THE PREDICTION OF NUCLEOPHILIC ATTACKING SITES VIA DETERMINANTS OF 'ACTIVE' FRONTIER AND NEAR-FRONTIER ORBITALS *

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Summary

A method for computing the most favourable initial attacking site for a nucleophile on a transition metal complex is described, and applied to the nucleophilic substitution and addition reactions of fluoromethane, and the cationic complexes $[BFe(CO)_3]^+$ ($B = C_6H_7$ and C_7H_9). The reactions considered are classified according to whether they are frontier or non-frontier orbitally or charge controlled. It is found that initial attack on the $(polyenyl)M(CO)_3$ cations is always predicted to occur at the $M(CO)_3$ moiety, in agreement with the experimental observation of intermediates in several such reactions and suggesting that the existence of these species is a general phenomenon.

Introduction

Attempts to develop computationally inexpensive yet reliable structure reactivity correlations for inorganic compounds have met with only partial success. The application of the symmetry rules [2,3] and reactivity indices [4,5] in wide use in mechanistic organic chemistry sometimes yields accurate results [6–9], but often fails to predict the site of nucleophilic attack on inorganic systems [10,11]. This is probably due to the fact that for many organic molecules, the frontier orbitals are relatively widely spaced in energy, and often "localised" on certain parts of the molecule, hence weighting the frontier index in favour of that site. The introduction of a metal atom leads to "bands" of closely spaced HOMOs and LUMOs not weighted greatly in favour of any particular site, and predictions based on indices then become less clear-cut. For example, despite intensive investigation, the factors governing the regioselectivity of nucleophilic addition to cyclic polyenetricarbonyl-metal complexes are still not clear. If such reactions are "frontier controlled", that

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* For a preliminary communication see ref. 1.

is, if they are dominated by the interaction of the highest occupied molecular orbital (HOMO) of the nucleophile with the lowest unoccupied molecular orbital (LUMO) of the substrate, then the site of nucleophilic attack might be expected to correlate with reactivity indices such as frontier charge density (ρ(LUMO)) [9]. In some compounds, for example the $AM(CO)_3$ series ($AM = (C_6H_6)Cr$, $(C_5H_5)Mn$, $(C_4H_4)Fe$, $(C_3H_5)Co$ and $(C_2H_4)Ni$), such a correlation between ρ(LUMO) and the initial site of nucleophilic attack has indeed been shown to exist [9]. In other cases, this approach is less successful – an INDO study of $(C_7H_6X)Cr(CO)_3$ ($X = H$, OCH_3, $COOCH_3$) showed that the site of attack did not correlate with any electronic parameter [11].

For nucleophilic addition and associative S_N2 reactions, the failure of such arguments to pinpoint the site of attack of an incoming nucleophile may be due to the absence of explicit inclusion of the nature of the nucleophile or of the medium in which reaction takes place. To rectify this situation would require not only the time-consuming calculation of transition state energies, an impractical task for most organometallic molecules, but also a consideration of the rôle of the solvent. The reactivity index approach to stereoselectivity in organometallic complexes may therefore be of limited value, and an incorporation of the structure of the nucleophile and substrate and also of solvent effects should be made. This was achieved in a recent application of the perturbation theory of reactivity [12–16] to the nucleophilic addition of the $AM(CO)_3$ and $[BFe(CO)_3]^+$ ($B = (C_6H_7)$, (C_7H_9)) series [17].

The interaction energy between a nucleophilic entity R and a substrate species S, denoted $(\Delta E_{RS})_{total}$ was expressed as a sum of charge and orbitally controlled terms [15]:

$$(\Delta E_{RS})_{total} = (\Delta E_{RS})_{solvation} + (\Delta E_{RS})_{orbital} \tag{1}$$

$$(\Delta E_{RS})_{solvation} = \frac{\sum_{r,s} q_r q_s}{R_{rs}\epsilon} \tag{2}$$

$$(\Delta E_{RS})_{orbital} = 2 \frac{\sum_{i=1}^{occ} \sum_{j=1}^{unocc} \left(c_\rho^i c_\sigma^j \beta_{rs} \right)^2}{(E_i - E_j)} \tag{3}$$

Interaction occurs between atoms r of R and s of S, separated by a distance R_{rs}; ϵ represents the dielectric constant of the medium in which interaction occurs, c_ρ^i and c_σ^j are the coefficients of the atomic orbitals ψ_ρ and ϕ_σ in the MOs Ψ_i^R and Φ_j^S on the isolated R and S systems, and q_r and q_s are the charges on r and s. β_{rs} is the "interaction parameter". This formulation has also been used to discuss the classification of nucleophiles as "hard" and "soft" and the relative sizes of the two terms in the equation forms a basis for the classification of reactions as "orbitally" or "charge" controlled [15].

