Molecular Orbital Calculations on Transition Metal Complexes. Part XIII.* Ground States and Bonding in $3d^5$ Bis-benzene Complexes

D. W. CLACK and W. SMITH

Department of Chemistry, University College, P.O. Box 78, Cardiff, CF1 1XL, Wales, U.K.

Received March 17, 1976

INDO SCF Molecular orbital results are reported for the bis-benzene complexes $V(C_6H_6)_2$, $Cr(C_6H_6)_2$ and $[Cr(C_6H_6)_2]^+$. In contrast to the $^2E_{2g}$ and $^6A_{1g}$ ground states previously obtained for the closely related ferricenium and manganocene, a $^2A_{1g}$ ground electronic configuration is computed for $V(C_6H_6)_2$ and $[Cr(C_6H_6)]^+$, in complete agreement with the known ground states of these species. An analysis of the charge distribution in these complexes convincingly shows the synergic nature of their bonding. The spin distribution in the paramagnetic complexes, and the electronic relaxation which occurs on ionisation of $Cr(C_6H_6)_2$ are also discussed.

Introduction

The axially symmetric d^5 system presents an interesting situation since there is the possibility of having three different ground states and in view of this there has recently been a considerable effort of both theoretical [1] and experimental [2, 3] natures directed towards establishing the factors involved in determining which ground state occurs in sandwich type compounds. Thus it has only recently been shown that manganocene may possess either a high spin $^6A_{1g}$ ground state or a low spin $^2E_{2g}$ ground state depending on its surrounding environment [3], with the sextet state marginally favoured in the gas phase [2]. On the other hand, ferricenium cation is known to have a low spin $^2E_{2g}$ ground state [4], while the bis-benzene complexes V(Benzene)$_2$ and [Cr(Benzene)$_2$]$^+$ both show the low spin $^2A_{1g}$ state as their ground states [5–7].

A number of one-electron calculations of the Wolfsberg–Helmholz type have been performed on these systems [7, 8], and while these are of some use in describing overall bonding patterns they suffer certain limitations due to the neglect of electron–electron interactions. Thus they should not be used to obtain ionisation energies or to specify ground states solely on the basis of the ordering of the one-electron energy levels, although this is frequently

done. We have recently reported S.C.F. molecular orbital results for manganocene and ferricenium cation which not only yielded the correct ground states for both molecules, but also indicated that manganocene lay very close to the high spin–low spin crossover point [9]. In view of the success of this method in distinguishing such ground states we have extended our work to bis-benzene complexes and we report herein results for the d^5 complexes VBz$_2$ and [CrBz$_2$]$^+$ using the same method of calculations. Also included are results for the neutral CrBz$_2$ species so that an analysis may be made of the charge redistribution which occurs on complexation and ionisation.

Method

The INDO SCF MO scheme for transitional elements has been described elsewhere [10]. Molecular geometries were taken from the available literature [11, 12].

Results

We begin firstly by describing the bonding within these benzene complexes and Figure 1 shows the molecular orbital diagram for [CrBz$_2$]$^+$ using the core terms of the Hamiltonian. The S.C.F. eigen values show differences in their ordering and will be discussed later. The results show that although there is considerable mixing between the ligand σ and π orbitals, the ligand $2p_\pi$ orbitals interact most strongly with the metal $3d$-orbitals, and it is primarily this interaction which splits the $3d$ subshell in the sequence $e_{2g} < a_{1g} < e_{1g}$. The lowering of the e_{2g} d-orbitals, occupied by four electrons, on complexation is clearly an important feature in the bonding within these systems. In addition it seems that there is a strong interaction between the lowest lying a_{1g}, a_{2u} and e_{2u} ring σ-orbitals and the metal $4s$ and $4p$ orbitals which also contributes to the bonding. Other workers have also found large bond orders between the ring and the metal $4s/4p$ orbitals [7]. Apart from the e_{2g} π^* ring orbital there is little

