

CORRELATION OF THE REACTIVITY OF COORDINATED π -HYDROCARBONS WITH ELECTRONIC PARAMETERS

IV *. INDO MOLECULAR ORBITAL CALCULATIONS ON THE CATIONS [[$(C_6H_5X)Fe(C_5H_5)$]⁺ (X = H, Me, OMe, COOMe)

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Summary

Molecular orbital calculations have been made for the series of cations [[$(C_6H_5X)Fe(C_5H_5)$]⁺ (X = H, Me, OMe, COOMe). The results provide some support for recent proposals concerning the relationship between the site of nucleophilic attack and the even or odd hapticity of the π -hydrocarbon ligands. However, the factors which determine the position of attack in a particular ring appear to be neither charge controlled nor influenced by the LUMO in the complex.

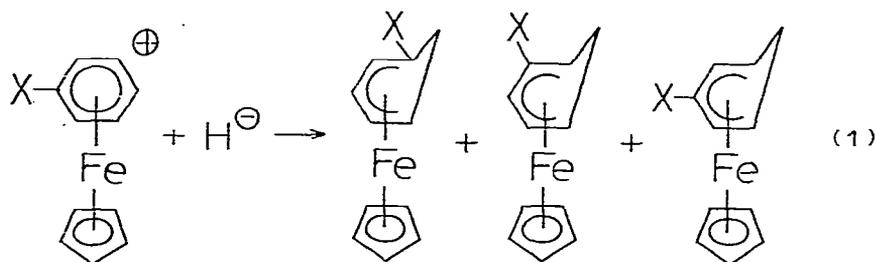
Introduction

Synthetic and more recently kinetic studies have established a variety of reaction pathways for nucleophilic attack on coordinated π -hydrocarbons. In an attempt to provide a quantitative theoretical basis for observed reactivity patterns, we recently commenced a programme [1] of INDO molecular orbital calculations on organometallic complexes. The present paper reports the results of such calculations on the cations [[$(C_6H_5X)Fe(C_5H_5)$]⁺ (I; X = H, Me, MeO, COOMe) together with the free arenes C_6H_5X .

Hydride ion has been shown [2–4] to add to these complexes according to eq. 1, in which the ratio of *ortho*, *meta*, and *para* addition is strongly influenced by the nature of the arene substituent X. The calculations establish the relative importance of arene carbon charge, σ - and π -electron density, free valency, and frontier

* For Part III, see ref. 1.

orbitals in determining the regioselectivity of addition. Further insights are also provided into the bonding in such complexes.



Experimental

Method

The calculational procedure has been outlined previously [5]. Lacking experimental geometries for these complexes we have taken Fe—C(benzene) and Fe—C(cyclopentadiene) as 2.07 Å and 2.17 Å, respectively, by analogy with similar complexes. The side-chain geometries have been estimated from data given in ref. 6.

Results and discussion

Stereochemical investigations [2–4] of reactions (I; X = Me, MeO, COOMe, Cl) have established the directing influence of various arene substituents (Table 1). While a methyl (+I) substituent exhibits no site preference for hydride addition, the electron-withdrawing COOMe (–I–R) and Cl (–I > +R) groups strongly activate the C(2) or *ortho* position relative to the *meta* and *para* sites. In contrast, a methoxide (–I < +R) substituent favours attack at C(3) i.e. the *meta* position. It has been suggested [4] that these variations in arene-site reactivities may be explained qualitatively by variations in the arene-carbon charges.

The present INDO molecular orbital calculations on $[(C_6H_5X)Fe(C_5H_5)]^+$ cations (I) allow this hypotheses to be tested quantitatively. The charge values in Table 2 for X = MeO (positive charge decreasing along the series C(3) > C(4) > C(2)) correctly predict the observed site preference for H[–] addition. Similarly, the much smaller variations in arene-carbon charges for X = Me (C(3) ≥ C(4) ≥

TABLE 1

ARENESITE REACTIVITIES FOR HYDRIDE ADDITION TO $[(C_6H_5X)Fe(C_5H_5)]^+$

X	Ratio of <i>ortho</i> , <i>meta</i> and <i>para</i> addition			Reference
	<i>ortho</i>	<i>meta</i>	<i>para</i>	
Me	1	1	1	2a
MeO	0.2	1	0.6	3
COOMe	12.7	1	1.1	4
Cl	4	1	0	2b

TABLE 2

ARENES CARBON ATOMIC CHARGES AND σ - AND π -ELECTRON OCCUPANCIES FOR C_6H_5X AND $[(C_6H_5X)Fe(C_5H_5)]^+$ (I)