Study of the (polyene)$M(CO)_3$ complexes showed that the position of attack depends on the nucleophilicity of the incoming species, and also on solvent polarity, with a possible changeover in site occurring on variation of these parameters [17].

Although these results are encouraging, such an approach has some disadvantages. The nucleophile and substrate are treated as point masses, and hence no consideration of the geometry of the (RS) system is made. In addition, the orbital interaction energy is treated as a summation of energies arising from pairwise

interactions of each of the MOs on R and S. Except in certain cases where the MOs considered each belong to a different irreducible representation of the molecular point group, this assumption is incorrect (see Fig. 1). Also, in certain cases where Ψ_i^R and Φ_j^S are very close in energy, $(\Delta E_{RS})_{orbital}$ may become unrealistically large. The most satisfactory way around these difficulties is probably to perform complete SCF calculations on RS supermolecules comprised of various chemically feasible geometrical arrangements of R and S, and express $(\Delta E_{RS})_{total}$ as the energy difference between the RS system and the sum of the energies of the fragments. Several schemes may then be used to decompose the interaction into charge transfer, electrostatic, correlation terms and so on. This method has been applied by Yamabe, Kitaura and Nishimoto to the problem of intermolecular hydrogen bonding in formic acid dimers [18]. Fujimoto, Koga and Fukui [19] have also discussed composite systems in terms of orbital interactions between fragments using an ab initio approach. Dedieu and Nakamura [20] have recently tackled the problem of nucleophilic attack on a transition metal carbonyl using ab initio methods. The attack of the hydride anion yielding formyl complexes was examined, and the existence of a low-lying empty orbital on the complex directed towards the attacked carbonyl ligand was identified as a driving force for activation of the reaction. Unfortunately, the difficulty in performing such rigorous calculations on large systems precludes the general application of these techniques to organometallic molecules at present.

The purpose of this paper is to present an alternative method for calculating $(\Delta E_{RS})_{orbital}$ which circumvents some of the problems inherent in the perturbation approach but is computationally inexpensive and may be applied to inorganic systems. A secular determinant based on MOs centred on R and S is constructed. Solution of this determinant yields energy levels and orbitals for the combined (RS) system. By populating the lowest levels of (RS) from the filled MOs of R and S a value of $(\Delta E_{RS})_{orbital}$ is obtained and then used below to discuss the nucleophilic addition reactions of some transition metal complexes.

Theoretical development

When two species R and S react to form a combined system RS, such a supermolecule will be described by eigenfunctions, Ω_{RS}, each of which satisfy the Schrödinger equation:

$$H_{RS}\Omega_{RS} = E_{RS}\Omega_{RS} \tag{4}$$

where H_{RS} is the Hamiltonian for the combined system, and E_{RS} the energy eigenvalue corresponding to a given wave function Ω_{RS}. Ω_{RS} can be expressed as a linear combination of the n_R MOs of R, Ψ_i^R, and the n_S MOs of S, Φ_j^S:

$$\Omega_{RS} = \sum_{i=1}^{n_R} a_i \Psi_i^R + \sum_{j=1}^{n_S} b_j \Phi_j^S \tag{5}$$

The energy associated with this function, E_{RS}, may be minimised with respect to the coefficients a_i and b_j by application of the variational procedure to equation 4. This

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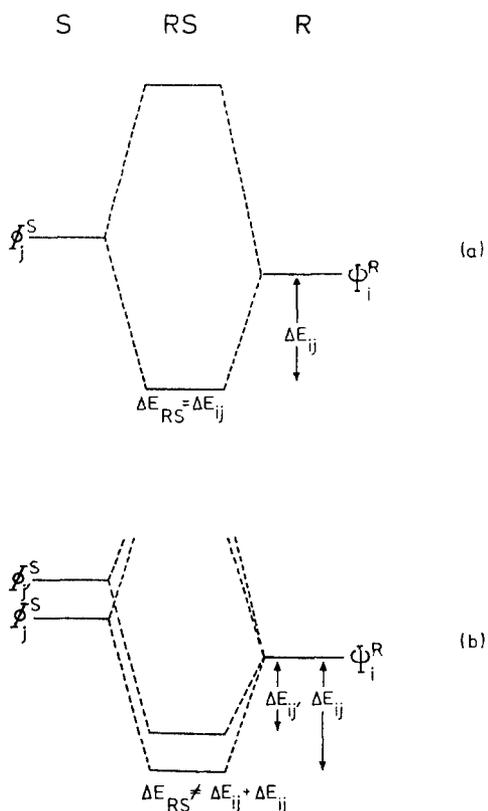
Fig. 1. Energy level diagrams showing the interpretation of the summation of interactions between the MOs of R and S.