---
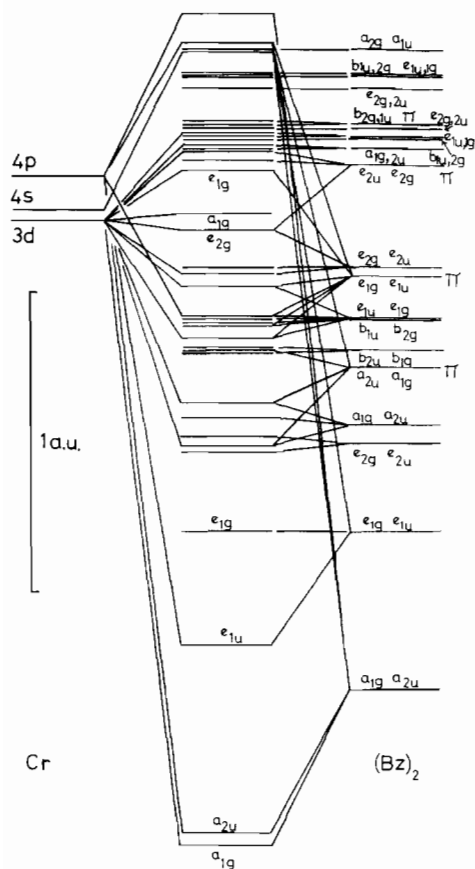*Part XII. D. W. Clack and M. Monshi, Rev. Roum. Chim., accepted for publication.

Figure 1. Molecular orbital diagram for $[Cr(benzene)_2]^+$.

TABLE I. Orbital Occupations for Benzene and Bis-benzene Chromium.

		CrBz$_2$	Benzene
Carbon	$2s$	0.9580	1.0350
	$2p_x$	0.9556	0.9696
	$2p_y$	0.9556	0.9696
	$2p_z$	1.0538	1.0000
Hydrogen	$1s$	1.0350	1.0258
Chromium	$3d_{xy}$	1.1540	
	$3d_{x^2-y^2}$	1.1540	
	$3d_{z^2}$	1.9182	
	$3d_{xz}$	0.2200	
	$3d_{yz}$	0.2200	
	$4s$	0.4490	
	$4p_x$	0.4984	
	$4p_y$	0.4984	
	$4p_z$	0.3964	

interaction of the vacant π^* ring orbitals with the metal.

A more detailed picture of the bonding may be obtained by comparing the electronic charge distribution before and after complexation and for convenience the closed shell CrBz$_2$ molecule will be examined. The situation is similar for the two d^5 complexes. The orbital occupancies for CrBz$_2$ and for free benzene are given in Table I. Substantial occupancies are observed for the formally empty $4s$, $4p_x$, $4p_y$, $4p_z$, $3d_{xz}$ and $3d_{yz}$ metal orbitals due to their significant involvement in the bonding. This build up of electronic charge on the metal is partially relieved by back donation from the metal $3d_{xy}$ and $3d_{x^2-y^2}$ orbitals to the ring π-system, with these former orbitals losing nearly half of their formal four electrons. In the ligand it appears that, compared to free benzene, the σ-type $2s$, $2p_x$ and $2p_y$ orbitals have decreased electron occupancy, while electron density in the π-type $2p_z$ orbitals has increased.

A consideration of all the atoms in the molecule shows that 1.2612 electrons are lost from the carbon atoms' $2s$, $2p_x$ and $2p_y$ σ-orbitals. It is reasonable to assume that some of this charge is lost to the hydrogen $1s$ orbitals (0.1104 electrons), since it is

