A Kinetic Study of the Mechanisms of S_NAr Reactions of Neutral and Cationic Metal-complexed Halogenoarenes with Methoxide Ion

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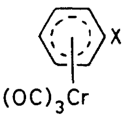
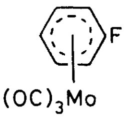
Rate studies have shown that the activation of halogenobenzenes towards nucleophilic attack by methoxide ion in methanol increases through the series of π-attached residues: $(OC)_3Cr < (OC)_3Mo \ll (\eta^5\text{-}C_5H_5)Fe^+ < (OC)_3Mn^+$. For a given ($\pi$-arene)metal system, the reactivity of halogenoarene ligands towards methoxide decreases through the series: fluorobenzene > chlorobenzene > chlorotoluene. Rates of reaction with methoxide are retarded in the presence of $NaClO_4$ or LiCl, but accelerated when the methanol solvent is diluted with tetrahydrofuran or 1,4-dioxan. Fluorobenchrotrene $(OC)_3Cr(\eta^6\text{-}PhCl)$ is slightly more reactive towards ethoxide in ethanol than towards methoxide in methanol. Evidence has been obtained that the cationic (halogenoarene)metal complexes readily form ion-pairs with methoxide, resulting in a reduction in their reactivity towards nucleophilic attack. Methoxide adds to $[(\pi\text{-methoxyarene})Mn(CO)_3]^+$ complexes to give (η^5-cyclohexadienyl) products which are reconverted into the cations by acid treatment.

ALTHOUGH unactivated halogenoarenes are inert to nucleophilic substitution under normal conditions,[1] their π-complexes with transition metal-ligand residues readily undergo S_NAr reactions with anionic and neutral nucleophiles.[2] Such activation was first reported[3] by Nicholls and Whiting who found that chlorobenchrotrene, *i.e.* $(OC)_3Cr(\eta^6\text{-}PhCl)$, reacts with methoxide ion under mild conditions to give the corresponding (η^6-anisole) complex. Kinetic studies[4-7] later established that π-attachment of the $(OC)_3Cr$ residue activates fluoro- and chloro-benzene towards nucleophilic substitution to an extent similar in magnitude to the effect of a 4-nitro-substituent, although different mechanisms of electron withdrawal operate for the two systems,[8] and that π-complexation with an $(\eta^5\text{-}C_5H_5)Fe^+$ residue exerts an even more marked effect.[9] Since (η^6-arene)-metal complexes are available in a wide diversity of structural types,[2,10] and in view of the current interest in the mechanistic details of S_NAr reactions,[11] we have measured the rates of reactions of a series of neutral and cationic (η^6-halogenoarene)metal complexes (1)—(4) with a range of anionic and neutral nucleophiles. In this paper,[12] we report the results of reactions with alkoxide ions.


(1)

a; X = F

b; X = Cl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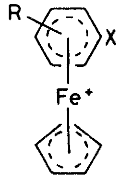

(3)

a; R = H, X = F

b; R = H, X = Cl

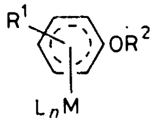
c; R = 2-Me, X = Cl

d; R = 4-Me, X = Cl


(4)

a; R = H

b; R = Me


(5)

a; R^1 = H, R^2 = Me, L_nM = $(OC)_3Cr$

b; R^1 = H, R^2 = Me, L_nM = $(\eta^5\text{-}C_5H_5)Fe^+$

c; R^1 = 2-Me, R^2 = Me, L_nM = $(\eta^5\text{-}C_5H_5)Fe^+$

d; R^1 = 4-Me, R^2 = Me, L_nM = $(\eta^5\text{-}C_5H_5)Fe^+$

e; R^1 = H, R^2 = Me, L_nM = $(OC)_3Mn^+$

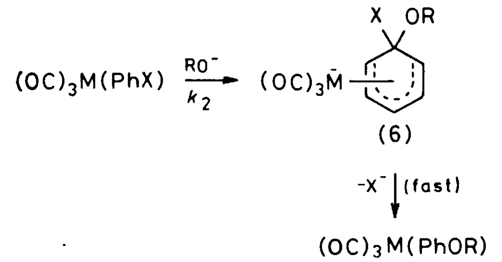
f; R^1 = 4-Me, R^2 = Me, L_nM = $(OC)_3Mn^+$

g; R^1 = H, R^2 = Et, L_nM = $(OC)_3Cr$

RESULTS

Synthesis of Substrates.—The neutral complexes (1a and b) and (2) were prepared by ligand-displacement reactions of $(MeCN)_3M(CO)_3$ with the halogenobenzenes. Attempts to prepare the 4-nitro-derivatives by this method were unsuccessful, low yields of 4,4′-dihalogenoazobenzenes resulting.[13] The cations (3a—d) were obtained from ferrocene by Al_2Cl_6-promoted ligand-exchange with the halogenoarenes[14] and isolated as $[PF_6^-]$ salts. Samples of the corresponding $[BF_4^-]$ salts were also prepared: borohydride reduction of (3) $[PF_6^-]$ gave the neutral (η^5-cyclohexadienyl) complexes[14] which were purified by chromatography and converted quantitatively into (3) $[BF_4^-]$ by treatment with triphenylmethyl tetrafluoroborate. The salts (4a, b) $[PF_6^-]$, obtained[15] from $BrMn(CO)_5$ by ligand-exchange with the chloroarenes in the presence of Al_2Cl_6 followed by treatment with HPF_6, were donated. For spectroscopic comparisons, the π-alkoxyarene complexes (5a—g) were prepared from the corresponding halogeno-substrates by treatment with alkoxide in alkanol. Methoxybenchrotrene (5a) and the cationic complexes (5b—d) were also prepared directly from hexacarbonylchromium and ferrocene, respectively, by ligand-exchange reactions with the methoxyarenes.