yields $(n_R + n_S)$ secular equations, which may be solved using a secular determinant:

$$\begin{vmatrix} H_{ij}^{RR} - E_{RS}S_{ij}^{RR} & H_{ij}^{RS} - E_{RS}S_{ij}^{RS} \\ \hline H_{ij}^{SR} - E_{RS}S_{ij}^{SR} & H_{ij}^{SS} - E_{RS}S_{ij}^{SS} \end{vmatrix} = 0 \tag{6}$$

where

$$S_{ij}^{RR} = \int \Psi_i^R \Psi_j^R d\tau \tag{7}$$

$$S_{ij}^{RS} = \int \Psi_i^R \Phi_j^S d\tau \tag{8}$$

$$H_{ij}^{RR} = \int \Psi_i^R H_{RS} \Psi_j^R d\tau \tag{9}$$

etc. Assuming that the MOs of R and S form independant orthonormal sets, then:

$$S_{ij}^{RR} = S_{ij}^{SS} = \delta_{ij} \tag{10}$$

leaving the H^{RS} and S^{RS} integrals to be evaluated. Each Ψ_i^R and Φ_j^S is in turn a linear combination of basis atomic orbitals on R and S:

$$\Psi_i^R = \sum_{\rho=1}^{n_R} c_{i\rho}^R \psi_\rho \tag{11}$$

$$\Phi_j^S = \sum_{\sigma=1}^{n_S} c_{j\sigma}^S \phi_\sigma \tag{12}$$

Hence

$$S_{ij}^{RS} = \sum_{\rho=1}^{n_R} \sum_{\sigma=1}^{n_S} c_{i\rho}^R c_{j\sigma}^S \int \psi_\rho^R \phi_\sigma^S d\tau \tag{13}$$

$$H_{ij}^{RS} = \sum_{\rho=1}^{n_R} \sum_{\sigma=1}^{n_S} c_{i\rho}^R c_{j\sigma}^S \int \psi_\rho^R H_{RS} \phi_\sigma^S d\tau \tag{14}$$

The coefficients $c_{i\rho}^R$ and $c_{j\sigma}^S$ are found from separate molecular orbital calculations on R and S. The overlap integrals S_{ij}^{RS} may be evaluated easily. The coulomb integrals H_{ij}^{RS} are more difficult. Rigorous evaluation would require as many integral computations as an SCF calculation. Therefore, in order to maintain the development at a semi-empirical level, they are approximated using parameters fitted from experimental data as in the extended Hückel formalism [21–23]. The diagonal elements are approximated by valence orbital ionisation potentials (VOIPs) [24] and non-diagonal elements calculated using the Wolfsberg–Helmholz formula [25]. It should be noted that use of this parameterisation introduces the weakness that even MOs widely separated in energy tend to interact well, if the overlap is good.

Solution of the determinant yields energy levels and molecular orbitals for RS. By populating the lowest levels from the filled MOs on R and S and calculating the change in total energy, a value for $(\Delta E_{RS})_{orbital}$ is obtained, thereby eliminating the "pairwise summation" approximation used in the perturbation treatment [15]. The evaluation of the overlap integrals between R and S means that the relative orientations of the attacking species are explicitly included, and therefore the preference for alternative paths of attack may be compared. Moreover, the determinant may include as many MOs from R and S as desired; for example, consideration can be restricted to a single HOMO–LUMO interaction, or alternatively, steric effects due to repulsions between the filled orbitals of R and S may be investigated by including such orbitals in the determinant. Examination of the effects of gradual augmentation of the 'active' orbital set with non-frontier MOs on the prediction of attacking site allows the classification of reactions as frontier and charge controlled.

Computational details

The calculations of (ΔE_{RS}) described in this work were carried out on IBM 4341 and AMDAHL 470 computers under VM/CMS, using a FORTRAN program developed in this laboratory. The program requires as input the geometry of the RS supermolecule, the coefficients of the "active" MOs of the isolated molecules R and S and the basis sets and semi-empirical parameters required to calculate the integrals between these MOs. $(\Delta E_{RS})_{orbital}$ is calculated as described above and combined

with the solvation term to yield a value for the total interaction energy. The integral evaluation routines were adapted from the FORTICON-8 program by Hoffmann and co-workers [26]. MO wavefunctions for use in the reactivity calculations were computed using the latter program. Details of the basis sets, semi-empirical parameters and geometrical structures used in the calculations are given in the appendix.

