$(AsF_6)_6$ and in Se_4^{2+}- and Te_4^{2+}-containing salts has been recently published.[40]

The S_4^{2+} units are arranged in a stack along the fourfold inversion axis separated by AsF_6^- ions, which are disordered. The most satisfactory description of these was with an As at $(^1/_4, ^3/_4, ^1/_2)$ surrounded by eight fluorine positions each with $^3/_4$ occupancy.

Registry No. $(S_7I)_4S_4(AsF_6)_6$, 74823-90-8; $[(S_7I)_2I](SbF_6)_3·2AsF_3$, 73381-83-6; SbF_5, 7783-70-2; AsF_5, 7784-36-3; S_8, 10544-50-0; I_2, 7553-56-2.

Supplementary Material Available: Tables of calculated and observed structure factors and isotropic and anisotropic thermal parameters for $[(S_7I)_2I](SbF_6)_3·2AsF_3$ and $(S_7I)_4S_4(AsF_6)_2$, bond distances and angles for SbF_6^- in $[(S_7I)_2I](SbF_6)_3·2AsF_3$, bond distances and angles for AsF_6^- in $(S_7I)_4S_4(AsF_6)_6$, and torsional angles in S_7I^+, $[(S_7I)_2I]^{3+}$, and the S_7 chair in S_{19}^{2+} (32 pages). Ordering information is given on any current masthead page.

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Contribution from the Chemistry Department,
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MO Theory of Organometallic Compounds. 16.[1] Perturbation Theory of the Reactivity of Metal Carbonyl Complexes

DAVID A. BROWN,* JOSEPH P. CHESTER, and NOEL J. FITZPATRICK

The perturbation theory of reactivity has been applied to the nucleophilic substitution and addition reactions of a series of metal carbonyl complexes, $AM(CO)_3$, $A = C_6H_6Cr$, C_5H_5Mn, C_4H_4Fe, or C_3H_5Co, and $[BFe(CO)_3]^+$, $B = C_5H_5$, C_6H_7, or C_7H_9, by both hard and soft reagents. For $C_6H_6Cr(CO)_3$ and $C_5H_5Mn(CO)_3$, attack by a hard nucleophile is predicted in the order metal > carbonyl > ring and the reverse for soft nucleophiles in polar solvents. In the cationic series, attack by a hard nucleophile may occur at either metal or carbonyl, while for a soft nucleophile, initial metal attack is predicted with a change to ring attack as solvent polarity increases.

Introduction

One of the most challenging problems facing theoretical inorganic chemistry is the development of structure–reactivity correlations of a degree of sophistication and success comparable to those used so widely in mechanistic organic chemistry.[2] Even in the case of simple substitution reactions of organometallic systems, it is still very difficult to predict a priori whether, for example, carbonyl substitution of a metal carbonyl complex will occur by an S_N1 dissociative or S_N2 associative mechanism.[3] In the former case, it is reasonable to assume that calculations of ground-state properties such as metal–carbon overlap populations using semiempirical MO methods should give a reasonable indication of relative reactivities. Such attempts at structure–reactivity correlations have proved quite successful in series of closely related molecules, for example, the metal carbonyl halides $M(CO)_5X$ (M = Mn, Re; X = Cl, Br, I).[4] In the case of nucleophilic addition to organo–transition-metal complexes, rules based on simple Hückel theory considerations of the HOMO of the polyene fragment have been applied to a wide range of complexes.[5] However, in general for associative S_N2 substitution reactions similar correlations are much less successful since explicit account is now required of the interaction between the nucleophile and substrate and thus of calculations of transition-state energies. Such calculations are still impracticable or prohibitively expensive for the large molecules under discussion, and consequently attempts to rationalize associative mechanisms have concentrated on correlations with various reactivity indices. For example, the site of attack of a nucleophile in an associative substitution reaction of a metal carbonyl complex might be expected to correlate with calculated charge densities. However, INDO calculations[6,7] for $[C_6H_7Fe(CO)_3]^+$ and $[C_7H_6XCr(CO)_3]^+$ showed the best correlation between bond index values and the effect of coordination on reactivity; however, the site of nucleophilic attack did not correlate with any electronic parameter in the latter case. If the interaction between the attacking nucleophile and substrate is frontier controlled, that is, if it is dominated by the interaction of the highest occupied orbital (HOMO) of the nucleophile with the lowest unoccupied orbital (LUMO) of the substrate, then, for a given nucleophile, correlation between reactivity and the frontier electron density (P_A^{LUMO}) at a given atom A, the site of attack of the substrate, should be observed. We have shown previously that such correlation does occur in both (a) the neutral $AM(CO)_3$ series (A = C_6H_6Cr, C_5H_5Mn, C_4H_4Fe, C_3H_5Co or C_2H_4Ni) and (b) the cationic series $[BFe(CO)_3]^+$ (B = C_5H_5, C_6H_7, or C_7H_9).[8] For example, in the $AM(CO)_3$ series, the values of P_M^{LUMO} increase in the series $C_2 \rightarrow C_6$ with the reverse trend in $P_{C(O)}^{LUMO}$ in accord with the facile S_N1 carbonyl substitution of the cobalt complex compared to the relative inertness of the chromium complex. In contrast, the cationic series gives the sequence $P_M^{LUMO} > P_{C(O)}^{LUMO} > P_{C(ring)}^{LUMO}$, indicating metal attack as the most common initial step. This agrees with evidence of metal attack by some nucleophiles but not apparently where ring adducts are obtained as the final products; however, care must be exercized in discussions of reaction mechanisms based simply on the nature of the final products.

