

Preliminary communication

**CORRELATION OF NUCLEOPHILIC SUBSTITUTION OF POLYENE-
 M(CO)₃ COMPLEXES WITH FRONTIER ORBITAL INDICES**

D.A. BROWN*, J.P. CHESTER and N.J. FITZPATRICK

Department of Chemistry, University College, Belfield, Dublin 4 (Ireland)

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Summary

Nucleophilic substitution is correlated with the frontier electron density parameter, the partial valence-inactive population (P_A^{LUMO}) for two series of polyene-M(CO)₃ complexes, AM(CO)₃ (A = C₆H₆Cr, C₅H₅Mn, C₄H₄Fe, C₃H₅Co and C₂H₄Ni) and [BFe(CO)₃]⁺ (B = C₅H₅, C₆H₇ and C₇H₉). In both series nucleophilic substitution by an S_N2 process is shown as probably occurring by initial attack at the metal atom.

One of the most important problems facing the theoretical chemist in the field of organometallic chemistry is the correlation of structure and reactivity.

In the case of S_N1 dissociative carbonyl substitution reactions proceeding by very similar transition states, correlation between kinetic parameters and the overlap population of the M—C(O) bond undergoing substitution would be expected. In previous papers [1–3], we have shown that, using the SCCMO method, such correlations exist for the dissociative carbonyl substitution of M(CO)₅X (M = Mn, Re; X = Cl, Br and I) [1], C₃H₅Co(CO)₃ [2] and for the trend in S_N1 activity in the series AM(CO)₃ (A = C₆H₆Cr, C₅H₅Mn, C₄H₄Fe and C₃H₅Co) [3]. However, discussion of the analogous associative S_N2 reaction is more difficult because of uncertainties in assigning a structure to the transition state and, indeed, uncertainties regarding the point of initial attack within a complex. In these calculations the standard SCCMO method was employed [4]. Table 1 gives the values of half the partial valence-inactive populations (P_A^{LUMO}) of atom A in the LUMO [5] for the central metal atom (P_M^{LUMO}), the carbonyl carbon atom ($P_{C(O)}^{LUMO}$) and the ring carbon atom ($P_{C(H)}^{LUMO}$), respectively, in the two series (a) AM(CO)₃ (A = C₆H₆Cr, C₅H₅Mn, C₄H₄Fe, C₃H₅Co and C₂H₄Ni) and (b) [BFe(CO)₃]⁺ (B = C₅H₅, C₆H₇ and C₇H₉). The P_A^{LUMO} value may be used as a measure of frontier electron density for nucleophilic reactions and, provided carbonyl substitution is frontier controlled, it should serve as an indication of the relative S_N2 reactivity in a series of closely related molecules. Table 1 shows an

TABLE 1

FRONTIER ELECTRON DENSITY (P_A^{LUMO}) values

AM	P_M^{LUMO}	$P_{C(O)}^{LUMO}$	$P_{C(H)}^{LUMO}$
$AM(CO)_3$			
C_2H_4Ni	0.096	0.381	0.010
C_3H_5Co	0.196	0.267	0.086
C_4H_4Fe	0.235	0.167	0.066
C_5H_5Mn	0.352	0.136	0.096
C_6H_6Cr	0.412	0.049	0.036
$[BFe(CO)_3]^+$			
B			
C_5H_5	0.311	0.087	0.059
C_6H_7	0.327	0.115	0.028
C_7H_9	0.336	0.113	0.024

immediate difference between the two series. In the $AM(CO)_3$ case the values of P_M^{LUMO} show the trend: $C(2) < C(3) < C(4) < C(5) < C(6)$, with the converse trend for $P_{C(O)}^{LUMO}$ such that for $C_6H_6Cr(CO)_3$, $P_{Metal}^{LUMO} > P_{C(O)}^{LUMO}$ whereas for $C_3H_5Co(CO)_3$, $P_{Metal}^{LUMO} < P_{C(O)}^{LUMO}$. This difference in frontier electron density correlates with the large S_N1 reactivity of the cobalt compound compared with the relative inactivity of the chromium complex and with the fact that when substitution of the latter does occur it involves direct attack by the nucleophile at the chromium atom and cleavage of the metal-arene bond [6]. In addition, the $P_{C(O)}^{LUMO}$ values suggest that loss of a carbonyl group is most probable for the C(3) (and C(2)) cases. Furthermore, the $P_{C(H)}^{LUMO}$ values are lower than the P_M^{LUMO} and $P_{C(O)}^{LUMO}$ values, hence in no case is initial ring attack predicted.

In contrast, the series $[BFe(CO)_3]^+$ shows in all cases the sequence: $P_{Metal}^{LUMO} > P_{C(O)}^{LUMO} > P_{C(H)}^{LUMO}$, which suggests that nucleophilic substitution in this series is likely to involve initial attack at the metal atom and to occur most probably by an S_N2 associative mechanism.

Synthetic studies of nucleophilic substitution of polyene- $M(CO)_3$ (for a recent summary see ref. 7) have shown that substitution can occur at the ring (polyene), at the metal and at the carbonyl carbon atom but there have been relatively few kinetic studies and so detailed reaction mechanisms have rarely been proven. However, in the case of $[CpFe(CO)_3]^+$ [8], and $[C_6H_7Fe(CO)_3]^+$ [9] nucleophilic substitution follows second-order kinetics presumably by an S_N2 mechanism in agreement with the above theoretical predictions. Second-order kinetics are also observed for the substitution of $[C_7H_7M(CO)_3]^+$ ($M = Cr, Mo, W$) by $P-n-Bu_3$ [9] but were interpreted in terms of ring attack. However, very recently stopped-flow Fourier transform NMR kinetic studies [10] of the substitution of $[C_7H_7M(CO)_3]^+$ ($M = Mo, W$) by iodide showed the rapid formation of an intermediate with a $M-I$ bond followed by iodide transfer to the polyene ring and formation of ring adduct intermediates (largely *exo* in structure but with a small contribution from the *endo*) and finally of the stable $C_7H_7M(CO)_2I$ as product. We have previously shown that nucleophilic substitution of $[C_7H_9Fe(CO)_3]^+$ (e.g. by N_3^-) probably proceeds through initial metal attack [11]. It is frequently assumed that formation of an *exo* ring-substituted product (or adduct) precludes direct

metal attack as an intermediate step. However, both the above observations and the calculations reported in this note suggest that, on the contrary, nucleophilic substitution by an S_N2 mechanism can occur for both the $AM(CO)_3$ and $[BFe(CO)_3]^+$ series by initial attack at the metal centre, even if the final product has an *exo* configuration.

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