $e_2(\text{Cot})$ level does indeed here lie below the metal 3d orbitals. Accordingly, to clarify this situation, we have made full basis set INDO SCF molecular orbital calculations for CpTiCot, using an established method [8], which has proved to give a good account of the electronic structures of metallocene [9, 10] and bis-arene [11] systems, and to reinforce the results of the ligand field approach [5, 7, 12, 13]. In this way the ordering of the dominantly metal d -orbitals has been determined and the composition of the highest filled e_2 level established: at the same time, as a check on the reliability of our results, we have compared experimental data relating to g values, proton hyperfine coupling constants, ionisation potentials, ring substitutions, and the effective charge on the metal, with the appropriate calculated quantities.

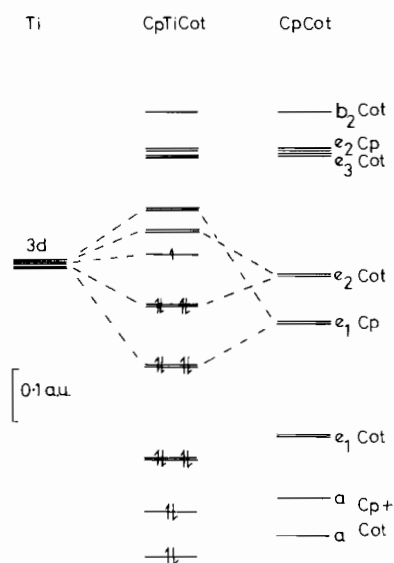


Figure 1. Molecular orbital diagram for π -cyclopentadienyl- π -cyclooctatetraenyltitanium, showing titanium 3d and ligand π -orbital interactions.

Method

The computations were carried out using the previously described INDO SCF molecular orbital method [8]. Metal 3d, 4s, and 4p orbitals, together with carbon 2s, 2p_x, 2p_y, and 2p_z and hydrogen 1s orbitals were included in the basis set, so that both σ - and π -bonding effects of the rings are taken into account. The structure adopted for CpTiCot was essentially that found by Kroon and Helmholdt [2], although we chose to use a geometry which made adjacent C-C distances for each of the two rings equal and also assumed the two rings to be parallel. Small (*ca.* 0.05 Å) variations in the metal-carbon bond lengths were found not significantly to affect the conclusions.

Results and Discussion

The calculations clearly indicate that CpTiCot is best formulated as a formally Ti(III) complex with only *one* principally 3d orbital singly occupied. This may best be understood in terms of a molecular orbital scheme, derived from the H^{core} terms, but since a diagram including the molecular orbitals arising from the whole basis set would be extremely complex we show in Figure 1, for the sake of clarity, only the interactions between the metal 3d orbitals and the ring π -orbitals. Thus, although there is also a significant interaction between the metal 4s and 4p levels and the ring σ -framework, as was similarly evident for the bis-arene compounds [12], the inter-

actions with the π -systems of the two rings constitute the primary cause of the splitting within the 3d orbital set.

Since the CpTiCot molecule cannot in fact possess a symmetry higher than C_2 the use of the D_5 and D_8 symmetry labels in Figure 1 is not strictly valid. However, apart from some mixing thus arising between the closely juxtaposed Cot e_3 and Cp e_2 levels, and between the Cot and Cp a_1 levels, which occurs even in the absence of the metal, the remaining non-complexed ligand levels are reasonably pure and well described by the symmetry designations of Figure 1. The lowest lying group of π -orbitals (Cp and Cot a_1 , Cot e_1) are stabilised by bonding to the metal 4s and 4p orbitals, whilst the highest group (Cot b_2 , Cot e_3 and Cp e_2) remain essentially unchanged on complexation. The primary interaction with the Ti 3d orbitals thus takes place through the Cot e_2 and Cp e_1 π -orbitals of the rings, but, as shown in the diagram, the free atom Ti 3d levels lie just slightly higher in energy than the Cot e_2 orbitals. Thus those molecular orbitals of e_2 symmetry which are mainly 3d in character are anti-bonding between the metal and the rings, and are therefore raised in energy compared with the free atom; similarly the e_1 orbitals, d_{xz} and d_{yz} , are also destabilised by interaction with the lower energy Cp e_1 orbitals in the same way as in the metallocene series. However, although the Cp e_1 level is further removed from the Ti 3d free atom level than are the Cot e_2 orbitals, its interaction, $H_{\mu\nu}$, with the appropriate 3d orbitals is approximately twice that between the 3d orbitals and the Cot e_2 level, by virtue of a more favourable overlap integral. In contrast the $3d_{z^2}$ (a_1) orbital remains virtually non-bonding, so that the overall 3d ordering becomes d_{z^2} (a_1) < d_{xy} , $d_{x^2-y^2}$ (e_2) < d_{xz} , d_{yz} (e_1). This sequence contrasts markedly with that found for other 3d sandwich systems, where the d_{xy} , $d_{x^2-y^2}$ pair lie lowest in energy on a one-electron basis, with $e_2 < a_1 < e_1$, but the present results clearly lead to the correct ground state by placing a single electron in the $3d_{z^2}$ orbital, in agreement with the esr results [3].