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As we show in the subsequent paper, kinetically controlled initial attack may not lead directly to the thermodynamically stable product.

Unfortunately, the above approach in terms of reactivity indices is of limited value since it takes no account of variations in structure of the attacking nucleophile nor of solvent effects and so may only be of use in special cases. Recently a more detailed CNDO–MO study has been made of nucleophilic substitution of the coordinated π-allyl ligand by the hydroxide ion.[9]

Perturbation Theory of Reactivity

In the general case of the interaction between two molecules R and S by means of orbitals on atom r of R and atom s of S, it can be shown[10,11] that the interaction energy ΔE is given by the expression

$$\Delta E = -\frac{q_r q_s}{R_{rs}\epsilon} + 2\sum_m^{occ} \sum_n^{unocc} \frac{(C_r{}^m C_s{}^n \beta_{rs})^2}{E_m - E_n}$$

where q_r and q_s are the net charges on atoms r and s before interaction. R_{rs} is the interatomic distance between atoms r and s, ϵ is the dielectric constant of the medium in which interaction occurs, $C_r{}^m$ and $C_s{}^n$ are the coefficients of the atomic orbitals ϕ_r and ϕ_s in molecular orbitals ψ_m and ψ_n, respectively, and E_m and E_n are the energies of the molecular orbitals ψ_m and ψ_n of the isolated R and S systems. In the case of a nucleophile R (charge q_r) attacking a substrate S at atom s (charge q_s), it is thus possible to calculate the interaction energy ΔE from the known molecular orbitals of the substrate and nucleophile. Related approaches have been used previously to discuss hard and soft acids and bases[12] and orientation effects in a range of substitution reactions of both aliphatic and aromatic molecules.[13] When the difference between E_m and E_n is large, very little charge transfer occurs and ΔE is determined primarily by the charges on the two reactants; that is, the interaction is "charge controlled". Conversely, if q_r and q_s are both small and E_m lies close to E_n, then the second term in the equation predominates and the interaction is "orbitally controlled".

In this paper, we describe an application of the above perturbation theory of reactivity to the above series of arene and dienylium metal carbonyl complexes in an attempt to correlate their behavior to nucleophilic substitution with the calculated interaction energies at various possible sites of attack within a molecule. In the subsequent paper, we describe our experimental studies of the substitution reactions of the tricarbonyl(η-1,5-cycloheptadienylium)iron cation with a range of nucleophiles.