Rate Measurements.—The electronic spectra of the complexed halogenoarenes (1)—(4) are closely similar to those of the corresponding alkoxyarene complexes (5). However, repetitive scans of the spectra during the course of reactions of the former with sodium alkoxide in alkanol revealed for each system wavelengths (Experimental) of appreciable absorbance change. Rates of reaction were then determined at 44.5 °C by following absorbance change with time at these wavelengths. For each reaction, a sufficient excess of alkoxide over complex was used such that pseudo-first-order conditions obtained, *i.e.* $k_\psi = k_2[RO^-]$ where k_ψ and k_2 are, respectively, the observed first-order rate constant and the apparent second-order rate constant for a given concentrate of alkoxide. For each substrate, the alkoxide concentration was varied over at least a ten-fold change where practicable. Typical k_ψ values are in Tables 1 and 2.



SCHEME 1

DISCUSSION

Neutral Substrates.—For reactions of the neutral complexes (1) and (2) with alkoxide in alkanol, plots of k_ψ against $[RO^-]$ were approximately linear through the range of nucleophile concentrations used and passed through the origin, showing that the rate of reaction with solvent alone is negligible. Values of the second-order rate constant $k_2 = k_\psi/[RO^-]$ obtained from the slopes are in Table 1.

TABLE 1

Second-order rate constants for reactions of neutral substrates with alkoxide[a]

Substrate	$[RO^-]$/M[b]	[Salt]/M	k_2/l mol^{-1} s^{-1}	Ref.[c]
(1a)	0.1—1.0		1.31×10^{-2}	
			1.23×10^{-2}[d]	4
	0.45	$NaClO_4$ (0.10)	1.30×10^{-2}	
	0.45	$NaClO_4$ (0.30)	1.15×10^{-2}	
	0.45	$NaClO_4$ (0.50)	0.88×10^{-2}	
	0.50	LiCl (0.10)	1.23×10^{-2}	
	0.25—1.0[e]		1.96×10^{-2}	
(1b)	0.5—3.0		2.70×10^{-5}	
			6.15×10^{-6}[d]	4
			4.25×10^{-5}[f]	7
(2)	0.1—1.0		3.80×10^{-2}	

[a] In alkanol at 44.5 °C, unless indicated otherwise. [b] Values of $k_2 = k_\psi[RO^-]^{-1}$ were constant through the range of $[RO^-]$ indicated; R = Me, unless indicated otherwise. [c] Unless this study. [d] Calculated from an Arrhenius plot (see Discussion section). [e] R = Et. [f] At 55.4 °C.

The rectilinear dependence of k_ψ upon $[RO^-]$, and the much greater reactivity (*ca.* 500 times) of fluorobenchrotrene (1a) compared with that of the chloro-analogue (1b), is in accord with an addition–elimination mechanism (Scheme 1) in which the first step is rate-limiting and the concentration of the anionic Meisenheimer-type intermediate (6) does not build up. The k_2 value for reaction of (1a) with methoxide in methanol at 44.5 °C is in good agreement (Table 1) with that obtained from an Arrhenius plot of earlier results of a titrimetric study[4] at lower temperatures; our k_2 value for the same reaction of (1b) is *ca.* 4 times greater than that similarly calculated from data reported[4] for higher temperatures, and *ca.* one-half the value measured[7] for reaction at 55.4 °C (Table 1). The molybdenum complex (2) is *ca.* 3 times more reactive towards displacement of fluoride by methoxide than the benchrotrenyl analogue (1a), suggesting that π-$Mo(CO)_3$ exerts a stronger electron-withdrawing effect in the transition state for nucleophilic addition than does π-$Cr(CO)_3$. For a given concentration of nucleophile, fluorobenchrotrene (1a) reacts faster with ethoxide in ethanol than with methoxide in methanol, as expected,* but the difference (Table 1) is small. The ether products (5a and g) are inert to further reaction with alkoxide; thus, (5a) was recovered unchanged following prolonged treatment with a large excess of sodium ethoxide in ethanol.

Salt and solvent effects on rate were studied for substitutions of (1a). Rates of reaction with methoxide in methanol are modestly retarded in the presence of $NaClO_4$ (0.1—0.5M) and LiCl produces a similar effect (Table 1). A large salt effect would not be expected because the rate-determining step (Scheme 1) involves the formation of an anionic intermediate (6). Dilution of the methanol solvent with tetrahydrofuran (THF) or 1,4-dioxan causes a marked acceleration of the rate of reaction of (1a) with methoxide (Figure 1), in harmony with the results of related studies; *e.g.* activated halogenoarenes are less reactive towards methoxide in methanol than in methanol diluted with a non-hydroxylic solvent (*e.g.* dimethyl sulphoxide, benzene),[17] in accord with the Hughes–Ingold theory [18] of solvent action.