probably *via* σ-bonding that such a charge could accumulate on the hydrogen atoms. Thus the remaining 1.1508 electrons are transferred to the chromium atom. On the basis of the bonding indicated in Figure 1 most of this charge is expected to enter the $4s$ and $4p$ orbitals, which are strongly bonded to the benzene σ-type orbitals. Similarly the charge lost from the $3d_{xy}$ and $3d_{x^2-y^2}$ orbitals is expected to enter the $2p_z$ orbitals of the benzene ring π-system. However, the 1.6922 electrons transferred exceeds the increase of 0.6454 electrons (12 $\times$ 0.0538) observed for these orbitals. It is therefore proposed that the $2p_z$ orbitals relay the excess charge into the $4s$, $4p_x$ and $4p_y$ and the $3d_{xz}$ and $3d_{yz}$ orbitals since these orbitals show a significant interaction with the $2p_z$ orbitals (Figure 1). The $3d_{xz}$ and $3d_{yz}$ orbitals are expected to acquire the bulk of their 0.440 occupancy in this manner, leaving the remaining 0.6067 electrons of the excess to enter the $4s$, $4p_x$ and $4p_y$ orbitals to account for most of the observed occupancy of 1.8414 electrons. This proposal is substantiated by the fact that the $4p_z$ occupancy is less than the $4s$, $4p_x$ and $4p_y$ occupancies, which follows from its smaller interaction with the ligand π-system. Schematically these proposals may be shown as follows:
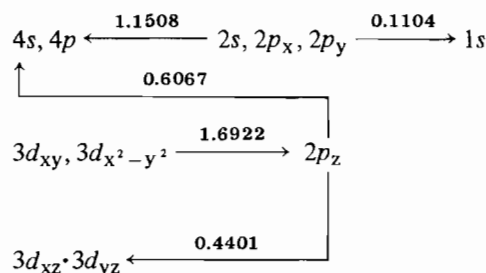
This scheme also shows the synergic nature of the bonding in dibenzenechromium. Electron charge is transferred from the ligand σ-orbitals to the $4s$ and $4p$ metal orbitals and also from the benzene π-orbitals to the $4s$, $4p_x$, $4p_y$, $3d_{xz}$ and $3d_{yz}$ orbitals. This charge migration is then partially compensated for by the charge donated by the $3d_{x^2-y^2}$ and $3d_{xy}$ orbitals to the ligand π-system.

The calculated reduction in occupancies of the benzene $2s$, $2p_x$ and $2p_y$ orbitals implies that σ-bonding within the ring will be weakened on complex formation. Furthermore the increased carbon $2p_z$ occupancy occurs *via* donation into the antibonding π^* orbitals, and on this basis the longer observed carbon–carbon separation in the benzene complex compared with free benzene may be attributed to both weaker in plane σ-bonds and π-bonds.

Although Fig. 1 suggests that electron loss from $CrBz_2$ should produce the cation $[CrBz_2]^+$ with the electronic configuration $e_{2g}^4 a_{1g}^1$, the S.C.F. eigenvalues show an inversion in the order of these orbitals and therefore indicate that the configuration $e_{2g}^3 a_{1g}^2$ should arise. In order to resolve this apparent anomaly we have computed the total energy for a number of states of $[CrBz_2]^+$ as a function of the metal–carbon distance. These are represented in Fig. 2 and clearly show that the $^2A_{1g}$ state has a

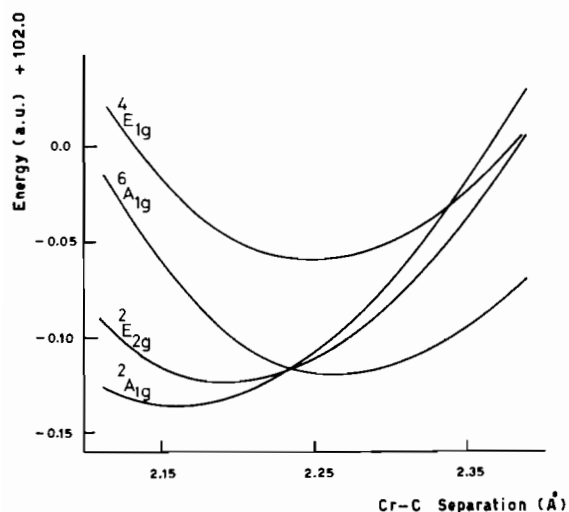Figure 2. Potential energy curves of $[Cr(benzene)_2]^+$.

lower equilibrium energy. The curves are very similar for VBz_2 although the $^2A_{1g}$ state is calculated to be slightly more favoured in this case. The computed equilibrium metal–carbon bond lengths compare favourably with the experimental values [11, 12] ($[CrBz_2]^+$: calculated 2.16 Å, experimental 2.07 Å; VBz_2: calculated 2.22 Å, experimental 2.17 Å). With manganocene previously [9] calculated to possess a $^6A_{1g}$ ground state and the ferricenium