Results and discussion

(A) Nucleophilic substitution at a saturated centre

To be of use in the prediction of attacking sites, it is important that the model be capable of distinguishing between alternative paths of attack. As a simple test, consider the reactions:

$$F^- + CH_3F \rightarrow CH_2F_2 + H^- \tag{a}$$

$$F^- + CH_3F \rightarrow CH_3F + F^- \tag{b}$$

Two main paths of attack are represented by these equations, "frontside" with substitution of hydride, or "backside" with substitution of fluoride. Theoretical studies have shown [27,28] that the "backside" pathway is preferred. Figure 2 shows the interaction energies calculated for $CH_3F_2^-$ supermolecules leading to the appropriate products at high and low solvent dielectric constants. In each case, all the MOs from both species were included in the "active set". The determinant interac-
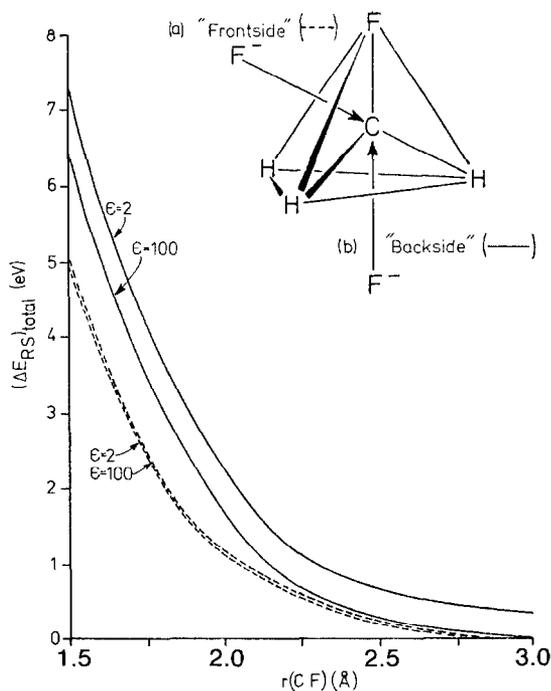
Fig. 2. Interaction energy "profiles" for attack by F^- on CH_3F in solvents of low ($\epsilon = 2$) and high ($\epsilon = 100$) dielectric constants. Path (a) shows "frontside" attack leading to displacement of hydride, and path (b) "backside" attack leading to displacement of fluoride.

tion method correctly predicts that "backside" attack is the most favourable, having the highest $(\Delta E_{RS})_{total}$ as the nucleophile approaches. Use of a truncated set of MOs, or simply the nucleophile HOMO and CH_3F LUMO does not yield the correct prediction, emphasising the importance of the "filled–filled" repulsion for this sytem and showing that the reaction is not frontier orbitally controlled. It should be stressed that the nucleophile–substrate distance is quite large here because the MOs of R and S were calculated for isolated systems, and a very close approach between nucleophile and substrate is inconsistent with the theoretical concept.

(B) Nucleophilic addition to [(C₆H₇)Fe(CO)₃] ⁺ and [(C₇H₉)Fe(CO)₃] ⁺

Having established that this model can successfully differentiate between alternative paths of attack by an incoming species, the reactions of nucleophiles with cyclodienyliumtricarbonylmetals are now considered. We attempt to correlate the known behaviour of the $[BFe(CO)_3]^+$ systems towards nucleophilic attack with the calculated interaction energies for various positions of attack within each molecule.

A range of nucleophiles was selected for study. We report results for hydroxide, a typical "hard" nucleophile, SH^- and I^-, typical "soft" nucleophiles, and the ambident nucleophile $[NCS]^-$, which may attack via the nitrogen or sulphur atom. In previous discussions of nucleophilic attack on metal complexes, attention has generally been focussed on the HOMO(nucleophile)–LUMO(substrate) interaction, but as described above, this may be unsatisfactory for metal complexes because of the presence of a "band" of relatively closely spaced orbitals lying near the LUMO of the complex. In addition, the question of deciding whether a reaction is orbitally or charge controlled must be considered. At low dielectric constants the charge term dominates, so that predictions made in such media will be due to charge control. As dielectric constant is increased, the orbital term becomes more important, and at

TABLE 1

COMPARISON OF PREDICTED SITE OF ATTACK BY HYDROXIDE AND IODIDE ON $[(C_6H_7)Fe(CO)_3]^+$ USING "ACTIVE" SETS OF SUBSTRATE MOs OF VARYING SIZE (ALL ENERGIES IN eV) [a]

Nucleophile	Substrate		Interaction energies						Prediction
	HOMOs	LUMOs	Ring		Metal		Carbonyl		
			exo	endo	C_3	side	exo	endo	
OH⁻ [b]	5	4	5.14	5.69	11.2	16.9	12.5	13.5	Metal
			2.64	0.89	3.17	9.24	7.35	10.6	Carbonyl
OH⁻ [c]	5	9	6.47	8.16	17.9	20.2	16.9	18.7	Metal
			3.97	3.36	9.86	12.5	11.8	15.8	Carbonyl
OH⁻ [d]	34	30	76.7	121	110	152	99.2	149	Metal
			74.1	117	105	147	95.2	147	Metal = Carbonyl
I⁻ [b]	5	4	32.9	36.7	47	41	38.7	34.1	Metal
			30.4	31.8	39.3	33.6	33.7	31.2	Metal
I⁻ [d]	34	30	88	117	111	136	91.3	130	Metal
			85.2	113	105	130	87.3	129	Metal