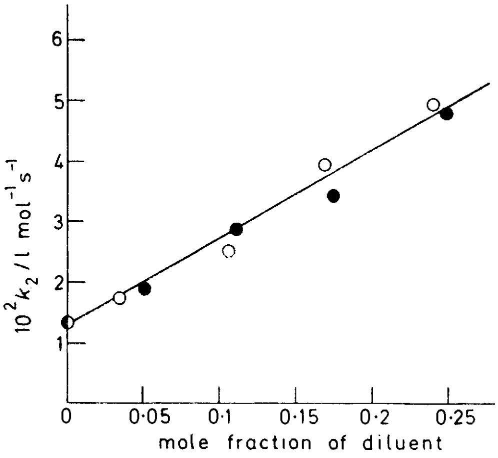


FIGURE 1 Effect of added THF (●) and 1,4-dioxan (○) upon second-order rate constant for reaction of (1a) with MeO^- in MeOH at 44.5 °C; a mole fraction of 0.25 corresponds to 4.93M-THF (40% v/v), 4.84M-1,4-dioxan (41% v/v)

Cationic Substrates.—Conversions of the cations (3a—d) into the corresponding methoxyarene complexes

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* The activation energies for S_NAr reactions of 4-nitrohalogenobenzenes with ethoxide in ethanol are 10—20 kJ mol^{-1} lower than those for corresponding reactions with methoxide in methanol.[16]

(5b—d) showed quite different kinetic features from those of reactions of the neutral substrates with methoxide. At each nucleophile concentration, good first-order kinetic behaviour was followed. However, although a plot of the observed first-order rate constants (k_ψ) *versus* [MeO$^-$] passed through the origin, k_ψ did not increase rectilinearly with increase in [MeO$^-$] in the manner expected of a second-order process where $k_\psi = k_2$[MeO$^-$]. Instead, values of the apparent second-order rate constant (k_ψ/[MeO$^-$]) decreased sharply with increasing [MeO$^-$] up to *ca.* 0.1M and then levelled off to approach a constant value at higher nucleophile concentrations; typical results are in Table 2. Similar behaviour was found for series of reactions conducted in the presence of inorganic salts (see later), indicating that the curvilinear dependence of k_ψ upon [MeO$^-$] is not due simply to an ionic-strength effect.

TABLE 2

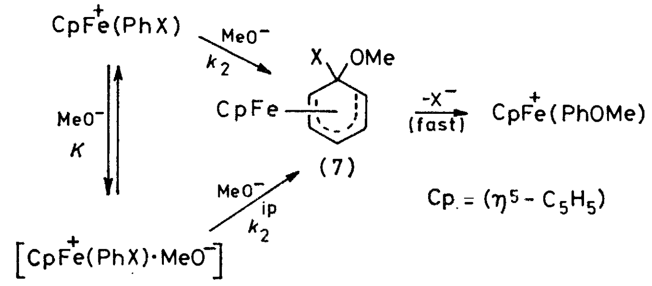
Second-order rate constants for reactions of cationic complexes with methoxide [a]

Cation [b]	10^2[MeO$^-$]/M	k_ψ[MeO$^-$]$^{-1}$/ l mol^{-1} s^{-1}
(3a)	0.48	3.12
	0.97	1.44
	2.41	1.00
	4.80	0.60
	9.70	0.34
	19.3	0.15
	38.5	0.098
(3b)	0.098	2.64
	0.49	1.86
	0.98	1.03
	4.88	0.51
	9.76	0.28
	19.5	0.24
(3c)	0.76	0.44
	5.40	0.18
	7.56	0.15
	10.8	0.10
	21.6	0.11
	32.4	0.081
(3d)	0.54	1.29
	0.65	1.15
	0.76	1.05
	0.86	0.96
	5.40	0.25
	10.8	0.14
(4a)	0.48	17.5
	0.57	12.1
	0.76	11.2
	0.96	7.82
	4.80	3.06
	28.8	0.15
(5e)	0.54	0.38
	1.08	0.27
	3.24	0.059
	5.40	0.026
	10.8	0.008
(5f)	0.43	0.52
	0.96	0.25
	4.80	0.10
	9.60	0.023
	19.2	0.014

[a] In methanol at 44.5 °C. [b] As [PF$_6^-$] salt; for reactions of the cations (3a—d), similar values were found for [BF$_4^-$] salts.

The conversion of (3b) into (5b) has been studied [9] by Nesmeyanov *et al.* who measured the second-order rate constant over a range of temperatures (5—25 °C) at constant [MeO$^-$] = [(3b)] = 1.82 × 10^{-2}M. Extrapolation of an Arrhenius plot of their results gives a rate constant of 0.85 l mol^{-1} s^{-1} at 44.5 °C, in reasonable agreement with our value (interpolated) of k_ψ/[MeO$^-$] = 0.76 l mol^{-1} s^{-1} at the same nucleophile concentration. The Russian group did not investigate the relationship between k_ψ and [MeO$^-$].

A mechanistic scheme involving reversible addition of methoxide to an arene ring carbon other than that bearing the halogen or to the cyclopentadienyl ring,* competitive with the S_NAr pathway, does not satisfactorily account for the kinetic behaviour observed. However, our results can be accommodated by the assumption that methoxide readily forms ion-pairs with the cations (3) in methanol, and that the products (5) result from reactions of methoxide with both the 'free' cation and the ion-pair, with the latter much less reactive. Evidence of ion-pairing in reactions of *pre-formed* carbocations with anionic nucleophiles is scanty, but a recent kinetic study [19] has shown that 1-ferrocenylalkyl cations [*i.e.* (π-cyclopentadienyl)(π-pentafulvene)iron cations], which are isoelectronic with (3) and possess a similar sandwich geometry, readily form ion pairs with anions in aqueous solution. For a reaction scheme involving the ion-pair (Scheme 2), the rate expression (1) can be derived where k_ψ, k_2, and k_2^{ip}



SCHEME 2

$$\frac{k_\psi}{[\mathrm{MeO^-}]} = \frac{k_2^{\mathrm{ip}}K[\mathrm{MeO^-}] + k_2}{K[\mathrm{MeO^-}] + 1} \qquad (1)$$

are, respectively, the observed first-order rate constant and the second-order rate constants for reactions of methoxide with the 'free' cation and the ion-pair, and K is the equilibrium constant for ion-pairing.