Atom	Total Charge		π -Electron density		σ -Electron density	
	C_6H_5X	I	C_6H_5X	I	C_6H_5X	I
	<i>X = H</i>					
C(1)–C(6)	+0.026	+0.148	1.000	0.950	2.97	2.90
	<i>X = Me</i>					
C(1)	+0.037	+0.163	0.981	0.919	2.98	2.92
C(2)	+0.014	+0.131	1.02	0.969	2.97	2.90
C(3)	+0.029	+0.151	0.992	0.942	2.98	2.91
C(4)	+0.019	+0.142	1.01	0.958	2.97	2.90
	<i>X = MeO</i>					
C(1)	+0.242	+0.368	0.951	0.897	2.81	2.73
C(2)	−0.050	+0.074	1.06	1.00	2.99	2.93
C(3)	+0.050	+0.164	0.980	0.938	2.97	2.90
C(4)	−0.003	+0.129	1.04	0.970	2.97	2.90
	<i>X = COOMe</i>					
C(1)	−0.047	+0.081	1.03	0.962	3.01	2.96
C(2)	+0.057	+0.163	0.970	0.939	2.97	2.90
C(3)	+0.017	+0.144	1.00	0.947	2.98	2.91
C(4)	+0.045	+0.152	0.974	0.945	2.98	2.90

C(2)) are consistent with the lack of regioselectivity in hydride attack on $[(C_6H_5Me)Fe(C_5H_5)]^+$. However, while the arene-carbon charges in the $X = COOMe$ cation do vary in the order expected ($C(2) \geq C(4) \geq C(3)$), the differences are no larger than those calculated for the $X = Me$ cation. Thus, the calculations suggest that charge variations alone cannot explain the very marked *ortho*-directing influence of the COOMe substituent.

Table 2 also shows that the positive charges on the arene carbon atoms increase on complexation to the $[Fe(C_5H_5)]^+$ moiety. However, the relative magnitude of these charges around the ring remain the same in complexes I as in the free arenes. This feature appears quite reasonable in view of the fact that the $Fe(C_5H_5)$ group is axially symmetric and should therefore, unlike a $M(CO)_3$ fragment, exhibit no directional properties.

A further interesting feature of the data in Table 2 is that charge considerations would clearly predict C(1) as the site for nucleophilic addition on the $X = MeO$ cation. C(1) is also the most positive arene carbon in the $X = Me$ complex. The failure to observe H^- addition at C(1) in any of the reactions 1 may arise from steric hindrance at this site.

Nevertheless, charge arguments do readily explain one of the characteristic features of reactions 1, namely that nucleophilic addition occurs exclusively at the arene ring rather than at the cyclopentadienyl ligand. The charges on each of the cyclopentadienyl-carbon atoms in all the cations I are calculated to fall in the narrow range +0.077, to +0.079, i.e. very much lower than the arene-carbon charges in Table 2. This observation supports a recent suggestion [7] that in 18-electron organometallic cations containing more than one unsaturated hydrocar-

bon ligand, ligands with an even hapticity will be invariably favoured over those with an odd hapticity as the site for attack by hard nucleophiles. This latter generalisation was given [7] a theoretical basis from Hückel-type calculations indicating a higher positive charge on even hydrocarbons, and was supported by an impressive body of stereochemical evidence.

However, our results here, and previous INDO calculations on the $[(C_6H_6Y)Fe(CO)_3]^+$ ($Y = H, Me, MeO$) and $[(C_7H_7Z)Cr(CO)_3]^+$ ($Z = H, MeO, Cl, COOMe$) cations [5,8,9] indicate that further suggestions [4,7] that the site reactivities on a particular hydrocarbon ligand are also controlled by charge are less well-founded. In none of the three systems that we have investigated to date do charge variations alone provide an adequate rationale for the regioselectivity on a single hydrocarbon. It is possible, as has been proposed [7] for some related reactions, that the products are not kinetically controlled and that rearrangements occur after initial nucleophilic addition. This ambiguity may be resolved by further spectroscopic and kinetic studies of these systems.

Attempts to correlate calculated σ - and π -electron densities (Table 2) with the site of nucleophilic addition on the arenes are no more fruitful. Although a reasonable correlation is observed for the $X = MeO$ cation, the fit for $X = Me$ and $X = COOMe$ is poor.

In view of our earlier observation [5] that the site of nucleophilic attack on the cation $[(C_6H_7)Fe(CO)_3]^+$ correlates well with the dienyl carbon free valencies (but not charge), C—C bond orders have also been calculated for the arene ligands in each of the complex I. If one excludes C(1) for steric reasons (see above), the C—C bond orders in Table 3 indicate that C(2) has the highest free valency in each case. This would suggest C(2) as the favoured site for formation of a bond with the incoming nucleophile in each complex, which (except for $X = COOMe$) is inconsistent with experimental observations.