[a] For each nucleophile, the first row of energies are calculated with $\epsilon = 2$, the second row with $\epsilon = 100$.
[b] Substrate MOs selected using criterion (a) (see text). [c] Substrate MOs selected using criterion (b) (see text). [d] Complete set of substrate MOs.

high dielectric constants, the reaction will be orbitally controlled. If the reaction is very sensitive to charge control, there will be a crossover as this term decreases in importance. If the reaction is not charge controlled, then no such crossover will occur. When a reaction is frontier-orbitally controlled, addition of non-frontier orbitals to the determinant does not affect the prediction of initial site of attack, whereas in the case of orbital control, addition of non-frontier orbitals will change the predicted site. The problem remains of choosing which non-frontier orbitals should be included in the determinant. Two criteria for determining the "cut-off" point for inclusion were investigated:-

(a) Starting from the HOMO and LUMO, other orbitals were included which occurred respectively downwards and upwards in energy for a distance of 1 eV in both directions. In this way five HOMOs from $[(C_6H_7)Fe(CO)_3]^+$ and four from $[(C_7H_9)Fe(CO)_3]^+$ were included together with four LUMOs in each case.

(b) Starting from the HOMO and LUMO, other orbitals were included which occurred respectively downwards and upwards in energy until a gap of 1 eV or larger was encountered. Using this method nine LUMO's were included (a gap of ap-

TABLE 2

INTERACTION ENERGIES, $(\Delta E_{RS})_{total}$, FOR NUCLEOPHILIC ATTACK ON $[(C_6H_7)Fe(CO)_3]^+$ (eV) [a]

Nucleophile	Substrate		Interaction energies						Prediction
	HOMOs	LUMOs	Ring		Metal		Carbonyl		
			exo	endo	C_3	side	exo	endo	
OH^{-}	0	1	2.71	5.07	8.40	7.82	7.44	3.46	Metal
			0.21	0.27	0.41	0.16	2.33	0.57	Carbonyl
OH^{-}	5	4	5.14	5.69	11.2	16.9	12.5	13.5	Metal
			2.64	0.89	3.17	9.24	7.35	10.6	Carbonyl
OH^{-}	5	9	6.47	8.16	17.9	20.2	16.9	18.7	Metal
			3.97	3.36	9.86	12.5	11.8	15.8	Carbonyl
SH[-]	0	1	3.00	5.87	12.2	8.20	9.87	5.21	Metal
			0.61	1.04	4.91	1.23	4.98	2.48	Metal = Carbonyl
SH[-]	5	4	9.84	3.97	19.4	19.9	18.7	15.8	Metal
			7.45	4.13	12.1	12.9	13.8	13.1	Carbonyl
SH[-]	5	9	12.2	12.7	29.4	25.6	23.2	19.2	Metal
			9.82	7.83	22.1	18.7	18.3	16.5	Metal
I[-]	0	1	11.6	15.7	20.2	17.6	16.1	12.7	Metal
			9.10	10.9	12.6	10.2	11.0	9.90	Metal
I[-]	5	4	32.9	36.7	47.0	41.0	38.7	34.1	Metal
			30.4	31.8	39.3	33.6	33.7	31.2	Metal
NCS[-] [b]	0	1	2.29	4.67	6.95	5.76	6.81	2.92	Metal
			0.25	0.66	1.33	0.31	2.70	0.63	Carbonyl
NCS[-] [b]	5	4	7.31	12.0	13.9	15.6	20.3	12.6	Carbonyl
			5.57	8.58	8.23	10.2	16.2	10.3	Carbonyl
NCS[-] [c]	0	1	1.96	3.99	5.52	4.68	7.04	2.91	Carbonyl
			0.21	0.51	1.44	0.67	3.58	1.01	Carbonyl
NCS[-] [c]	5	4	3.30	7.20	8.28	10.6	22.3	8.00	Carbonyl
			1.55	3.72	4.20	6.60	18.8	6.09	Carbonyl

[a] For each nucleophile, the first row of energies are calculated with $\epsilon = 2$, the second row with $\epsilon = 100$.
[b] Attack via the nitrogen atom. [c] Attack via the sulphur atom.
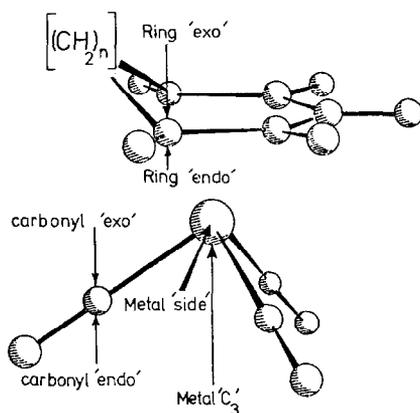
Fig. 3. Pathways of attack by nucleophiles on $[(C_6H_7)Fe(CO)_3]^+$ and $[(C_7H_9)Fe(CO)_3]^+$ used in the calculations of (ΔE_{RS}).