From plots of k_ψ/[MeO$^-$] against [MeO$^-$] for reactions of the cations (3a—d), estimates of the rate constants k_2 and k_2^{ip} were obtained, respectively, from the intercepts ([MeO$^-$] = 0) and limiting values of k_ψ/[MeO$^-$] approached at high methoxide concentrations. From equation (1), it is evident that equation (2) holds when

$$k_\psi/[\mathrm{MeO^-}] = (k_2^{\mathrm{ip}} + k_2)/2 \qquad (2)$$

[MeO$^-$] = K^{-1}. The equilibrium constants could then be calculated from the values of [MeO$^-$] obtained from

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* We did not detect any spectroscopic evidence of addition of methoxide to the parent complex (3; R = X = H) in methanol.

the plots by interpolation, using the estimated values of the rate constants. Close agreement was found between the experimental k_ψ values and those calculated from equation (1) using the estimated rate and equilibrium constants, which are in Table 3. This is illustrated in Figures 2 and 3 which show the fit of experimental data points to the calculated $k_\psi/[MeO^-]$ *versus* $[MeO^-]$ curves for reactions of (3a and b), respectively; the results for the other cations (3c and d) were also well fitted by equation (1). Because $k_2 \gg k_2^{ip}$ for all of these cations, accurate estimation of values of the latter rate constants is difficult; the values given (Table 3) are less reliable than those of k_2 and K, and probably represent upper limits.

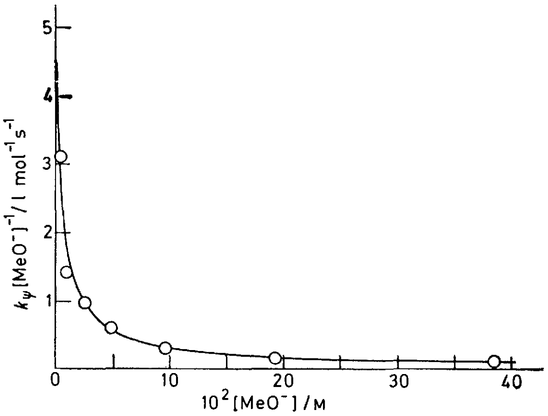


FIGURE 2 Fit of experimental values to curve calculated from equation (1) for reactions of (3a) with MeO^- in MeOH at 44.5 °C

Comparison of k_2 values for the neutral (1a and b) and cationic complexes (3a and b) shows that complexation of a halogenobenzene with an $(\eta^5\text{-}C_5H_5)Fe^+$ residue activates the molecule towards nucleophilic attack to an extent much greater than that resulting from $(OC)_3Cr$ π-attachment; *e.g.* (3a) is *ca.* 350 times more reactive than (1a) and (3b) is *ca.* 10^5 times more reactive than (1b). However, although the fluoride is more reactive than the chloride for both systems, the difference is much smaller for the cationic complexes; *i.e.* while (1a) is *ca.* 500 times more reactive than (1b), the reactivity of (3a) is only about twice that of (3b). Thus the much greater ability of the attached $(\eta^5\text{-}C_5H_5)Fe^+$ group to stabilise the transition state for nucleophilic addition to the arene ring, compared with the effect of $(OC)_3Cr$ complexation, reduces in importance the reactivity effect resulting from the difference in electronegativity of the halogeno-substituents. A similar situation obtained with S_NAr reactions of uncomplexed halogenoarenes where the nucleophilic addition step is rate determining, *i.e.* the difference in reactivity at a given temperature between fluoro- and chloro-substrates becomes generally smaller as the system is progressively activated by introduction of electron-withdrawing substituents (see ref. 1, pp. 139—164).

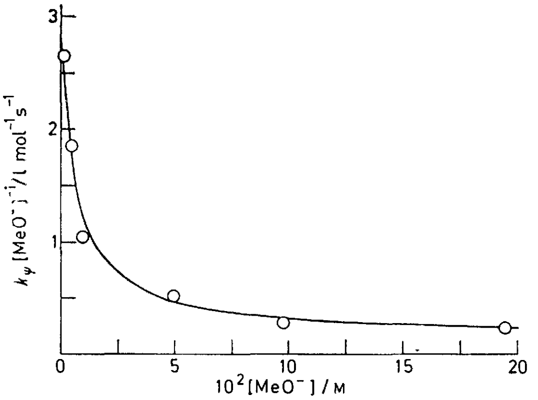


FIGURE 3 Fit of experimental values to curve calculated from equation (1) for reactions of (3b) with MeO^- in MeOH at 44.5 °C

The equilibrium constants (Table 3) for pairing of the cations (3) with methoxide, which are relatively insensitive to the substituents in the arene ring, are large; the cations are >90% ion-paired at a methoxide concentration of 0.1M. Comparison of k_2 and k_2^{ip} values for each substrate shows that ion-pairing causes a substantial (*ca.* 20-fold) reduction in reactivity of the arene ligand towards nucleophilic addition. This can be related to the work required to separate the counter-ions in formation of the neutral intermediate (7) which is common to the k_2 and k_2^{ip} pathways (Scheme 2). It is also conceivable that ion-pairing with methoxide may attenuate the electron-withdrawing power of the $(\eta^5\text{-}C_5H_5)Fe^+$ residue.