cation to have a $^2E_{2g}$ electronic configuration, this scheme of calculation has therefore differentiated most successfully between the three known ground states in the sandwich compounds of the $3d^5$ metal ions. There appear to be two reasons for favouring occupation of the e_{2g} orbital in the bis-benzene complexes compared with the ferricenium ion leading to the respective ground state configurations of $^2A_{1g}$ and $^2E_{2g}$. Firstly the e_{2g} * ligand orbital has a more negative one-electron H^{core} for a six-membered ring than for a five-atom ring and it will therefore interact more strongly with the metal d_{xy}, $d_{x^2-y^2}$ orbitals. In addition, since the e_{2g} molecular orbital is more delocalised than the a_{1g} molecular orbital, more electronic charge can be lost from the metal if the e_{2g} rather than the a_{1g} molecular orbital is occupied. This is of obvious importance in the bis-benzene complexes where the metal is in a low oxidation state (either 0 or I), and the build up of charge on the metal *via* the $4s$, $4p$ and $3d_{xz}$, $3d_{yz}$ orbitals can best be relieved by *full* occupation of these e_{2g} orbitals. On the other hand the metal has a formal oxidation state of III in ferricenium and has no desire to further lose electronic charge to the rings with the result that *full* a_{1g} occupancy is favoured.

It is possible from these results to evaluate the first two photoelectron bands of $CrBz_2$ by taking vertical energy differences from the minimum of the $^1A_{1g}$ curve of $CrBz_2$. The calculated values of 5.03 and 5.71 eV arise from ionisation to the $^2A_{1g}$ and $^2E_{2g}$ states respectively of $[CrBz_2]^+$ (Fig. 2), and these agree very well in magnitude with the experimental values of 5.43 and 6.38 eV, and their assignment based on the intensity ratio of the two bands [13]. Application of Koopmans' theorem to the S.C.F. eigenvalues would have yielded values of 5.06 eV (e_{2g}) and 6.48 eV (a_{1g}), which although showing better numerical agreement with experiment are incorrect in their ordering. The results show that one of the inherent assumptions within Koopmans' theorem, namely that of negligible charge redistribution on ionisation, is not true for these molecules. Thus of the electron charge present in the a_{1g} molecular orbital in $CrBz_2$, 93.08% lies in the metal $3d_{z^2}$ orbital. Ionisation from this molecular orbital is therefore expected to change the total charge on the chromium atom from -0.5075 to $+0.4233$ if it is assumed that no subsequent electronic relaxation occurs. However, the calculated charge in the $^2A_{1g}$ state of the cation is -0.3818, indicating that a substantial charge redistribution has occurred. Similarly, the ionisation from the e_{2g} orbital is expected to remove 0.4768 of an electron from either the $3d_{x^2-y^2}$ or the $3d_{xy}$ orbital, thereby reducing the charge on the metal to -0.0307. However, the actual metal charge for the $^2E_{2g}$ state of the cation is -0.4962, which again indicates considerable relaxation.

TABLE II. Net Orbital Occupancy in $[CrBz_2]$ and $[CrBz_2]^+$.

Orbital	Occ. $^1A_{1g}$	Occ. $^2A_{1g}$	$^2A_{1g} - {}^1A_{1g}$	Occ. $^2E_{2g}$	$^2E_{2g} - {}^1A_{1g}$
$4s$	0.4490	0.4344	−0.0146	0.4483	−0.0007
$4p_z$	0.3964	0.4208	0.0064	0.3968	0.0004
$4p_x + 4p_y$	0.9968	1.0103	0.0135	1.0081	0.0113
$3d_{z^2}$	1.9182	0.9943	−0.9239	1.9356	0.0174
$3d_{xz} + 3d_{yz}$	0.4400	0.5512	0.1112	0.4709	0.0309
$3d_{xy} + 3d_{x^2-y^2}$	2.3080	2.9888	0.6808	2.2365	−0.0715
$2s$	11.4960	11.5669	0.0709	11.5813	0.0853
$2p_z$	12.6456	11.8465	−0.7991	11.6805	−0.9651
$2p_x + 2p_y$	22.9344	23.3444	0.4100	23.3371	0.4027
$1s$	12.4200	11.8614	−0.5586	11.9030	−0.5170

It is of interest to examine the charge redistribution on ionisation in terms of the atomic orbital occupations since this offers a further insight into the bonding and charge distribution of the neutral molecule. Table II shows the net orbital occupancies, including both spins, for all the orbitals of the molecule and its ion and the changes they undergo on vertical ionisation.

