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Preliminary communication

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

I. INDO CALCULATIONS ON THE CATION $[(C_6H_7)Fe(CO)_3]^+$

D.W. CLACK, M. MONSHI, and L.A.P. KANE-MAGUIRE*
Chemistry Department, University College, Cardiff, P.O. Box 78, Cardiff, Wales
(Great Britain)

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Summary

INDO calculations on the cation $[(C_6H_7)Fe(CO)_3]^+$ suggest that there is a correlation between the bond index (or free valence) values at each dienyl carbon and the site of nucleophilic addition.

Despite considerable current interest in nucleophilic attack at coordinated π-hydrocarbon molecules, the factors governing the reactivity of such ligands are still not clearly understood. While reaction site preferences and rate trends have frequently been rationalised in qualitative electronic terms, it is noteworthy that apart from one brief report on $[(C_6H_7)Fe(CO)_3]^+$ [1] and some calculations on $[(\text{arene})M(CO)_3]$ (M = Cr, Mo, W) systems [2,3], no quantitative molecular orbital treatment has been applied to such reactions. As part of a programme of such studies, we report calculations on the cation $[(C_6H_7)Fe(CO)_3]^+$ (I). These were carried out to determine whether the observed position of nucleophilic attack may be rationalized in terms of electronic quantities, such as electron density, overall charge, or free valence, obtained from SCF MO computations.

The method of calculation follows the intermediate neglect of differential overlap (INDO) scheme [4], in which metal 3*d*, 4*s*, 4*p*, carbon and oxygen 2*s*, 2*p*, and hydrogen 1*s* valence orbitals are considered. Bond lengths and angles were taken from single-crystal X-ray data [5] for the related cation $[(MeOC_6H_6)Fe(CO)_3]^+$. The positions of the C(1)—C(5) carbons in the ring least squares plane were modified slightly to create the equivalent pairs C(1), C(5) and C(2), C(4). We propose to employ the term bond index of an atom

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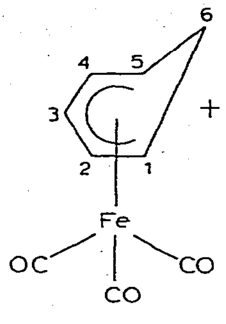
*To whom correspondence should be addressed.



(I)

for the parameter $\sum_{\nu}^{B} P_{\mu\nu}S_{\mu\nu}$, where the summation extends over all atoms B which are bonded to the atom. The total bond index of atom A is given by $\sum_{\mu}^{A} \sum_{\nu}^{B} P_{\mu\nu}S_{\mu\nu}$, and therefore represents the overlap density [6]. The use of this modified valence parameter is required since bond orders between a variety of different atoms and orbital types occur in species such as I. Bond order contributions from overlap of C(1) and C(5) orbitals with the methylene C(6) as well as contributions involving the metal, which were neglected in the simple model of Lewis et al. [1] are considered in calculating the bond index values. Table 1 summarises the electronic parameters calculated for the C(1), C(2) and C(3) positions of I and also for the free $C_6H_7^+$ species.

TABLE 1

CALCULATED ELECTRONIC PARAMETERS FOR DIENYL CARBONS IN FREE $(C_6H_7)^+$ AND $[(C_6H_7)Fe(CO)_3]^+$

Species	Parameters	Position		
		C(1)	C(2)	C(3)
$(C_6H_7)^+$	Charge	+0.186	−0.024	+0.239
	π-electron density	0.700	1.034	0.662
	Bond index (σ)	1.404	1.554	1.546
	Bond index (π)	0.263	0.313	0.272
$[(C_6H_7)Fe(CO)_3]^+$	Charge	+0.140	+0.226	+0.159
	π-electron density	0.993	0.848	0.964
	Bond index (σ)	1.582	1.690	1.702
	Bond index (π)	0.364	0.378	0.376

Coordination of $C_6H_7^+$ to the $Fe(CO)_3$ moiety is seen to cause an increase in the positive charge at C(2) which arises mainly via π-electron interactions. The bond index at each dienyl carbon also increases on coordination.

Interestingly, no correlation exists between the magnitude of the dienyl carbon positive charges and the site of nucleophilic attack on I. The charge data in Table 1 would predict the site preference C(2) > C(3) > C(1), whereas nucleophiles are known [1] to add to cation I exclusively at C(1). Although addition of a nucleophile must involve interaction with the π-electron cloud of the dienyl ring, there is also no apparent correlation between the π-electron density at each carbon atom and the site of attack. Consideration of the carbon σ-electron densities is similarly unfruitful.

However, the bond index values in Table 1 correctly predict the site of nucleophilic addition (C(1) $\gg$ C(3) > C(2)). Separation of the bond index values into σ and π contributions results in the same site order prediction for each component. A low bond index value would imply a high "free valence" for formation of a bond with the incoming nucleophile. Similar correlations between "free valence" and reactivity have been extensively reported for electrophilic substitution on aromatic substrates [6]. Such a relationship would only be expected for reactions involving an early transition state. In this respect, it is interesting that recent kinetic studies [7] of the addition of amines to the related cation $[(MeOC_6H_6)Fe(CO)_3]^+$ indeed suggest an early transition state. For addition of anions to I a possible early transition state is an ion-pair.

Finally, the increased stability of the $C_6H_7^+$ species on coordination to $Fe(CO)_3$ is also consistent with the higher bond index values calculated for the complexed dienyl carbons (Table 1). Calculations on related organometallic cations are in progress to determine whether a general correlation exists between bond index values and reactivity.

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