Organometallic clusters with face capping arene ligands

II *. The electronic structure of $(CpCo)_3(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-benzene})$

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Abstract

Fenske–Hall quantum chemical calculations have been performed on the model complex $(CpCo)_3(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)$. It is shown that benzene acts as a π-donor and π-acceptor to the $(CpCo)_3$ cluster. A diminution of conjugation, due to a mixing of the benzene e orbitals, is responsible for the observed Kekulé-type distortion of the μ_3-benzene ligand.

Introduction

Organometallic molecular clusters are commonly used as models for the adsorption states of small molecules on metal surfaces [1]. Benzene has been extensively studied on a variety of metal surfaces by many different methods, e.g. LEED [2], HREELS [3], ARUPS [4], STM [5] and TDS [6]. Under ultra-high vacuum conditions, benzene is adsorbed molecularly on atomically flat metal surfaces with the plane of the benzene ring parallel to the surface [2–6]. However, no general agreement seems to exist under the various authors about the distortion from D_{6h} symmetry of the adsorbed benzene, or even the exact site of adsorption. Theoretical calculations favour location of benzene on top of three surface metal atoms ('hollow' adsorption site, C_{3v} (σ_d) symmetry) [7,8]. There is experimental evidence [2–5] for both 'on top' (C_{6v} symmetry) and 'hollow' adsorption geometries even on the same or very similar metals.

The first molecular models for chemisorbed benzene, $Os_3(CO)_9(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)$ and $Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_6)(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)$, were described in 1985 [9].

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Table 1

Selected bond lengths (Å) for benzene in various molecular complexes and on some metal surfaces

Compound	d(C–C) [a]	d(M–C)	Ref.
$Os_3(CO)_9(C_6H_6)$	1.41(3), 1.51(3) [b]	2.33(3) [b]	9
$Os_3(CO)_8(C_2H_4)(C_6H_6)$	1.41(3), 1.46(3) [b]	2.31(3) [b]	12
$Ru_6C(CO)_{11}(C_6H_6)_2$	1.39(2), 1.48(2) [b]	2.27(1) [b]	9
$(CpCo)_3(C_6H_5CH=C(H)Me)$	1.420(5), 1.446(5) [b]	2.029(2) [b]	10
$(CpCo)_3(C_6H_5C(Ph)=CH_2)$	1.418(4), 1.449(4) [b]	2.016(2) [b]	13
$Rh(111)/C_6H_6/CO$	1.33(15), 1.81(15)	2.35(5) [c]	2a
$Rh(111)/C_6H_6/2CO$	1.46(15), 1.58(15)	2.30(5) [c]	2b
$Pt(111)/2C_6H_6/4CO$	1.65(15), 1.76(15)	2.25(10) [d]	2c
$Cr(CO)_3(C_6H_6)$ [e]	1.401(2), 1.420(2) [b]	2.229(2) [b]	25a

[a] μ_3-Benzene resp. phenyl. [b] Mean values. [c] Hollow site ($C_{3v}(\sigma_d)$). [d] Bridge site (C_{2v}). [e] η^6-Benzene.

X-ray crystallographic data, although of limited precision, indicated a substantial expansion and Kekulé-type distortion of the face capping benzene rings in these compounds. Similar bond length alternation, but much more pronounced, was observed in benzene coadsorbed with CO on Rh(111) [2] (Table 1). We have recently developed a simple high-yield synthetic route to a novel class of μ_3-arene trimetal clusters, $(CpCo)_3(\mu_3-\eta^2 : \eta^2 : \eta^2$-subst. vinylbenzene) [10,11]. In these compounds, distortion of the bridging arene from hexagonal geometry is fairly small, but nevertheless significant (Table 1).

Here we report the results of theoretical SCF–MO–LCAO studies on a model compound, $(Cp(Co)_3(\mu_3-\eta^2 : \eta^2 : \eta^2-C_6H_6)$ (1).

Calculational details

The molecular orbital (MO) technique used in this study involved an approximation to the Hartree–Fock–Rothaan method, namely the Fenske–Hall procedure [14]. This iterative self-consistent field (SCF) calculation employs the atomic basis functions and the molecular geometry as only adjustable parameters. The geometry of 1 was derived from the crystal structure of $(CpCo)_3(\mu_3-\eta^2 : \eta^2 : \eta^2$-trans-$\beta$-methyl-styrene) [10] by omitting the propenyl side chain and idealising the molecular symmetry to C_3. The resulting bond lengths were Co–Co 2.50 Å, Co–C(benzene) 2.025 Å, Co–C(Cp) 2.11 Å and C–C(benzene) 1.43, 1.45 Å. The usual basis functions were used for Co [15], C [16] and H [17] atoms. The molecule was partioned into fragments with chemical meaning (see below). After convergence of the SCF calculation the atomic basis set was transformed into a basis set of the fragment orbitals to make the calculations easier to interpret. The energies of the fragment orbitals in the MO diagrams are diagonal elements of the Fock matrix from the calculation on the complete molecules. To avoid problems with counter-intuitive orbital mixing [18], which is quite common in cyclopentadienyl metal complexes, the lowest σ orbitals of the ligands were treated as 'frozen', i.e. as non-interacting with the metals [19].