TABLE 3

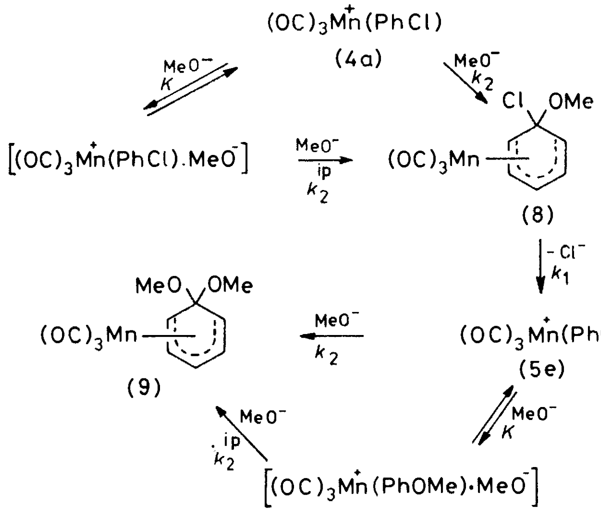
Rate and equilibrium constants for reactions of cationic complexes with methoxide [a]

Cation	$k_2/l\ mol^{-1}\ s^{-1}$	$k_2^{ip}/l\ mol^{-1}\ s^{-1}$	$K/l\ mol^{-1}$
(3a)	4.5	0.02	140
(3b)	2.8	0.15	145
(3b) [b]	0.60	0.15	100
(3b) [c]	0.39	0.15	100
(3c)	0.98	0.07	145
(3d)	2.0	0.13	135
(4a)	23.0	0.10	150
(5e)	0.55	0.005	100
(5f)	0.70	0.001	150

[a] In methanol at 44.5 °C. [b] In the presence of 0.05M-$NaClO_4$. [c] In the presence of 0.10M-$NaClO_4$.

Methyl substitution in the arene ring of (3b) causes a small reduction in reactivity towards nucleophilic attack, with the effect of 2-substitution greater than that of 4-substitution. Electron donation by the methyl group presumably stabilises the cation and lowers the electrophilicity of the reactive arene carbon atom; a 2-methyl group may additionally introduce some steric hindrance to nucleophilic addition at C(1). A similar effect has been reported[7] for benchrotrenyl analogues; for reactions with methoxide in methanol, relative k_2 values for (1b) and its 2- and 4-methyl derivatives are 1 : 0.28 : 0.36, respectively, and for (3b—d) are 1 : 0.35 : 0.71, respectively. Other workers have shown[6] that introduction of an electron-withdrawing arene substituent (CO_2Me) lowers the activation energy for the conversion of (1b) into (5a).

The effect of added $NaClO_4$ (0.05 and 0.10M) upon the rates of reaction of (3b) with methoxide in methanol was also studied. A general depression of the observed pseudo-first-order rate constants (k_ψ) was found, which was more marked at lower methoxide concentrations where the effect was much larger than that found previously for reactions of the neutral substrate (1a). Plots of $k_\psi/[MeO^-]$ against $[MeO^-]$ at constant $[NaClO_4]$ showed the same 'dog-leg' appearance as that found for reaction in the absence of added salt (see Figure 3) and were again well fitted by equation (1) with the values of k_2, k_2^{ip}, and K shown in Table 3. Similar behaviour was found for reactions in the presence of LiCl but detailed study was prevented by the problem of precipitation. Because addition of methoxide to the cation (3b) gives a neutral intermediate (7; X = Cl) (Scheme 2), reduction in the k_2 value brought about by added $NaClO_4$ (Table 3) can be attributed to a normal salt effect (added $NaClO_4$ retards the addition of anionic nucleophiles to preformed carbocations in solution)[20], although ion-pairing may also be of importance. Because of the difficulty noted earlier in estimation of k_2^{ip} values, the salt effect on this rate constant could not be assessed.



SCHEME 3

Reactions of the cations (4a and b) with methoxide in methanol were likewise studied over a range of nucleophile concentrations under pseudo-first-order conditions. Not surprisingly, π-attachment of an $(OC)_3Mn^+$ group to chlorobenzene causes greater activation towards nucleophilic attack than that resulting from $(\eta^5\text{-}C_5H_5)Fe^+$ complexation such that conversion of (4a) into the intermediate (8) (Scheme 3) is essentially complete before consumption of the latter by loss of chloride becomes significant. Accordingly, it was possible to measure independently rates of formation of (8) and of its subsequent conversion into the anisole complex (5e). Pseudo-first-order rate constants (k_ψ) were measured for the conversion of (4a) into (8) over a range of methoxide concentrations; typical results are in Table 2. A plot of $k_\psi/[MeO^-]$ against $[MeO^-]$ had the same 'dog-leg' appearance as that characteristic of reactions of the cations (3), suggesting that ion-pairing is again important (Scheme 3). Values of k_2, k_2^{ip}, and K (Table 3) were calculated as before, and the good fit of experimental data to equation (1) is shown in Figure 4. A similar study of the 4-methyl-substituted derivative (4b) was attempted. However, this substituent retards addition of methoxide to the cation (see earlier results) to the extent that the rate of loss of chloride from the (η^5-cyclohexadienyl) product [to give (5f)] is competitive with its rate of formation from (4b), and the equilibrium and rate constants could not be evaluated.