Method

The molecular orbitals of the arene series $AM(CO)_3$ (AM = C_6H_6Cr, C_5H_5Mn, C_4H_4Fe, or C_3H_5Co) and those for the cationic series $[BFe(CO)_3]^+$ (B = C_5H_5, C_6H_7, or C_7H_9) were obtained from previous SCCC($\sigma + \pi$) calculations.[8] A preliminary simulation-type calculation of ΔE for the interaction of $[C_7H_9Fe(CO)_3]^+$ in a solvent of low polarity ($\epsilon = 1$) with a wide range of nucleophiles was performed first. The range of single donor orbital energies was taken from $E_m = -2$ to -14.0 eV with small energy intervals in the area where E_m lies close to the band of LUMOs of $[C_7H_9Fe(CO)_3]^+$ ($E_n = -8.2$ to -9.5 eV). Two ideal hard and soft nucleophiles, OH^- and

Table I. Calculated Interaction Energies between Interacting Nucleophile and $[C_7H_9Fe(CO)_3]^+$

E_m	E_n	ΔE ($\epsilon = 1$)	
-2.0		M > C(O) > C(H)	charge controlled
-7.0		M > C(O) > C(H)	
-7.8		M > C(O) > C(H)	
-7.9	-7.9	C(O) > M > C(H)	orbitally controlled
-8.0		C(O) > M > C(H)	
-9.0		M > C(H) > C(O)	
	-9.5		
-11.0		M > C(O) > C(H)	charge controlled
-14.0		M > C(O) > C(H)	

I^-, respectively, were then considered and their energies obtained by standard methods. For an average of steric effects, it was assumed that (a) R_{rs} was a constant (1.0 Å) and (b) that β_{rs} was also a constant (1.0 eV). The summation of E_m was taken over all occupied orbitals of the attacking nucleophile R; however, the summation of E_n for the substrate S involves in principle all unoccupied orbitals, and this raises the problem of the nature of the virtual orbitals in molecular orbital theory. Certainly, a summation over all virtual orbitals is a very dubious procedure indeed, in view of the unreal energies obtained for some of these. We have already discussed this problem in our previous calculations of the ^{13}C NMR shifts in these complexes.[14] Fortunately, in the present discussion, it is possible to consider only a limited summation over the virtual orbitals because the more the energy gap between E_m and E_n increases the smaller the contribution of its term is to the above series. Moreover, in all the molecules under consideration, the virtual orbitals given by the SCCC($\sigma + \pi$) method consist of a group (6–10 levels) of closely similar energies, followed by a gap, averaging 3 eV, before the next level, and so summation was taken over this group in each case. The electrostatic term is dependent on the magnitude of the calculation substrate charge q_s, which obviously depends on the theoretical MO method used,[15] but since we are comparing trends in reactivity between closely related molecules the use of the relatively simple SCCC–MO method should be valid. The calculations were repeated for a range of values of ϵ, the dielectric constant of the solvent.

Results and Discussion

The values of ΔE calculated for a wide range of nucleophiles in a nonpolar solvent may be used to compare the ease of attack at (a) the metal atom (M), (b) a carbonyl carbon atom (C(O)), and (c) an averaged ring carbon atom (C(H)). The relative values of these three quantities for the above range of nucleophiles ($E_m = -2$ to -14 eV) are given in Table I.

It is clear that unless the donor energy of the attacking nucleophile lies close to the band of LUMOs of the substrate, that is, close to -8.0 eV, the reaction is charge controlled for both hard and very soft nucleophiles with use of the normal terminology.[10] When the donor orbital energy lies close to E_n (ca. -8.0 eV), then the reaction is orbitally controlled and the predicted position of the initial attack varies from the metal to a carbonyl carbon atom. These conclusions also apply to calculations of ΔE in polar solvents (e.g., $\epsilon = 80$) although then very hard nucleophiles ($E_m = -10.0$ to -14 eV) are predicted to give initial ring attack. These simple calculations using a single donor orbital indicate that nucleophilic substitution of tricarbonyl(η-1,5-cycloheptadienylium)iron will be charge controlled for both hard and very soft nucleophiles, giving either ring or metal attack depending on solvent polarity, but that for a certain range of moderately soft nucleophiles initial attack at both metal and carbonyl carbon may occur.