Results and discussion

Extended Hückel MO (EHMO) calculations on C_{3v} $[(CO)_3Fe]_3(\mu_3$-benzene) were briefly discussed by Schilling and Hoffmann in their comprehensive study of M_3L_9
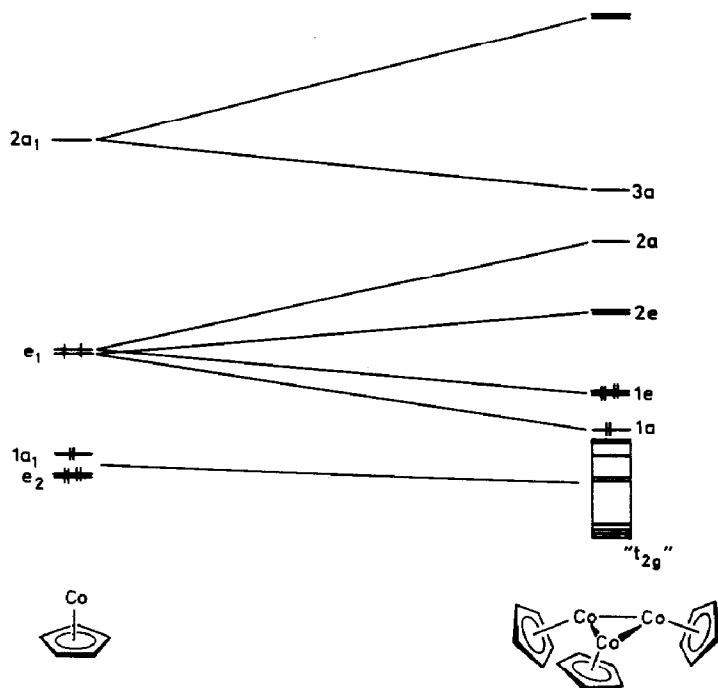
Fig. 1. Interaction diagram for (CpCo)$_3$ under C_3 symmetry.

(ligand) complexes [20]. Because of the isolobal relationship of the (CO)$_3$Fe and CpCo fragments [21] the electronic structures of the [(CO)$_3$Fe]$_3$ and (CpCo)$_3$ clusters are expected to be quite similar. Fenske–Hall MO (FHMO) calculations on C_{3v} [(CO)$_3$Fe]$_3$ generate basically the same sequence of frontier orbitals as those obtained by the EHMO-method [20]. We chose to build up the (CpCo)$_3$ fragment from three CpCo units. The frontier orbitals of the latter have been described in detail [22] and need not be explained here. D_{3h} (CpM)$_3$ clusters (M = Co [23], Rh [24]) (i.e. with the Cp rings perpendicular to the Co$_3$ plane) have been analysed earlier using the FHMO and EHMO methods. The somewhat different orbital scheme resulting from the interaction of three CpCo fragments under C_3 symmetry (i.e. the Cp ligands are bent towards one side of the Co$_3$ triangle and twisted to avoid close contacts between the Cp hydrogens) is shown in Fig. 1.

The lower lying 'pseudo t_{2g}' [21] orbitals of the three CpCo groups do not interact very much with one another. The main stabilisation of the (CpCo)$_3$ cluster arises from the CpCo e_1 fragment orbitals. Compared to C_{3v} [(CO)$_3$Fe]$_3$ the virtual cluster $3a$ orbital (in phase combination of the three CpCo $2a_1$ hybrid orbitals) has risen in energy while the metal metal antibonding cluster $2a$ orbital (a_2 for C_{3v}) has come down below $3a$. In addition, $1a$ is now below $1e$. For (CpCo)$_3$, orbitals up to $1e$ are filled.

Interaction of (CpCo)$_3$ and benzene is depicted schematically in Fig. 2.