proximately 3 eV separates LUMO (9) and (10) on each cation), but no gap between any two adjacent HOMOs of this size was found. Therefore, in order to maintain the number of HOMOs at a reasonable computational level, criterion (a) was applied to this group. Application of either of these criteria to the nucleophiles results in inclusion of the same number of HOMOs: two on OH^- and SH^-, three on I^- (three $5p$ orbitals) and three on $[NCS]^-$. Unoccupied orbitals on the nucleophiles were not included in the determinant. Since such a cut-off process is rather arbitrary, some calculations were performed for attack of $[(C_6H_7)Fe(CO)_3]^+$ by hydroxide and iodide including all of the MOs of the substrate in the active set. In both cases it was found that while the magnitude of the total interaction energy differs, the site prediction remains the same as that calculated using an active set selected according to criteria (a) and (b) (Table 1).

Interaction energies were calculated for geometries corresponding to ring, metal and carbonyl attack respectively (Fig. 3) at a fixed distance of 1.0 Å between the site of attack and the interacting atom of the nucleophile. The results are set out in Table 2 for $[(C_6H_7)Fe(CO)_3]^+$ and in Table 3 for $[(C_7H_9)Fe(CO)_3]^+$.

For both complexes, it is immediately obvious that in all cases initial attack is predicted at the carbonylmetal moiety. This conclusion holds for a wide range of solvent polarities and for both single HOMO–LUMO interactions and inclusion of many HOMOs and LUMOs (on either of the above criteria). The difference in interaction energies between ring and metal/carbonyl attack is so consistently large as to give confidence in the theoretical prediction despite the use of semi-empirical methods here. We now consider the results in detail, first for $[(C_6H_7)Fe(CO)_3]^+$.

For hydroxide, carbonyl attack is predicted in solvents of high polarity, with a "crossover" to metal attack occurring as the dielectric constant of the medium is decreased (Fig. 4). The site prediction does not change whether interaction is restricted to the frontier orbitals, or whether a more extended group of HOMOs and LUMOs is included in the determinant. However, the orientation of attack at each site does change on inclusion of non-frontier MOs (Table 1). Metal attack switches from a "C_3" to a "side" trajectory in passing from the frontier to the non-frontier case, and for carbonyl attack, the path switches from "exo" to "endo". In the case of

TABLE 3

INTERACTION ENERGIES, $(\Delta E_{RS})_{total}$, FOR NUCLEOPHILIC ATTACK ON $[(C_7H_9)Fe(CO)_3]^+$ (eV) [a]

Nucleophile	Substrate		Interaction energies						Prediction
	HOMOs	LUMOs	Ring		Metal		Carbonyl		
			exo	endo	C_3	side	exo	endo	
OH⁻	0	1	2.60	4.27	7.87	7.39	7.11	3.24	Metal
			0.27	0.27	0.34	0.15	2.19	0.46	Carbonyl
OH⁻	4	4	3.06	5.04	9.83	15.2	11.0	12.8	Metal
			0.73	1.04	2.30	7.99	6.10	9.98	Carbonyl
OH⁻	4	9	3.82	6.76	16.8	17.7	16.1	18.7	Carbonyl
			1.49	2.75	9.27	10.5	11.2	15.9	Carbonyl
SH⁻	0	1	3.14	5.00	12.5	8.39	9.65	4.86	Metal
			0.89	0.96	5.64	1.83	4.92	2.23	Metal
SH⁻	4	4	4.58	7.68	19.9	19.3	15.0	15.3	Metal
			3.33	3.63	13.0	12.8	10.3	12.6	Carbonyl
SH⁻	4	9	6.59	11.0	29.1	23.3	15.7	19.3	Metal
			4.33	7.00	22.3	16.7	20.5	16.7	Metal
I⁻	0	1	12.2	15.6	20.9	18.0	16.1	12.8	Metal
			9.90	11.6	13.7	11.0	11.3	10.1	Metal
I⁻	4	4	30.7	36.5	48.6	42.1	36.7	35.3	Metal
			28.4	32.5	41.3	35.2	31.8	32.6	Metal
NCS⁻ [b]	0	1	2.26	3.55	6.64	5.62	5.86	2.74	Metal
			0.32	0.13	1.33	0.44	1.86	0.53	Carbonyl
NCS⁻ [b]	4	4	5.73	12.9	13.0	15.8	14.2	12.0	Metal
			3.78	9.47	7.64	10.6	10.2	9.76	Metal
NCS⁻ [c]	0	1	2.03	3.45	5.74	4.58	6.17	2.73	Carbonyl
			0.34	0.42	1.86	0.74	2.77	0.89	Carbonyl
NCS⁻ [c]	4	4	2.56	6.36	8.80	9.91	9.50	7.72	Metal
			0.86	3.33	4.93	6.06	6.11	5.88	Metal = Carbonyl

[a] For each nucleophile, the first row of energies are calculated with $\epsilon = 2$, the second row with $\epsilon = 100$.
[b] Attack via the nitrogen atom. [c] Attack via the sulphur atom.