An examination of the $^2A_{1g}$ state of the cation reveals that the bulk (92%) of the lost electron has been removed from the $3d_{z^2}$ orbital as expected. This is coupled with a large increase (0.68) in the occupancies of the $3d_{xy}$ and $3d_{x^2-y^2}$ orbitals and a moderate increase (0.11) in the $3d_{xz}$ and $3d_{yz}$ orbital occupancies. The former reflects a reduction of the back bonding from the $3d_{xy}$ and $3d_{x^2-y^2}$ orbitals to the benzene π-system *i.e.* a decrease in the covalency of these orbitals, while the latter indicates an increased covalency for the $3d_{xz}$ and $3d_{yz}$ orbitals. Both these effects are consistent with the increase in oxidation state of the chromium, which leads to a greater electronegativity for the metal atom. It is also clear that these changes in $3d_{xy}$, $3d_{x^2-y^2}$, $3d_{xz}$ and $3d_{yz}$ occupancy are almost exactly balanced by the loss (0.80) of electrons from the benzene π-system. This is consistent with the charge migration scheme proposed for dibenzenechromium given earlier. Thus the synergic effect can be seen to be much reduced on ionisation from a a_{1g} molecular orbital.

The situation regarding the ionisation of the e_{2g} molecular orbitals is more complicated. In the $^2E_{2g}$ state of the cation there appears to be little electron loss from the metal $3d_{xy}$ and $3d_{x^2-y^2}$ orbitals despite their involvement in the ionised molecular orbital. There are two reasons for this. Firstly, most of the e_{2g} molecular orbitals (> 50%) are comprised of ligand $2p_z$ orbitals in the neutral molecule. Secondly, what charge is lost from the metal is readily compensated for by the decrease in covalency of the $3d_{x^2-y^2}$ and $3d_{xy}$ orbitals, hence reducing the back donation to the $2p_z$ orbitals from these orbitals. Consequently most of the lost electron (97%) appears

to come from the ligand π-system. This loss of $2p_z$ charge also means that there is less charge transferred to the $3d_{xz}$ and $3d_{yz}$ orbitals on ionisation, compared to the a_{1g} molecular orbital.

It is also interesting to note that from both states there is a loss of $1s$ electron charge, leading to a positively charged hydrogen atom and a corresponding increase in the $2s$, $2p_x$ and $2p_y$ occupancies. It is probable that the cause of this migration is the loss of considerable electron charge from the carbon $2p_z$ orbitals.

Although these two d^5 complexes possess a single unpaired electron in an essentially localised a_{1g} molecular orbital, small amounts of spin are transferred to the ring orbitals, notably to the hydrogen $1s$ orbitals where their presence may be detected by electron spin or nuclear magnetic resonance spectroscopy [5, 7, 14, 15]. Three different processes (Fig. 3) may contribute to the delocalisation of spin
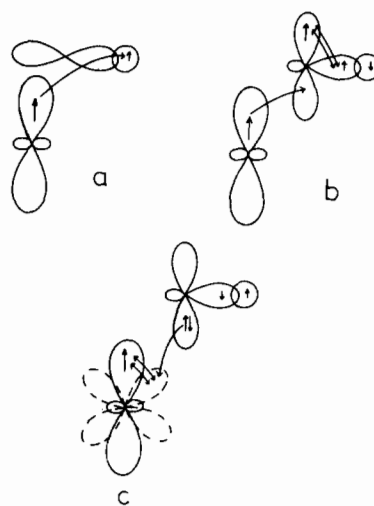
Figure 3. Spin transfer mechanisms within $[Cr(benzene)_2]^+$.