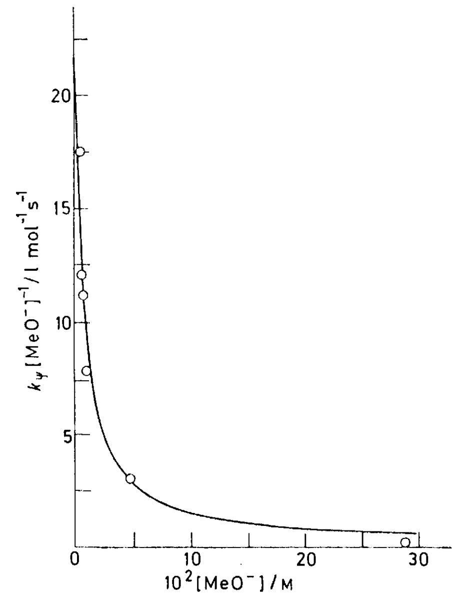


FIGURE 4 Fit of experimental values to curve calculated from equation (1) for reactions of (4a) with MeO^- in MeOH at 44.5 °C

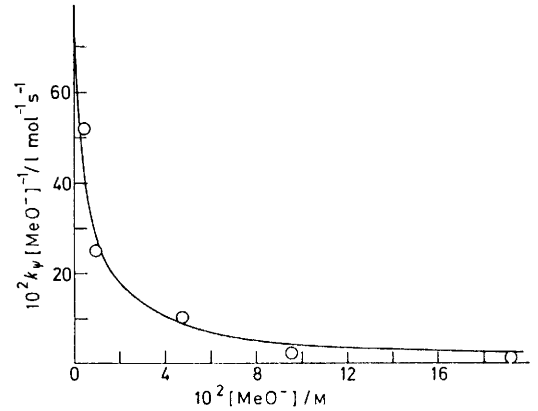


FIGURE 5 Fit of experimental values to curve calculated from equation (1) for reactions of (5f) with MeO^- in MeOH at 44.5 °C

The rate of conversion of the addition product (8) into the anisole complex (5e) (Scheme 3) was followed spectroscopically and the observed first-order rate constant (k_1 1.7×10^{-3} s^{-1}) was found to be independent of [MeO$^-$] in solution at the concentrations used. Thus, at [MeO$^-$] 5×10^{-3}M, for example, the rate of formation of (8) from (4a) at 44.5 °C is *ca.* 50 times faster than that of its conversion into (5e).

In contrast to the behaviour of the cationic sandwich complex (5b), which is inert to methoxide in methanol, the related cationic tricarbonylmanganese complex (5e) undergoes relatively slow addition of methoxide to give a product to which the (η^5-6,6-dimethoxycyclohexadienyl) structure (9) (Scheme 3) is assigned.* Similar behaviour was found for the 4-methyl derivative (5f). Rate constants (k_ψ) were determined under pseudo-first-order conditions as before for reactions of the cations (5e and f) with methoxide; typical values are in Table 2. For both cations, the kinetic behaviour was again in accord with ion-pairing (*cf.* Scheme 3) and good agreement was found between k_ψ/[MeO$^-$] values and those calculated from equation (1) using the k_2, k_2^{ip}, and K values in Table 3. The good fit of experimental to calculated k_ψ/[MeO$^-$] values is illustrated in Figure 5 for reactions of (5f); similar agreement was found for reactions of (5e).

Although the cationic chlorobenzene complexes (3b) and (4a) have a similar propensity towards ion-pairing with methoxide, comparison of k_2 values (Table 3) shows that the latter is the more reactive towards nucleophilic addition by a factor of *ca.* 8. This effect is not surprising in that the $(OC)_3Mn^+$ residue, by virtue of its stronger electron-withdrawing power than that of (η^5-C_5H_5)Fe$^+$, would better stabilise the transition state for addition. The effect of positive charge upon reactivity is striking; replacement of the $(OC)_3Cr$ residue in (1b) by the isoelectronic and isostructural $(OC)_3Mn^+$ group results in a *ca.* 10^6-fold enhancement in the reactivity of the arene ligand towards nucleophilic addition. For the cationic tricarbonylmanganese substrates, the chlorobenzene complex (4a) is *ca.* 40 times more reactive towards addition of methoxide than the anisole analogue (5e), reflecting the stronger $-I$ effect of the chloro-substituent.

From a knowledge of the k_1, k_2, and k_2^{ip} values (Table 3) for the stepwise conversion of (4a) into (9) (Scheme 3), reaction conditions could be chosen such that substantial concentrations of either of the neutral cyclohexadienyl complexes (8) or (9) could be generated in methanol containing a known [MeO$^-$] (see Experimental section). Addition of a predetermined excess of HCl to these solutions caused loss of methanol and regeneration of the cationic precursors; *i.e.* (8) was converted back into (4a) and (9) into (5e). Similar behaviour was found for acid treatment of the corresponding neutral intermediates formed by addition of methoxide to (4b) and (5f). The rates of these acid-promoted reactions, which were followed spectroscopically, were first order for a given acid concentration but the pseudo-first-order rate constants (k_ψ) did not increase linearly with increase in [H$^+$] and further study was not carried out. The non-linear relationship between k_ψ and [H$^+$] may arise because of the nature of the experiments which perforce were carried out in the presence of different concentrations of NaCl resulting from neutralisation of the NaOMe originally present; earlier work [20b] has shown that the rates of acid heterolysis of (1-hydroxyalkyl)-ferrocenes to give the corresponding carbocations, a mechanistically similar process, are very sensitive to the presence of inorganic salts such as NaCl.

In summary, it is clear that π-complexation of a halogenoarene with a metal–ligand residue results in a marked enhancement of reactivity towards nucleophilic displacement of halide, and that the extent of activation is highly sensitive to the nature of the π-attached residue. The ease of synthesis of such complexes and of subsequent removal of the activating metal–ligand group suggest obvious applications in organic synthesis which have, as yet, been little explored.[2]

EXPERIMENTAL

All preparative reactions were carried out under nitrogen. Neutral products were purified by column chromatography on Spence Grade H alumina which had been partially deactivated by exposure to the atmosphere for 6 h. Light petroleum refers to the fraction of boiling range 40—60 °C. M.p.s were determined in sealed evacuated capillaries and are uncorrected. ^{1}H N.m.r. spectra were determined using a Perkin-Elmer R32A spectrometer (90 MHz) and ^{13}C n.m.r. spectra using a JEOL FX90Q Fourier transform spectrometer (22.5 MHz), with tetramethylsilane as internal reference. Electronic spectra were recorded and kinetic experiments were performed using a Pye-Unicam SP1700 spectrometer coupled to an SP1803 wavelength selector, an SP1805 program controller, and an AR25 linear recorder.