SH⁻, using frontier orbitals only, metal attack is most favourable at low ϵ, with metal and carbonyl attack almost equally favourable at high ϵ. As the number of non-frontier MOs is increased, metal attack becomes the most favourable at all polarities. Iodide is also predicted to attack at the metal atom in all solvents, independant of the number of MOs included in the determinant. In the case of [NCS]⁻ the most favourable site of attack is at the carbonyl group via the sulphur atom, irrespective of solvent polarity or the number of MOs included.

Considering $[(C_7H_9)Fe(CO)_3]^+$, most of the predictions are identical to those described above, except in cases where small changes in interaction energy result in several sites presenting very similar choices. Most notable is attack by [NCS]⁻, where a drop in the favourability of the carbonyl site means that metal attack is almost equally favourable, particularly in high polarity solvents in the non-frontier case. Furthermore attack via nitrogen is now more favourable.

These results agree with the pattern outlined in previous papers [9,17] which is in general well supported by experimental results. Hard, non-polarizable nucleophiles such as alkoxides and azides are known to attack initially at the carbonyl group or
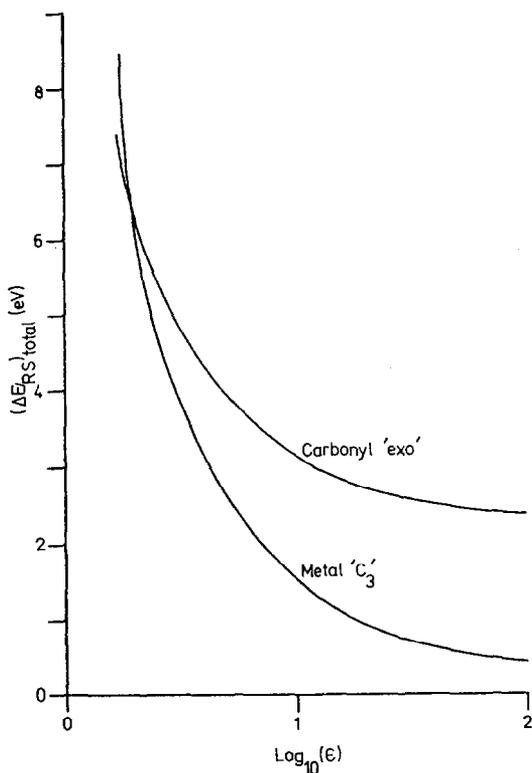
Fig. 4. $(\Delta E_{RS})_{total}$ plotted as a function of solvent dielectric constant for attack by OH^- on $[(C_6H_7)Fe(CO)_3]^+$.

metal atom respectively in solvents of high dielectric constant such as CH_2Cl_2 [29,30]. For the analogous $[(C_5H_5)Fe(CO)_3]^+$ cation, hydrazine [31] and azide attack at the carbonyl carbon in methanol [31–34], while in the less polar THF, NCO^- attacks the metal [35]. On the other hand, the soft nucleophile I^-, has been shown to attack at the metal to yield the dicarbonyliodo complex [36]. Phosphines, although soft, form 5-*exo* and 5-*endo* ring substitution products with the cycloheptadienylium complex, but this is thought to be due to their large size, which makes approach to other sites very difficult.

The prediction of carbonyl attack by hydroxide with a crossover to metal attack as solvent polarity is lowered, while SH^- attacks at the metal is in agreement with experiment. However, I^- is observed to attack initially at the ring [37], although Powell and co-workers found that at low temperatures attack by iodide on tricarbonyltropyliummetal cations does indeed occur initially at the $M(CO)_3$ group [38]. For $[NCS]^-$, initial attack is experimentally observed to occur at the ring via the nitrogen atom, to yield the 5-*exo* substituted isothiocyanate, which subsequently rearranges to the sulphur-bonded thiocyanate isomer [39]. This is inconsistent with the predicted site of attack, although it is possible that a so-far undetected carbonyl addition intermediate does occur. Considering attack by $[NCS]^-$ at the ring only, the data in Tables 2 and 3 show that attack occurs preferentially via nitrogen for both cations.

