Preliminary communication

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

II. INDO CALCULATIONS ON THE CATIONS $[(C_7H_6X)Cr(CO)_3]^+$ (X = H, OMe, COOMe)

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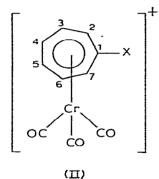
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Summary

INDO calculations show that, despite an increase in ring carbon positive charge, the decrease in reactivity of the $C_7H_7^+$ ion towards nucleophiles upon coordination to $Cr(CO)_3$ can be explained in terms of increased bond index values; the site of nucleophilic attack in $[(C_7H_6X)Cr(CO)_3]^+$ (X = OMe, COOMe) systems does not in general correlate with any specific electronic parameter, and several factors may be involved.

As part of a programme to determine whether the patterns of nucleophilic attack at coordinated π-hydrocarbon molecules can be rationalized in terms of electronic quantities, we recently reported [1] INDO calculations on the cation $[(C_6H_7)Fe(CO)_3]^+$ (I). No correlation was observed between the magnitude of the dienyl carbon positive charges and the site of nucleophilic attack on I. Similarly, no correlation was found with the σ- and π-electron densities at the ring carbons. However, calculated bond index (or free valence) values at each dienyl carbon correctly predicted nucleophilic attack at C(1) (or C(5)). In order to gain further insight into the influence of electronic factors on ligand reactivity, we have carried out similar INDO calculations on the cations II (X = H, OMe, COOMe).

Calculation procedures have been previously summarised [1]. Geometric parameters for $[(C_7H_7)Cr(CO)_3]^+$ were estimated from X-ray structural data [2] for the analogous molybdenum cation, and consideration of differences between $[(C_7H_8)M(CO)_3]$ and $[M(CO)_6]$ (M = Cr, Mo) complexes [3,4]. Ring C—C distances were assumed to be unaffected by OMe and COOMe

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(II)

substituents.. For II (X = COOMe), calculations were made for two extreme conformations: (i) the COOMe group in the ring plane, and (ii) perpendicular to the plane. The modified valence parameter, bond index, is employed once more since bond orders between a variety of different atoms and orbital types are involved in species II.

Table 1 summarises the electronic parameters calculated for the C(1)-C(7) positions of II together with values for free $C_7H_6X^+$ (X = H, OMe) cations. Coordination of $C_7H_7^+$ or $C_7H_6OMe^+$ to a $Cr(CO)_3$ moiety is seem to cause an increase in the positive charge at each ring C atom, in keeping with the established electron-withdrawing character of the $Cr(CO)_3$ unit when attached to arene ligands [5]. Since complexation is also seen to increase the π-electron

TABLE 1

CALCULATED ELECTRONIC PARAMETERS FOR FREE $C_7H_6X^+$ AND $[(C_7H_6X)Cr(CO)_3]^+$

Species	Position [a]	Charge	Electron density	Bond index (σ)	Bond index (π)
$C_7H_7^+$	avg	+0.11	0.86	2.256	0.314
$[(C_7H_7)Cr(CO)_3]^+$	avg	+0.18	0.92	2.407	0.374
$C_7H_6OMe^+$	C(1)	+0.33	0.82	2.263	0.373
	C(2)	+0.02	0.94	2.258	0.310
	C(3)	+0.12	0.86	2.258	0.316
	C(4)	+0.09	0.88	2.258	0.314
	C(7)	+0.002	0.94	2.253	0.309
$[(C_7H_6OMe)Cr(CO)_3]^+$	C(1)	+0.40	0.86	2.475	0.421
	C(2)	+0.09	1.00	2.408	0.370
	C(3)	+0.21	0.88	2.407	0.370
	C(4)	+0.16	0.94	2.357	0.375
	C(7)	+0.08	1.00	2.406	0.364
$[(C_7H_6COOMe)Cr(CO)_3]^{+}$ [b]	C(1)	+0.09	0.94	2.403	0.405
(i)	C(2)	+0.19	0.92	2.408	0.371
	C(3)	+0.17	0.92	2.408	0.368
	C(4)	+0.17	0.92	2.414	0.374
	C(7)	+0.19	0.90	2.402	0.367
(ii)	C(1)	+0.09	0.90	2.391	0.368
	C(2,7)	+0.18	0.94	2.344	0.371
	C(3)	+0.18	0.90	2.405	0.367
	C(4)	+0.17	0.94	2.401	0.373