An explanation for the stereochemistry of reactions 1 may also be sought in frontier orbital terms. In the unsubstituted cation ($X = H$) the LUMO is a doubly degenerate pair of orbitals corresponding essentially to the vacant $\pi^* e_2$ level of

TABLE 3

ARENE π -BOND ORDERS FOR C_6H_5X AND $[(C_6H_5X)Fe(C_5H_5)]^+$ (I).

Bond	C_6H_5X	$[(C_6H_5X)Fe(C_5H_5)]^+$ (I)
<i>X = H</i>		
All C—C bonds	0.666	0.578
<i>X = Me</i>		
C(1)—C(2)	0.652	0.570
C(2)—C(3)	0.670	0.582
C(3)—C(4)	0.664	0.580
<i>X = MeO</i>		
C(1)—C(2)	0.642	0.560
C(2)—C(3)	0.672	0.582
C(3)—C(4)	0.664	0.580
<i>X = COOMe</i>		
C(1)—C(2)	0.638	0.558
C(2)—C(3)	0.674	0.588
C(3)—C(4)	0.662	0.578

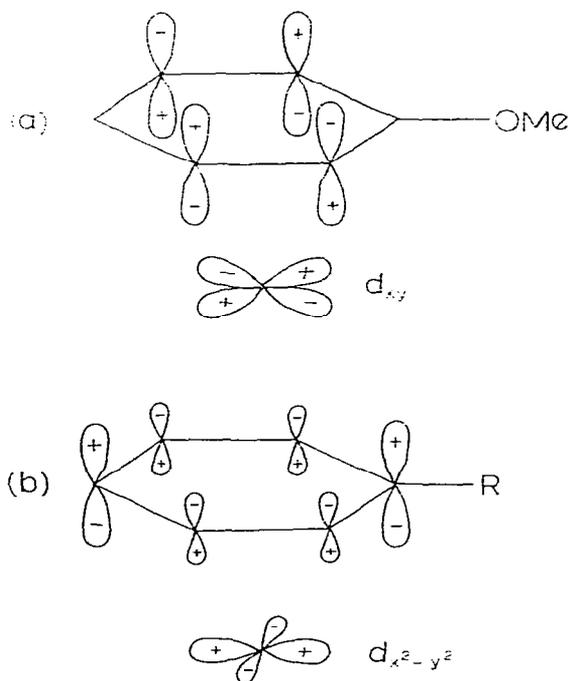


Fig. 1. Lowest unoccupied molecular orbitals for $[(C_6H_5X)Fe(C_5H_5)]^+$ cations: (a) $X = OMe$; (b) $X = Me, COOMe$.

benzene, with a small contribution (ca. 7%) from the iron $3d_{xy}$ and $3d_{x^2-y^2}$ orbitals. There is a negligible contribution to this LUMO from the cyclopentadienyl ring orbitals, which is also consistent with the proposals of Green et al. [7] concerning the relationship between the site of attack and the even or odd hapticity of the hydrocarbon ligand.

When the benzene ring is substituted, the degenerate LUMO becomes split and the lowest components of these for the various substituted complex cations I are shown in Fig. 1. The coefficients of the arene carbon $2p_\pi$ orbitals are listed in Table 4. Inspection of these coefficients shows that if frontier orbital interactions with the nucleophile HOMO were dominant, addition would be expected at C(4), C(3), and C(4) for the $X = Me, MeO,$ and $COOMe$ cations, respectively (neglecting C(1) for steric reasons). These predictions conflict with the product stereochemistries in Table 1. The apparent unimportance of frontier orbital factors in reactions 1 is perhaps not surprising in view of the hard nucleophile employed.

The general *exo*-configuration of the addition products would seem to rule out initial nucleophilic attack at the metal* and the calculations provide further support for this view. Thus the only metal $3d$ orbitals which are vacant and there

* This oft-quoted general conclusion is considerably weakened by recent studies [11] of the reaction of MeO^- with $[(C_6H_7)Os(CO)_3]^+$. The final product, $[(C_6H_6OMe)Os(CO)_3]$, has an *exo*-configuration although initial MeO^- addition occurs on a carbonyl ligand.

TABLE 4

COEFFICIENTS OF THE ARENE CARBONS IN THE LOWEST UNOCCUPIED MO OF $[(C_5H_5)X]Fe^+$ CATIONS

X	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)
Me	-0.550	+0.274	+0.265	-0.530	+0.265	+0.274
MeO	0	-0.476	+0.482	0	-0.482	+0.474
COOMe	-0.470	+0.304	+0.196	-0.447	+0.189	+0.311

fore able to accommodate an incoming nucleophile are the $3d_{xz}$, $3d_{yz}$ pair. These lie considerably higher in energy than the LUMO (ca. 1.5 eV), and moreover are aligned spatially most unfavourably with respect to an approaching nucleophile since their lobes are orientated directly at the two rings.

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