TABLE 4

CLASSIFICATION OF THE REACTIONS ACCORDING TO CONTROL

Substrate	Nucleophiles				
	OH⁻	SH⁻	I⁻	[NCS]⁻	
				N Attack	S Attack
[(C₆H₇)Fe(CO)₃]⁺	F.O./ Charge [a]	Orbital	Frontier orbital	Frontier orbital	Frontier orbital
[(C₇H₉)Fe(CO)₃]⁺	F.O./ Charge [a]	Frontier orbital	Frontier orbital	Orbital	Orbital

[a] Crossover occurs from frontier orbital to charge control as the dielectric constant increases.

These results suggest that for attack of iodide on both cations and SH⁻ on [(C₇H₉)Fe(CO)₃]⁺, the reaction is frontier orbitally controlled. This is also true of attack by [NCS]⁻ on the [(C₆H₇)Fe(CO)₃]⁺ cation. On the other hand, attack of [NCS]⁻ on the cycloheptadienylium cation or of SH⁻ on the cyclohexadienylium cation is non-frontier orbitally controlled. For hydroxide, the reaction changes from frontier orbital control at high polarity to charge control at low polarity, as evidenced by the crossover. These results are summarised in Table 4. Predictions of the actual orientation of attack at any site are difficult to verify. For example, although *exo*-ring addition products are often observed as the final complexes from nucleophilic addition to the cations, it is incorrect to assume that attack at the *exo* position of the ring is necessarily the initial choice, as for example in the case of methoxide attack on the cycloheptadienylium cation, where initial attack yields a carbomethoxy species [30], although the final product is 5-*exo*-addition at the ring. Even in the case of tropyliumtricarbonylmetal complexes long known to give 7-*exo* derivatives as stable products, it is now clear that in certain solvents, initial attack occurs at both metal and carbon atoms [40].

These results suggest that the formation of metal and carbonyl attack intermediates is a quite general phenomenon requiring special low-temperature techniques for their observation in certain cases.

Appendix

Choice of semi-empirical and geometrical parameters

The following bond lengths and angles were used for CH_3F and the nucleophiles: $r(C-H)$ 1.105 Å, $r(C-F)$ 1.385 Å, $A(H-C-H)$ 109°54′, $A(H-C-F)$ 109°02′, $r(O-H)$ 0.96 Å, $r(S-H)$ 1.329 Å, $A(N-C-S)$ 180°, $r(N-C) = 1.25$ Å, $r(C-S)$ 1.59 Å. The structure of $[(C_6H_7)Fe(CO)_3]^+$ was adapted from that of the manganese analogue [41], and that of $[(C_7H_9)Fe(CO)_3]^+$ was derived from that of azulenehexacarbonyldimanganese [42]. For ring attack, nucleophiles were oriented perpendicular to the η^5-plane of the ring, above (*exo*) and below (*endo*). C_3 metal attack corresponded to attack along the C_3 axis of the $Fe(CO)_3$ group, while "side" attack corresponded to the C_3 trajectory rotated by 120° about an axis through the metal parallel to the ring plane and lying in the C_2 plane of the complex. "*Exo*" and "*endo*" carbonyl attack were again vertical approaches to the carbonyl group as shown in Fig. 3.

TABLE 5

SEMI-EMPIRICAL PARAMETERS USED IN THE CALCULATIONS

Atom	n	ns	np	$(n-1)d$			
				C_1	ζ_1	C_2	ζ_2
Exponents and Coefficients							
Fe	4	1.4296	0.9717	0.4847	5.6528	0.6610	2.3246
C	2	1.5533	1.4500				
O	2	2.1632	2.1739				
N	2	1.8596	1.8166				
F	2	2.4652	2.5173				
S	3	2.0199	1.6886				
I	5		2.1573				
H	1	1.3000					
Valence orbital ionisation potentials (eV)							
Fe	4	-7.104	-3.707	-9.390			
C	2	-20.31	-10.71				
O	2	-32.34	-15.80				
F	2	-40.12	-18.65				
N	2	-25.57	-13.19				
S	3	-20.67	-11.58				
I	5		-3.52				
H	1	-13.60					

The basis set for the iron atom consisted of valence Slater-type $3d$, $4s$ and $4p$ atomic orbitals, and for the first row atoms $2s$ and $2p$ AOs were used. $1s$ orbitals only were included on the hydrogen atoms. The radial wave functions computed by Fitzpatrick and Murphy [43] as a best least-squares fit to the SCF functions of Herman and Skillman [44] were chosen. Double-zeta functions were used to represent the d-orbitals. A value of 1.30 was used as the exponent for the hydrogen $1s$ orbitals. $5p$ exponents for the iodide anion were approximated by reducing the values for the neutral atom by 0.07. Valence orbital ionization potentials [24,45] for nine configurations of the metal atom and two configurations of first row atoms were used as approximations to the diagonal elements of the coulomb matrix. All the parameters used are summarised in Table 5.

Acknowledgements

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