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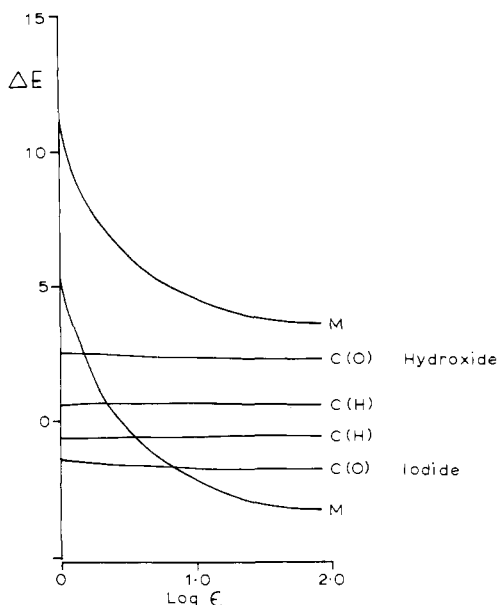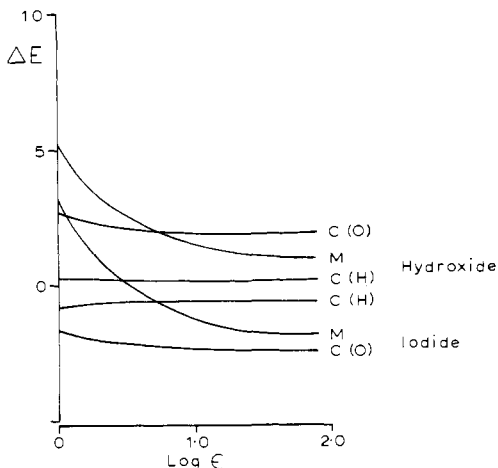(15) P. J. Hay, *J. Am. Chem. Soc.*, **103**, 1390 (1981).

Figure 1. Plot of interaction energy (ΔE) vs. the logarithm of the dielectric constant of the solvent (log ϵ) for the interaction of OH$^-$ and I$^-$ with $C_6H_6Cr(CO)_3$.

Figure 2. Plot of interaction energy (ΔE) vs. the logarithm of the dielectric constant of the solvent (log ϵ) for the interaction of OH$^-$ and I$^-$ with $C_3H_5Co(CO)_3$.

In view of this general pattern we now discuss more detailed calculations of ΔE for the hydroxide and iodide ions allowing for summation of their interactions with the substrate LUMO levels E_n.

The values of ΔE(eV) for attack at the metal atom, ΔE-(metal), a carbonyl carbon atom, ΔE(carbonyl), and the average value for a ligand (ring) carbon atom, ΔE(ring), for both the hydroxide and iodide ions (hard and soft nucleophiles, respectively) were plotted against log ϵ. These results are presented graphically for $C_6H_6Cr(CO)_3$ (Figure 1), C_3H_5-Co(CO)$_3$ (Figure 2), and [$C_7H_9Fe(CO)_3$]$^+$ (Figure 3).

AM(CO)$_3$ Series. It is instructive to consider the neutral series separately from the cationic series. For both the $C_6H_6Cr(CO)_3$ and $C_5H_5Mn(CO)_3$ complexes as illustrated in Figure 1 for $C_6H_6Cr(CO)_3$, ΔE is much greater for metal attack by a hard nucleophile than for the carbonyl attack and this order is independent of solvent; however, for the iron and cobalt complexes, as illustrated in Figure 2 for $C_3H_5Co(CO)_3$, there is a "crossover" as ϵ increases so that in polar solvents initial carbonyl attack is preferred to metal attack by hard nucleophiles. In all cases, ΔE(ring) is small and so initial ring attack is not predicted. In the case of attack by a soft nucleophile, there is now a "crossover" for ΔE for all members
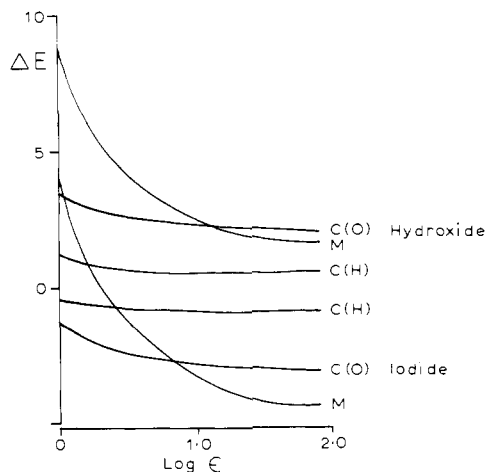