The eigenfunctions reveal that, despite the closeness in energy of the Cot e_2 and metal 3d levels, the bonding e_2 orbital contains only about 19% metal 3d character, so that the central titanium atom is justifiably formulated as $3d^1$ rather than $3d^5$. On the other hand the strongly bonding Cp e_1 level contains only 8.5% 3d character, but the metal 4p orbitals make a significant contribution of some 4%, this latter mixing being permitted by the absence of a centre of symmetry in the molecule.

The bonding in the complex may therefore be regarded as solely due to electron donation from the two rings, involving both σ - and π -orbitals, to the metal 3d, 4s, and 4p orbitals, with no significant synergic contribution. This contrasts with the situa-

tion found in the metallocenes and more particularly the bis-arene complexes where metal \rightarrow ligand back-donation is an important factor contributing to the stability of these systems. Back donation would however be expected to be less profitable for CpTiCot since the metal is already in a relatively high formal oxidation state which should therefore inhibit the loss of electron density in this way.

The ordering of the SCF orbital energies, ϵ_i , closely resembles that of Figure 1 except in as much as the highest filled level ($\epsilon = -8.03$ eV) corresponds to the Cot e_2 orbital whilst the open-shell, mainly $3d_{z^2}$, a_1 level lies deeper at -10.12 eV. On the basis of Koopman's theorem this would imply that ionisation from the mainly ligand Cot e_2 level occurred more readily than electron loss from the metal $3d_{z^2}$ (a_1) orbital, but the photoelectron spectrum [6] is best assigned assuming the first peak at 5.67 eV to correspond to a metal ionisation, with the higher bands (at 7.62, 8.63, and 10.51 eV) attributed [5] to ligand ionisations. Calculations were therefore performed on the molecular ion [CpTiCot] $^+$, for the electronic configurations corresponding to both metal $3d_{z^2}$ ionisation (... $e_2^4 a_1 \rightarrow \dots e_2^4$) and ligand ionisation (... $e_2^4 a_1 \rightarrow \dots e_2^3 a_1$) and the appropriate ionisation energies calculated from the energy differences between these ionised states and the neutral molecule. The value calculated for the ligand Cot e_2 ionisation (7.23 eV) is fairly well represented by its SCF orbital energy (-8.03 eV), and agrees well with experiment (7.62 eV), but very considerable relaxation accompanies ionisation from the $3d$ a_1 orbital; thus with $\epsilon_1 = -10.12$ eV the calculated ionisation energy is only 1.7 eV, which is rather lower than the experimental 5.67 eV, but does restore the correct ionisation sequence, $a_1 < e_2$.

The electronic relaxation on ionisation takes place however through the bonding e_1 and e_2 , mainly ligand, levels by substantially changing the amounts of admixed metal character therein. Thus the d-electron configuration for the neutral molecule is given by $a_1^{0.99} e_2^{0.79} e_1^{0.52}$, whilst for the molecular ion produced by loss of the a_1 electron the $3d$ population is $a_1^{0.05} e_2^{1.36} e_1^{0.74}$. Consequently, despite the formal loss of one electron from the metal, the charge thereon is diminished only by 0.15 units. Interestingly, the one-electron ordering of levels (Figure 1) matches up very well with the observed photoelectron bands and it appears, at least for this system, that changes in the eigenvalues induced by the two-electron terms in the ϵ_i effectively cancel out the consequences of any relaxation effects which may occur on ionisation. Because of the low actual symmetry of the molecule it was not possible, due to convergence to more stable states, to calculate by difference the ionisation energies for the lower lying, mainly ligand, levels. However, the H^{core} ordering suggests that the ring σ -orbital ionisations may also occur in the low energy

region below 12 eV, in addition to those from the metal $3d$ and ligand π (Cot and Cp) levels.

There are, unfortunately, no electronic spectral data for CpTiCot, but the lower energy d-d transition, $a_1 \rightarrow e_2$ (${}^2A_1 \rightarrow {}^2E_2$) is calculated to lie at 9.8 kK. Similarly the $a_1 \rightarrow e_1$ excitation (${}^2A_1 \rightarrow {}^2E_1$) is estimated at 13.9 kK, and the low energy charge-transfer transition, $e_2(\text{Cot}) \rightarrow a_1(3d_{z^2})$ (${}^2A_1 \rightarrow {}^2E_2$), at 19.6 kK.

However, where experimental data are available good agreement with the calculated properties is in most cases found. Thus for the esr g values simple ligand field theory [5] yields $g_{\parallel} = 2.0023$ and $g_{\perp} = 2.0023 - 6 \xi/\Delta E$, where ξ is the effective spin-orbit coupling constant and $\Delta E = E(e_1) - E(a_1)$. Neglecting the ligand contribution to ξ one may write $\xi = c_1 c_2 \cdot \xi(\text{Ti})$, where c_1 and c_2 ($= 0.9600$ and 0.7547 respectively) are the metal coefficients for the mainly metal $3d$ a_1 and e_1 orbitals, and with ΔE calculated as 13.9 kK, the experimental g_{\perp} value ($g_{\parallel} = 1.998$) yields $\xi(\text{Ti}) = 93 \text{ cm}^{-1}$. Since this is very close to the range of ξ values found by Cole and Garrett [15] for Ti^0 and Ti^+ , the agreement between theory and experiment is most satisfactory.