The standard (D_{6h}) labelling of the benzene orbitals is used, although the true symmetry is of course reduced. The main bonding interaction in the complete molecule amounts to donation from the filled e_{1g} orbitals of benzene into the virtual (CpCo)$_3$ $2e$ set, accompanied by back donation from (CpCo)$_3$ $1e$ into benzene e_{2u} (Fig. 3).
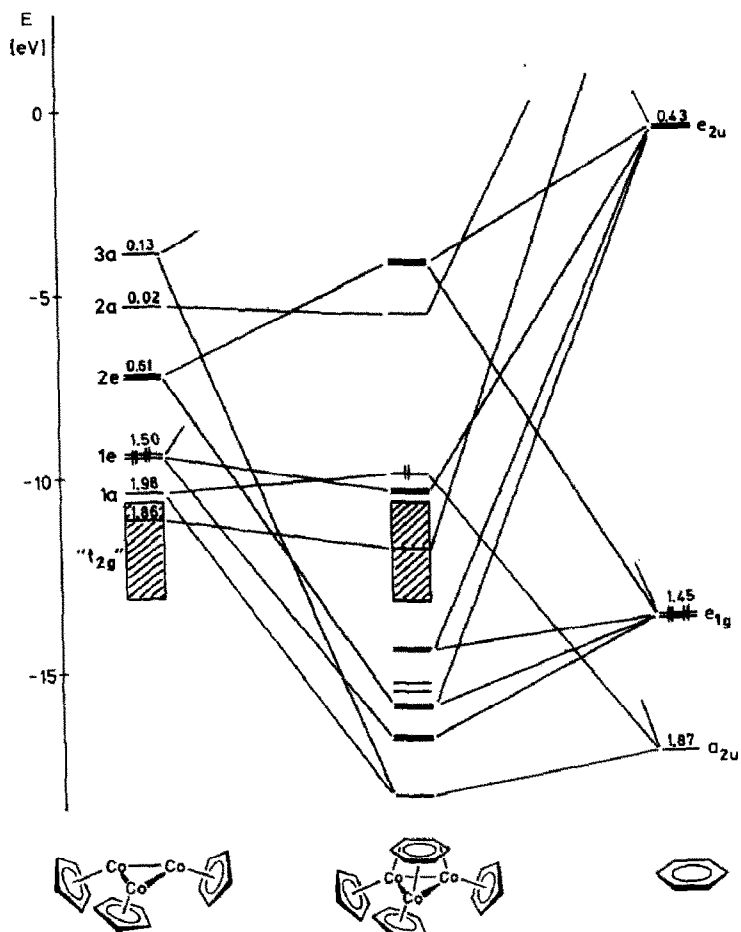
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Fig. 2. Interaction diagram for $(CpCo)_3(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-benzene})$ (1). The numbers above the fragment orbital energy levels are Mulliken populations.

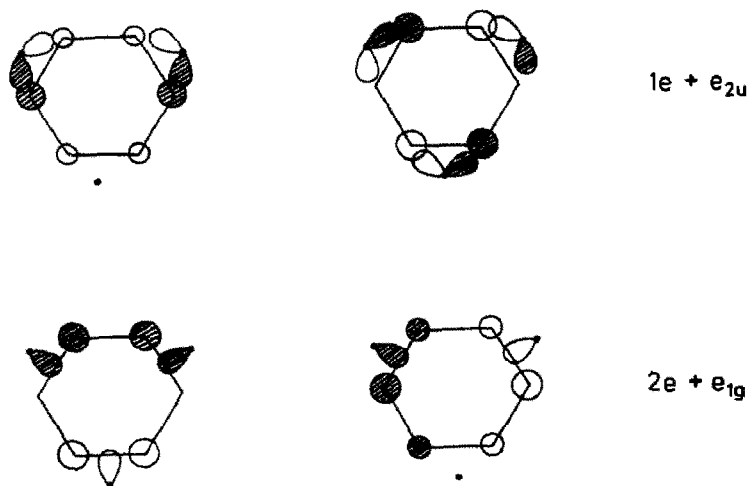Fig. 3. Pictorial representation of important donor–acceptor orbital interactions in 1: $(CpCo)_3$ $1e$ and benzene e_{2u} (top); $(CpCo)_3$ $2e$ and benzene e_{1g} (bottom). Black dots denote positions of the cobalt atoms.

Table 2

Fragment–fragment Mulliken overlap populations for the formation of **1** from $(CpCo)_3$ and benzene

MO in $(CpCo)_3$	MO in benzene					
	a_{2u}	e_{1g}		e_{2u}		b_{2g}
46						0.106
49 (1a)	0.002					0.005
50 (1e)		0.013	0.068	0.025	0.136	
51 (1e)		0.068	0.013	0.136	0.025	
52 (2e)		0.234	0.034	0.049		
53 (2e)		0.034	0.234		0.049	
55 (3a)	0.167					
56		0.048				
57			0.048			

Additional stabilisation is gained from interaction of one of the $(CpCo)_3$ 'pseudo t_{2g}' orbitals with benzene b_{2g}. Several weak repulsive four electron interactions of benzene a_{2u} with low lying $(CpCo)_3$ orbitals, although evident, are comparatively unimportant for bonding. Mulliken overlap populations are summarised in Table 2. Both HOMO (89% $(CpCo)_3$ with a small contribution (5%) of benzene a_{2u}) and LUMO (94% $(CpCo)_3$, 2% benzene b_{2g}) of **1** are essentially non bonding with respect to $(CpCo)_3$ and benzene.