Figure 3. Plot of interaction energy (ΔE) vs. the logarithm of the dielectric constant of the solvent (log ϵ) for the interaction of OH$^-$ and I$^-$ with [$C_7H_9Fe(CO)_3$]$^+$.

of the series. This is from M > C(H) > C(O) to C(H) > C(O) > M ($C_6H_6Cr(CO)_3$, $C_5H_5Mn(CO)_3$, $C_4H_4Fe(CO)_3$) or to C(H) > M > C(O) ($C_3H_5Co(CO)_3$) for increasing ϵ values. In general, in polar solvents ΔE(ring) is greater than either ΔE(metal) or ΔE(carbonyl) and so initial ring attack is favored. In summary, for polar solvents the predicted site of attack by a hard nucleophile on $C_6H_6Cr(CO)_3$, as indicated by the magnitude of ΔE, is

<div align="center">metal > carbonyl > ring</div>
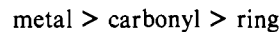
and the reverse for attack by a soft nucleophile. The order changes as we move from the chromium to the cobalt complex: carbonyl > metal > ring with again the reverse for attack by a soft nucleophile. In general, these theoretical predictions agree well with the observed substitution behavior (albeit limited) of the series: for example, the susceptibility of the cobalt complex to undergo S_N1 carbonyl substitution[16] and the relative inertness of the chromium complex,[17] although ring addition by reactive carbanions have been noted recently.[18]

[BFe(CO)$_3$]$^+$ Series. The calculated interaction energies for this series show distinct differences from those calculated for the neutral AM(CO)$_3$ series. Thus for the hard hydroxide nucleophile, the difference between ΔE(metal) and ΔE(carbonyl) is much smaller in the cationic series at low ϵ than that in $C_6H_6Cr(CO)_3$ and the crossover between these quantities now occurs as ϵ increases for all members of the series as illustrated in Figure 3 for [$C_7H_9Fe(CO)_3$]$^+$. In other words, as solvent polarity is increased, initial carbonyl attack is predicted in preference to metal attack. In contrast, in the AM(CO)$_3$ series, neither the chromium nor the manganese complex showed such a crossover.

For a soft nucleophile in solvents of low polarity, initial metal attack is predicted with a crossover to ring attack as the solvent polarity increases so that the predicted order of site attack becomes

<div align="center">ring > carbonyl > metal</div>
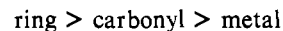
Again these predictions are in reasonable accord with the observed substitution pattern of the complexes. For example, both hydrazine in chloroform and azide in polar solvents such as acetone, methanol, and water[19] attack the carbonyl carbon

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of $[C_5H_5Fe(CO)_3]^+$ to give the isocyanate derivative, whereas in the less polar THF, attack by isocyanate was shown clearly by the use of labeled NCO⁻ to involve direct attack at the metal atom with displacement of CO.[20] Finally, the soft nucleophile iodide gives direct metal attack and formation of the corresponding $BFe(CO)_2I$ (B = C_6H_7, C_7H_9)[21] although this occurs in a polar solvent (acetone). In the case of cyclohexadienyliron tricarbonyl cation, soft nucleophiles, except iodide, give ring attack as the final product[22,23] but there is some evidence of carbonyl attack by the hard alkoxide nucleophile.[24] The behavior of the seven-membered ring cation is discussed fully in the following paper, but in summary only metal attack is observed for the iodide ion and a range of substituted hydrazines. For the azide ion, there is an indication of initial metal interaction followed by ring addition to give the stable 5-exo product;[25] however, the reaction with alkoxide