Moreover, the open-shell a_1 orbital is described by the wave function

$$|\Psi a_1\rangle = 0.9600 |d_{z^2}\rangle + 8(0.0321) |^1\text{H}(\text{Cot})\rangle + 5(0.0497) |^1\text{H}(\text{Cp})\rangle + 8(0.0544) |2p_{\pi}(\text{Cot})\rangle + 5(0.0312) |2p_{\pi}(\text{Cp})\rangle + 8(0.0070) |2s(\text{Cot})\rangle + 5(0.0090) |2s(\text{Cp})\rangle + \text{very small } |2p_{\sigma}\rangle \text{ contributions,}$$

and is the least admixed of the d-orbitals. The ligand contributions here derive almost entirely from the carbon $2p_{\pi}$ and hydrogen $1s$ orbitals from both ring systems, the latter being largely responsible for the significant spin transfer to the hydrogen atoms which manifests itself as proton coupling in the esr spectrum. The calculated spin transfer yields $A_{\text{H}}(\text{Cp}) = +2.27$ G and $A_{\text{H}}(\text{Cot}) = +1.03$ G, as compared with the measured values [3] of 3.2 and 1.6 G respectively, the agreement being very satisfactory for this type of calculation, especially for the ratio $A_{\text{H}}(\text{Cp})/A_{\text{H}}(\text{Cot})$.

Of the ionisation potentials only those for the two highest filled orbitals (a_1 , mainly metal, and e_2 , mainly ligand) could be calculated (*vide supra*). For the e_2 ionisation the calculated and experimental values were seen to be in excellent agreement, and although the a_1 ionisation energy was substantially

underestimated such a discrepancy is not too surprising when ionisation is accompanied by such substantial relaxation. On the other hand the calculated net charge on the metal in the neutral molecule (+ 0.275) is in excellent agreement with the value of +0.40 deduced by Vlieg *et al.* [16] from ESCA measurements.

Finally, metallation of CpTiCot by n-BuLi was found [16] to take place predominantly in the Cp ring, this being interpreted as indicating that the Cp ring is the more negatively charged. However, such metallation reactions normally proceed [17] via *nucleophilic* attack of the incipiently negative n-Bu moiety on the ring hydrogen atoms, so that if the substitution is dependent on charge densities it should occur more readily in the ring bearing the more positively charged hydrogen atoms. Thus, contrary to the supposition of Vlieg *et al.* [16], our calculations indicate that both the carbon and the hydrogen of the Cp ring are more positively charged than their Cot counterparts (C(Cp) = +0.010, H(Cp) = -0.010, C(Cot) = +0.001, H(Cot) = -0.035). This is nevertheless fully consistent with the experimental result, assuming the nucleophilic mechanism outlined above.

References

- 1 H. O. Van Oven and H. J. De Liefde Meijer, *J. Organometal. Chem.*, **19**, 373 (1969).
- 2 P. A. Kroon and R. B. Helmholdt, *J. Organometal. Chem.*, **25**, 451 (1970).
- 3 J. L. Thomas and R. G. Hayes, *Inorg. Chem.*, **11**, 348 (1972).
- 4 R. D. Fischer, *Theoret. Chim. Acta*, **1**, 418 (1963).
- 5 K. D. Warren, *Structure and Bonding*, **27**, 45 (1976).
- 6 S. Evans, J. C. Green, S. E. Jackson, and B. Higginson, *J. Chem. Soc. Dalton*, 304 (1974).
- 7 K. D. Warren, *J. Phys. Chem.*, **77**, 1681 (1973).
- 8 H. D. Amberger, R. D. Fischer, and B. Kanellakopoulos, *Theoret. Chim. Acta*, **37**, 105 (1975).
- 9 D. W. Clack, *Mol. Phys.*, **27**, 1513 (1974).
- 10 D. W. Clack, *Theoret. Chim. Acta*, **35**, 157 (1974).
- 11 D. W. Clack and M. Monshi, *J. Organometal. Chem.*, **116**, C41 (1976).
- 12 D. W. Clack and W. Smith, *Inorg. Chim. Acta*, **20**, 93 (1976).
- 13 K. D. Warren, *Inorg. Chem.*, **13**, 1243 (1974).
- 14 K. D. Warren, *Inorg. Chem.*, **14**, 2279 (1975).
- 15 G. M. Cole and B. B. Garrett, *Inorg. Chem.*, **9**, 1898 (1970).
- 16 M. Vlieg, C. J. Groenenboom, H. J. De Liefde Meijer, and F. Jellinek, *J. Organometal. Chem.*, **97**, 67 (1975).
- 17 J. March, "Advanced Organic Chemistry", p. 469, McGraw-Hill, New York (1968) and references therein cited.