The bonding situation in **1** can be compared with that in the mononuclear complex $(CO)_3Cr(benzene)$ [25]. The frontier orbitals of $(CO)_3Cr$ [25b] (which is isolobal with $(CpCo)^{2+}$), a 'pseudo t_{2g}' ($1a_1 + 1e$) set below and a set of three orbitals ($2e$, $2a_1$) above, are to be compared with the right hand side of Fig. 1. In $(CO)_3Cr$, $1a_1$ and $1e$ are filled, which results in a configuration quite similar to that of $(CpCo)_3$. Hence, $(CO)_3Cr(benzene)$ and $(CpCo)_3(benzene)$ have many features in common. The similarity of the small Kekulé distortion of the coordinated benzene found experimentally in both types of complexes is remarkable (Table 1), though ring expansion is more pronounced in the cluster-bound benzene. In our calculations on **1** it is evident from the C–C overlap populations. These are reduced from 1.130 ($0.293\pi + 0.837\sigma$) and 1.102 ($0.271\pi + 0.831\sigma$) in D_{3h} (Kekulé distorted) free benzene to 1.011 ($0.184\pi + 0.827\sigma$) and 0.936 ($0.114\pi + 0.822\sigma$) in **1**. The larger values are for the bonds closest to the cobalt atoms. Additional calculations with regular hexagonal benzene reproduce this trend fairly closely, indicating that it is not an artefact from the geometry used for **1**. The weakening of the conjugation in the face capping benzene, however, is much less pronounced than that in $L_2Pd_2(\mu$-X)(benzene) [26], where benzene is bound in η^4-fashion across a Pd–Pd bond [27].

It has been suggested that the Kekulé-type distortion of the benzene hexagon in $(CO)_3Cr(benzene)$ is caused by a mixing of the benzene e_{2u} and e_{1g} orbitals, which are both e under the reduced threefold molecular symmetry of the complex (and can therefore mix) [25b,28]. The same conclusion was derived from the calculations of benzene adsorbed in threefold sites on metal surfaces and slabs [8]. In **1** mixing of the bonding benzene e_{1g} and antibonding e_{2u} orbitals is also evident (Fig. 2); it is however present in various $(CpCo)_3(\mu_3$-benzene) molecular orbitals and not associated mainly with one particular metal fragment orbital, as it is the case in $(CO)_3Cr(benzene)$ [28].

In mononuclear complexes of benzene, the C–H bonds are bent towards the metal in order to maximise the overlap between the benzene e_{1g} and suitable metal orbitals [22]. For M_3 face-capping benzene, the opposite distortion is expected from geometrical arguments. Moving the hydrogen atoms out of the C_6 plane away from the metal does indeed increase the total inter-fragment overlap populations. Analogous conclusions were reached from EHMO band calculations of benzene on various clusters of nuclearity 3 to 17 and two-dimensional slabs of the late transition metals [7,8]. Our crystallographic data for $(CpCo)_3(\mu_3\text{-}\eta^2 : \eta^2 : \eta^2\text{-}trans\text{-}\beta\text{-methyl-}$ styrene) [10] and $(CpCo)_3(\mu_3\text{-}\eta^2 : \eta^2 : \eta^2\text{-}1,1\text{-diphenylethene})$ [13] as well as the available data for benzene in threefold adsorption sites do indeed reveal a displacement (0.3 Å in the molecular clusters) of the arene hydrogen atoms away from the metals.

Conclusion

Our calculations underline the considerable stability of the $\mu_3\text{-}\eta^2 : \eta^2 : \eta^2\text{-benzene}$ tricobalt cluster 1. The main stabilising interactions are π donation from benzene e_{1g} into empty metal orbitals, accompanied by π back-donation into benzene e_{2u} orbitals. Structural details, such as the small Kekulé-type bond length alternation in the coordinated benzene ring (attributed to a diminution of conjugation caused by a mixing of the benzene e_{1g} and e_{2u} orbitals), and the bending of the benzene C–H bonds away from the metals, are reproduced by our calculations. With respect to the properties of their frontier orbitals, the mononuclear $(CO)_3Cr$ fragment, the trinuclear $(CpCo)_3$ cluster and a threefold site on a close packed metal surface of the late transition metals have a lot in common, and this is reflected in the structural similarities of the coordinated benzene ligands.

Acknowledgment

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