[a] C(3), C(6) and C(4), C(5) are equivalent pairs. [b] (i) COOMe in ring plane, (ii) COOMe perpendicular to ring plane.

density at the ring C atoms, the overall electron-withdrawal must occur from ring σ-orbitals. It is interesting that despite its higher ring positive charge, $[(C_7H_7)Cr(CO)_3]^+$ is less susceptible to nucleophilic attack than the free tropylium cation e.g. while the complex is stable for hours in water the free ion is attacked rapidly to yield the corresponding alcohol [6]. The decrease in reactivity on coordination is, however, consistent with both the general increase in π-electron density and bond index values of the ring C atoms. A high bond index value implies a low "free valence" for formation of a bond with an incoming nucleophile. These results are thus similar to our earlier obervations [1] on the $[(C_6H_7)Fe(CO)_3]^+$ system, in which ring C bond index values were also shown to be more important than charge in determining reactivity towards nucleophiles.

On the other hand the data in Table 1 for the cations $[(C_7H_6X)Cr(CO)_3]^+$ (X = OMe, COOMe) do not reveal a general correlation between the site of nucleophilic attack and any particular electronic parameter. For X = OMe, weak nucleophiles such as methoxide ion have been shown to add almost exclusively at C(1) (indicating that steric factors are not important), while hydride ions attack at C(3) [7]. The charge and π-electron density data in Table 1 for $[(C_7H_6OMe)Cr(CO)_3]^+$ both correctly predict C(1) and C(3) as the preferred sites for nucleophilic attack {C(1)>C(3)}. However, there is no correlation with the carbon bond index values (these would suggest C(1) and C(3) as the least likely sites of attack). For X = COOMe, each of the nucleophiles OMe$^-$, CN$^-$, and H$^-$ add exclusively at C(2) [7]. Interestingly, the electronic parameters for this complex do not vary greatly with ring position and would not suggest exclusive attack at C(2).

The present results indicate that while bond index values may correctly predict the effect of coordination on the overall reactivity of π-hydrocarbon molecules, the factors that control the site of nucleophilic addition in $[(C_7H_6X)Cr(CO)_3]^+$ systems are uncertain and perhaps multiple. Furthermore, the change in site preference with the nature of the nucleophile observed [7] for $[(C_7H_6OMe)Cr(CO)_3]^+$ may simply arise from a qualitative change in the character of the transition state.

References

1 D.W. Clack, M. Monshi and L.A.P. Kane-Maguire, J. Organometal. Chem., 107 (1976) C40.
2 G.R. Clark and G.J. Palenik, J. Organometal. Chem., 50 (1973) 185.
3 (a) P.E. Blaikie and O.S. Mills, J. Chem. Soc. A, (1968) 2704;
  (b) J.D. Dunitz and P. Pauling, Helv. Chim. Acta, 43 (1960) 2188.
4 Interatomic Distances and Configurations in Molecules and Ions, Chemical Society Special Publication no. 11, London, 1958.
5 D.A. Brown and J.R. Raju, J. Chem. Soc., (1966) 40 and ref. therein.
6 G.A. Olah and P.R. Schleyer, Carbonium Ions, Vol. IV, John Wiley-Interscience Ltd., New York, 1973, Ch. 29.
7 P.L. Pauson and K.H. Todd, J. Chem. Soc. C, (1970) 2638.