throughout the molecule. Firstly there is 'direct' delocalisation, which occurs by an inclusion of small amounts of ligand orbitals into the essen-

tially metal wavefunction as a result of molecular orbital formation (case a). Secondly (case b) it is possible for unpaired electrons to be delocalised into the ring π-orbitals which then polarise the C–H σ-bonds and produce negative spin density at the protons, similar to that encountered with aromatic radical ions. This effect was taken into account empirically in the one-electron calculations of Drago *et al.* [7]. Lastly, the metal unpaired electrons may polarise the metal–carbon bonds and produce a negative spin density within the carbon orbitals, thereby leading to positive spin density at the protons (case c). All three mechanisms are automatically incorporated into the calculations with the present INDO method. The computed hydrogen $1s$ spin densities yield coupling constants, using Pople's value [16] for the factor

$$\frac{4\pi}{3} g \beta \gamma h \langle S_z \rangle^{-1} | \Phi_0 |^2,$$

which are in good agreement with the measured values [$(CrBz_2)^+$: calculated +2.21 gauss, experimental +3.15 and 3.46 gauss; VBz_2: calculated +3.40 gauss, experimental +4.0 gauss]. Negative coupling constants result in both complexes for the $^2E_{2g}$ state. The bulk of the spin transferred to the hydrogens in the $^2A_{1g}$ state arises by direct delocalisation with the third mechanism also contributing to some extent, since all the metal orbitals have a small excess of positive spin while the carbon $p\pi$ orbitals show a net negative spin density. It is noteworthy that less than 0.0002 spins are transferred to the carbon $2s$ orbitals.

The e.s.r. spectra of both molecules have also yielded metal hyperfine coupling constants, the isotropic portion of which is influenced by small admixtures of a $4s$ component in the open-shell a_{1g} orbital. The present calculations suggest that the $4s$ orbital contains $\sim$ +3% and +1.5% spin density in VBz_2 and $[CrBz_2]^+$ respectively. Unfortunately it

is not possible to evaluate accurately this contribution to the coupling constant because the desired wavefunctions are not available, however using the values [17] for $[\Psi_{4s}^0]^2$ we estimate the $4s$ term to make a positive contribution of $\sim$ 20 gauss to the observed negative coupling constant of -63 gauss for VBz_2, and a negative contribution of about -2 gauss for $[CrBz_2]^+$.

References

1 K. D. Warren, *Inorg. Chem., 14*, 2279 (1975).
2 S. Evans, M. L. H. Green, B. Jewitt, G. M. King and A. F. Orchard, *J. Chem. Soc. Far. II, 70*, 356 (1974).
3 a) J. H. Ammeter, R. Bucher and N. Oswald, *J. Am. Chem. Soc., 96*, 7833 (1974). b) M. E. Switzer, R. Wong, M. F. Rettig and A. H. Maki, *J. Am. Chem. Soc., 96*, 7669 (1974).
4 a) R. Prins, *Mol. Phys., 19*, 603 (1970). b) M. D. Rowe and A. J. McCaffery, *J. Chem. Phys., 59*, 3786 (1973).
5 S. E. Anderson and R. S. Drago, *J. Am. Chem. Soc., 92*, 4244 (1970).
6 E. O. Fischer and U. Piesbergen, *Z. Naturforsch. 11b*, 758 (1956).
7 R. Prins and F. J. Reinders, *Chem. Phys. Letters, 3*, 45 (1969).
8 S. E. Anderson and R. S. Drago, *Inorg. Chem., 11*, 1564 (1972).
9 D. W. Clack, *Theor. Chim. Acta, 35*, 157 (1974).
10 D. W. Clack, *Mol. Phys., 27*, 1513 (1974).
11 O. V. Starovskii and Y. T. Struchkov, *Dokl. Akad. Nauk. SSSR, 135*, 620 (1961).
12 a) E. O. Fischer, H. P. Fritz, J. Manchot, E. Priebe and R. Schreider, *Chem. Ber., 96*, 1418 (1963).
b) A. Haaland, *Acta Chem. Scand., 19*, 41 (1965).
13 S. Evans, J. C. Green and S. E. Jackson, *J. Chem. Soc. Far. II, 68*, 249 (1972).
14 Y. S. Karinov, C. M. Chibrikin and I. F. Shchegolev, *J. Phys. Chem. Solids, 24*, 1683 (1963).
15 K. H. Hauser, *Z. Naturforsch. 16a*, 1190 (1961).
16 J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory", McGraw-Hill (1970).
17 B. A. Goodman and J. B. Raynor, *Adv. Inorg. and Radiochem., 13*, 135 (1970).