Tris(acetonitrile)tricarbonylchromium.—A solution of hexacarbonylchromium (2.2 g, 10 mmol) in acetonitrile (75 ml) was heated under reflux for 16 h. The solvent was then evaporated leaving the title complex,[21] a yellow solid pyrophoric in air, which was used immediately.

Halogenobenchrotrenes (1).—A solution of $(MeCN)_3Cr(CO)_3$ (10 mmol) in the halogenarene (65 ml) was heated under reflux for 3 h. The resulting brown solution was filtered through Kieselguhr, evaporated to low bulk under reduced pressure, and chromatographed. In each case, the sole yellow product was eluted with benzene and purified by sublimation: fluorobenchrotrene (1a); yield 31%; m.p. 119—121 °C (lit.,[3] 122—123 °C); δ_H ($CDCl_3$) 4.8 (1 H) and 5.4 (4 H) (2 m, Ph); δ_C ($CDCl_3$) 79.2 (C-2, -6), 86.3 (C-4), 93.3 (C-3, -5), 146.5 (C-1), and 231.6 p.p.m. (CO); $\lambda_{\mathrm{max.}}$ (MeOH) 311 nm (ε 8 900); chlorobenchrotrene (1b); yield 33%; m.p. 99—101 °C (lit.,[3] 102—103 °C); δ_H ($CDCl_3$) 5.0 (1 H) and 5.4 (4 H) (2m, Ph); δ_C ($CDCl_3$) 88.0 (C-4), 91.1 (C-2, -6), 93.1 (C-3, -5), 113.0 (C-1), and 231.5 p.p.m. (CO); $\lambda_{\mathrm{max.}}$ (MeOH) 315 nm (ε 7 300).

Tricarbonyl(η^6-fluorobenzene)molybdenum (2).—A solution of hexacarbonylmolybdenum (0.26 g, 1 mmol) in acetonitrile (50 ml) was heated under reflux for 12 h. The solvent was then evaporated leaving yellow crystals (pyrophoric in

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* It is possible that this product is a mixture of isomeric tricarbonyl(η^5-n,6-dimethoxycyclohexadienyl)manganese complexes in (n = 1, 2, 3, or 6).

air) of $(MeCN)_3Mo(CO)_3$ [21] which were immediately dissolved in ice-cold fluorobenzene (50 ml). The solution was stirred at 0 °C for 24 h, then filtered through Kieselguhr, and the solvent was evaporated at low temperature under reduced pressure leaving the title complex [22] (0.06 g, 22%), which was purified by sublimation; m.p. 80—85 °C; δ_H ($CDCl_3$) δ 7.1 (1 H) and 7.5 (4 H) (2m, Ph).

Alkoxybenchrotrenes.—(a) Fluorobenchrotrene (0.23 g, 1 mmol) was dissolved in alkanol (50 ml) containing sodium alkoxide (10 mmol) and the solution was maintained at 45 °C for 17 h. The solution was then diluted with water (50 ml) and extracted with ether. The extract was washed (H_2O), diluted with light petroleum, dried ($MgSO_4$), and evaporated. A single yellow product, purified by sublimation, was obtained in each case: methoxybenchrotrene (5a); yield 95%; m.p. 83—85 °C (lit.,[3] 86—87 °C); δ_H ($CDCl_3$) 3.7 (3 H s, OMe), and 5.0 (4 H) and 5.5 (1 H) (2m, Ph); δ_C ($CDCl_3$) 55.4 (OMe), 78.2 (C-2, -6), 85.5 (C-4), 95.1 (C-3, -5), 143.3 (C-1), and 233.2 p.p.m. (CO); $\lambda_{max.}$ (MeOH) 311 nm (ε 5 000): ethoxybenchrotrene (5g); yield 69%; m.p. 65—67 °C; δ_H ($CDCl_3$) 1.1 (3 H, t, Me), 3.8 (2 H, q, CH_2), and 4.6—5.6 (5 H, m, Ph).

(b) A solution of hexacarbonylchromium (4 g, 18 mmol) in a mixture of anisole (25 ml), di-n-butyl ether (120 ml), and tetrahydrofuran (10 ml) was stirred and heated to 140 °C for 20 h. The solution was then evaporated to low bulk under reduced pressure and cooled (liquid nitrogen) giving crystals of the complex (5a) (2.7 g, 60%), identical with the product described under (a).

(η^5-Cyclopentadienyl)(η^6-halogenoarene)iron Salts.—(a) The [PF_6^-] salts of the cations (3a—d) were prepared in 30—70% yields from ferrocene by ligand-exchange with the halogenoarene in the presence of Al_2Cl_6–Al powder, as described previously,[14] and were purified by recrystallisation from acetone–ether. Their ^1H n.m.r. spectra were identical with those reported [14] earlier; their ^{13}C n.m.r. resonances ([$^2H_6$]acetone) were as follows: (3a) δ_C 79.1 (Cp), 79.0, 88.0, and 88.4 (C-2—6), and 138.8 p.p.m. (C-1); (3b) δ_C 79.9 (Cp), 88.3, 89.3, and 89.9 (C-2—6), and 108.2 (C-1); (3c) δ_C 19.6 (Me), 80.1 (Cp), 77.9, 80.1, 89.4, 90.1, and 103.3 (C-2—6), and 108.5 (C-1); (3d) δ_C 20.2 (Me), 80.4 (Cp), 89.1, 89.6, and 104.3 (C-2—6), and 106.8 (C-1).