ions provides a clear example of the dangers of using the formation of a thermodynamically stable product to infer the site of initial attack. At room temperature, the stable 5-exo ring alkoxy addition product is formed. However, reaction at lower temperatures gives an indication of initial metal interaction followed by carbonyl attack and formation of the dicarbonyl carboalkoxy derivative, which rearranges by a dissociative mechanism to the 5-exo ring product on raising the temperature.[26] Finally, the reaction with phosphines yields either the 5-exo or 5-endo ring product, depending on the steric requirements of the phosphine and solvent polarity. In polar solvents there is again an indication of metal interaction both during substitution and during interconversion of the exo and endo isomer (see the following paper).

It is clear that the prediction of the site of initial attack in these carbonyl complexes is a difficult matter, but the above application of perturbation theory provides a rational theoretical framework in which to discuss the very varied behavior exhibited by these systems.

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Nucleophilic Substitution and Addition Reactions of the Tricarbonyl(η-1,5-cycloheptadienylium)iron Cation

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The substitution pattern for nucleophilic attack on the tricarbonyl(η-1,5-cycloheptadienylium)iron cation is reported for a series of nucleophiles. Amines attack the ring directly to give 5-exo ring products with no evidence of preliminary interaction at either the metal or the carbonyl carbon atom. Alkoxides give carbonyl attack at low temperatures with formation of carbalkoxy derivatives, which rearrange spontaneously as the temperature is raised to give 5-exo ring alkoxy derivatives. By "tuning" the nucleophilicity of substituted hydrazines it is possible to obtain either metal or carbonyl carbon substituted derivatives. Finally, by careful choice of both phosphine and solvent, both the 5-exo and the 5-endo phosphine ring adducts are obtained. The substitution pattern is discussed in terms of the perturbation theory of reactivity of the preceding paper.

Introduction

The preceding paper[1] discussed the application of the perturbation theory of reactivity[2] to the substitution and addition reactions of two series of (polyene)metal carbonyl complexes, first, the neutral $AM(CO)_3$ series (AM = C_6H_6Cr, C_5H_5Mn, C_4H_4Fe, C_3H_5Co, or C_2H_4Ni) and, second, the cationic $[BFe(CO)_3]^+$ series (B = C_5H_5, C_6H_7, or C_7H_9). Behavior contrasting to nucleophilic substitution was predicted for the two series. In the former case, substitution by a hard or very soft nucleophile was predicted to involve initial metal attack with no crossover in the curves of ΔE (calculated interaction energies) against log ϵ (ϵ = dielectric constant of solvent) between the metal and carbonyl carbon atoms. In no case was initial ring attack predicted for a hard nucleophile whereas the curves for a soft nucleophile such as iodide or phosphine generally indicated ring attack.

In contrast, in the case of attack by a hard nucleophile the cationic series gave much smaller differences between ΔE(metal) and ΔE(carbonyl) with a crossover occurring between these quantities as ϵ increases. Thus the theory predicts for the cations that a hard nucleophile may give initial attack at either the metal atom or carbonyl carbon depending on reaction conditions. Attack by a soft nucleophile is predicted in the sequence

$$\text{ring} > \text{carbonyl} > \text{metal}$$
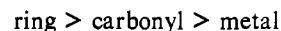
although initial metal attack may occur in solvents of low polarity. In this paper, we compare the above theoretical predictions with experimental studies of the substitution and addition reaction products of the tricarbonyl(η-1,5-cycloheptadienylium)iron cation for a wide range of nucleophiles.

In general, (cyclic diene)metal carbonyl complexes such as the title compound (I) and the closely related tricarbonyl(η^5-cyclopentadienyl)- and tricarbonyl(η^5-cyclohexadienyl)iron cations may undergo nucleophilic attack at the diene ring,[3]

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