(b) Each of the salts (3a—d) [PF_6^-] was reduced with sodium borohydride in 1,2-dimethoxyethane, as described previously.[14] The resulting (η^5-cyclohexadienyl) neutral products were purified by chromatography, dissolved in dichloromethane, and the solutions were treated with an equimolar amount of triphenylmethyl tetrafluoroborate [23] in the same solvent. Upon dilution of these solutions with ether, there was precipitated in almost quantitative yields the [BF_4^-] salts of the cations (3a—d) whose ^1H and ^{13}C n.m.r. and electronic spectra were identical with those of the corresponding [PF_6^-] salts.

(η^5-Cyclopentadienyl)(η^6-methoxyarene)iron Salts.—Solutions of the salts (3b—d) [PF_6^-] (2.5 mmol) in methanol (30 ml) containing sodium methoxide (25 mmol) were stirred at 25 °C until reaction was complete. Addition of saturated aqueous ammonium hexafluorophosphate solution gave precipitates of the corresponding salts (5b—d) [PF_6^-] (60—80% yields) whose ^1H n.m.r. spectra were identical with those of the [BF_4^-] salts reported [24] previously. The ^{13}C n.m.r. resonances ([$^2H_6$]acetone) for (5b) were as follows: δ_C 57.3 (OMe), 77.3 (Cp), 75.2, 84.9, and 87.5 (C-2—6), and 135.8 (C-1).

Tricarbonyl(η^6-chloroarene)manganese Salts.—Pure samples of the salts (4a, b) [PF_6^-] [15] were generously donated by Professor P. L. Pauson.

Tricarbonyl(η^6-methoxybenzene)manganese Hexafluorophosphate (5e) [PF_6^-].—A solution of the salt (4a) [PF_6^-] (0.2 g, 0.5 mmol) in methanol (20 ml) containing sodium methoxide (6 mmol) was stirred at room temperature for 0.25 h. An excess of aqueous HPF_6 solution (65%) was then added, whereupon the title salt was precipitated as a yellow solid (90 mg, 45%), m.p. 200—205 °C (lit.,[15] 203—205 °C); δ_H ([$^2H_6$]acetone) 4.15 (3 H, s, OMe) and 7.0—7.25 (5 H, m, Ph).

Kinetic Measurements.—The following general procedure was used. A stoppered cuvette (1 cm path length) containing a solution (3 ml) in alkanol of sodium alkoxide at a predetermined concentration was allowed to reach a constant temperature in the cell compartment of the spectrometer. A solution (10—50 μl) of the complex in methanol or acetone was then added with thorough mixing, such that the molar excess of alkoxide over complex was at least 50-fold; the concentration of complex was always $\leqslant 5.5 \times 10^{-4}$M. From a repetitive scan (220—350 nm) of the absorbance of the solution during the course of reaction, a suitable wavelength of maximum absorbance change was identified for each substrate; *viz.* 313 nm for the neutral substrates (1a and b) and (2) and 265 nm for the cations (3a—d), (4a and b), and (5e and f). The experiment was then repeated and the rate of change with time of the absorbance (*A*) at the selected wavelength was recorded; maximum absorbance scale change was arranged by appropriate adjustment of the base-line and scale-expansion spectrometer controls.

For each reaction, at least two independent kinetic runs at each nucleophile concentration were carried out to ensure reproducibility of results. For the faster reactions, the pseudo-first-order rate constants (k_ψ) were determined conventionally from a plot of log ($A_\infty - A_t$) *versus* t, using a least-squares best-fit computer program. For the slower reactions, particularly those of chlorobenchrotrene (1b), where determination of A_∞ values was difficult due to slow decomposition of the complexes in solution, the pseudo-first-order rate constants were calculated using the Guggenheim analysis procedure.[25] In either case, data points over four half-lives (*ca.* 95% reaction) were taken, and runs giving correlation coefficients <0.999 for calculation of rate constants were disregarded. Reactions in the presence of inorganic salts were carried out similarly. Typical results are in Tables 1 and 2.

Reactions of (η^5-Cyclohexadienyl)manganese Complexes.—(a) The salt (4a) [PF_6^-] was converted into the cyclohexadienyl complex (8) by treatment with a predetermined excess of sodium methoxide in methanol at 44.5 °C, and the course of the reaction was monitored spectroscopically by following absorbance change at 265 nm, as described previously. At the methoxide concentrations used (0.005—0.05M), this reaction was essentially complete within 60 s (see $k_\psi[MeO^-]^{-1}$ values; Table 2). The subsequent much slower conversion of (8) into (5e) by loss of chloride was then followed at the same wavelength. The rate of reaction ($t_{\frac{1}{2}}$ *ca.* 400 s) was independent of [MeO^-] through the range used.

(b) A solution (3 ml) of the complex (8) in methanol containing sodium methoxide was prepared in a u.v. cell as described under (a). An aqueous solution (<50 μl) of HCl was then added immediately to give an excess of acid in solution. Conversion of (8) back into (4a) was observed.

(c) Treatment of the salt (5e) [PF_6^-] with sodium methoxide in methanol at 44.5 °C caused slow conversion into the cyclohexadienyl complex (**9**), and rates were followed spectroscopically as before. Rate constants for this reaction and for the corresponding reaction of (5f) [PF_6^-] are in Table 2.

(d) A solution of the complex (9) in methanol containing sodium methoxide was prepared as described under (c). Upon addition of an excess of aqueous HCl, conversion of (**9**) back into (5e) was observed. Addition of methoxide to (5f) was similarly reversed upon acid treatment.

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