Kinetics and Mechanism of Halide Promoted Migratory CO Insertion of *fac*-$[FeMe\{o\text{-}C_6H_4(AsMe_2)_2\}(CO)_3]ClO_4$

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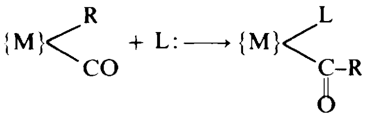
The kinetics for the iodide and bromide promoted carbonyl insertion of *fac*-$[FeMe\{o\text{-}C_6H_4(AsMe_2)_2\}(CO)_3]ClO_4$ have been examined at +10 °C in methylene chloride, acetone, and mixed aqueous–acetone solvents. In the presence of excess halide the insertion rate is first order in Fe substrate. The pseudo-first-order rate constants, $k_{obs.}$, show a complicated dependence both on halide concentration and on solvent, which is analysed in terms of a mechanism involving a pre-equilibrium ion-pair formation between the cationic substrate complex and the promoting halide. The proposed mechanism is used to account for the known solvent-dependent regiospecificity of the insertion.

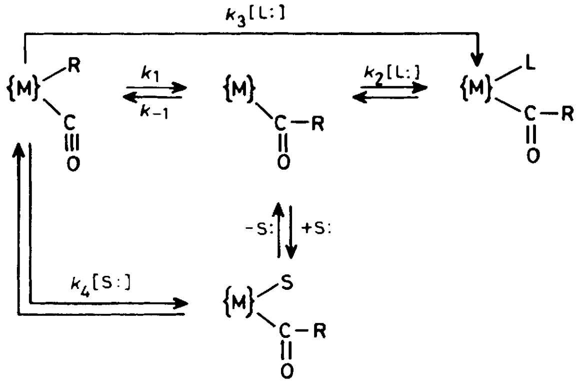
Extensive mechanistic studies of Lewis-base promoted migratory carbon monoxide insertion on transition-metal substrates [*cf.* equation (1)] provide evidence for several distinct rate laws and stoicheiometric mechanisms.



$$\{M\}(R)(CO) + L: \longrightarrow \{M\}(L)(C(=O)R) \qquad (1)$$

(**1**) (**2**)

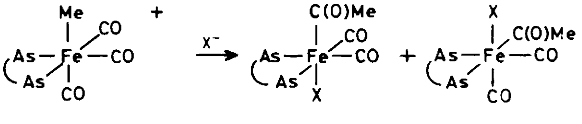
Unimolecular {rate = k[(**1**)]}, bimolecular {rate = k[(**1**)][L:]}, as well as parallel uni- and bi-molecular or mixed-order rate laws have all been reported and interpreted in terms of the generalized mechanism shown in Scheme 1, where {M} represents the transition-metal substrate.[1–3]



Scheme 1.

The extent of associative character, or bond making, between the promoting base, L:, or donor solvent, S:, and {M} on approach to the transition state for acyl formation, given by the relative importance of the dissociative ({M}–C bond breaking dominant) k_1 path and the associative ({M}–L or {M}–S bond making dominant) k_3 and k_4 paths of Scheme 1, remains a crucial point not yet clearly understood. Convincing evidence has been presented which argues both for[4–8] and against[9–16] an associative interaction with L: or S:.

In this paper we present the results derived from a kinetic study of the previously reported[17] halide promoted migratory carbon monoxide insertion reaction of the cationic substrate (**3**) which represents a charge type not previously examined in detail [*cf.* equation (2); $X^- = I^-$ or Br^-; As–As = *o*-phenylenebis(dimethylarsine)]. Specifically, reaction (2) is of current interest from a number of perspectives. First, although we presented[11] earlier evidence which established that the phosphine promoted migratory carbon monoxide insertion of the alkyl complex (**3**) according to equation (1) was a clean, first-order reaction with a rate *independent* of [L:] or donor solvent and concluded that the insertion step was essentially a unimolecular process,† we felt in the present case that electrostatic considerations would favour an associative interaction for equation (2) and thereby provide a more stringent test of the intimate mechanism for d^6 substrates. Secondly, the role which halides in general and iodide in particular play in facilitating carbon–carbon bond formation in homogeneous catalytic reactions involving a migratory carbon monoxide insertion step is not yet clarified.[19] Finally, although ion pairing has been shown to catalyze strongly the rate of alkyl migration in *anionic* alkyl complexes,[20] and to be relevant to the mechanism of catalysis for systems involving ionic catalysts,[21] the role of ion aggregates derived from cationic alkyls remains unexplored.



(2)

(**3**) (**4a**) (**4b**)

Experimental

General.—Weighings were carried out under an atmosphere of dry nitrogen in a glove-box fitted with a gas recirculating train containing heated DeOx catalyst (Alpha), Drierite, and activated (450 °C, 4 h) type 4A molecular sieves. Spectral grade (Baker) acetone was distilled from activated 4A molecular sieves under a dry, nitrogen atmosphere immediately before use.

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† Further corroboration of the unimolecular nature of the phosphine promoted migratory carbon monoxide insertion of complex (**3**) follows from the observation of a distinct steric acceleration of the reaction rate found[18] for the carbon monoxide insertion reaction of monophosphine substituted derivatives, $[FeMe(pdma)(CO)_2(PR_3)]^+$, with increasing steric requirements of PR_3.

Methylene chloride (MCB) was dried by percolation through a column of activated basic alumina immediately before use. Solutions were transferred under a positive pressure of nitrogen by means of a nitrogen-filled syringe or a double-ended needle inserted through a tight-fitting rubber septum.

fac-[FeMe(pdma)(CO)$_3$]BF$_4$ [pdma = *o*-phenylenebis(dimethylarsine)] was prepared as described previously.[17] The corresponding perchlorate salt was prepared in an analogous manner from the reaction of anhydrous AgClO$_4$ (Aldrich) with [FeI(pdma)(CO)$_2${C(O)Me}],[17] and was purified by several recrystallizations from methylene chloride–diethyl ether. The compound was stored under a nitrogen atmosphere protected from light [m.p. >164 °C (violent decomp.); Found: C, 30.95; H, 3.65. Calc. for $C_{14}H_{19}As_2ClFeO_7$: C, 31.10; H, 3.50%]. Its ^{1}H n.m.r. spectrum (CDCl$_3$) was identical with that of the tetrafluoroborate salt previously reported.[17] Tetrabutylammonium salts were purchased from Aldrich and dried *in vacuo* before use.

Kinetic Measurements.—All measurements were made on a Cary 17 or Perkin-Elmer 356 spectrophotometer at 340 (bromide) or 350 nm (iodide). In the case of the Cary instrument, optical density *vs.* time profiles were recorded and stored as digitized (Hewlett-Packard 3421A, Hewlett-Packard 86B) resistance of a precision potentiometer (Novo Technik) mechanically coupled to the spectrophotometer chart recorder. The Novo Technik potentiometer was calibrated against optical density readings from the spectrophotometer by means of a fourth order polynomial obtained from *ca.* 100 readings. A 10% filter was used to calibrate the Cary 17 instrument against a Shimatzu 260 spectrophotometer. The two instruments were found to be consistent within ±0.005 absorbance units. Measurements on the Perkin-Elmer instrument were obtained from an analog 4V output which was digitized, calibrated against the filter, and stored (Hewlett-Packard 3421A, Hewlett-Packard 86B).

Kinetic runs were conducted in an all-glass/Teflon stopped-flow type cell fitted directly into the sample compartment of the spectrophotometer. The reagents [(3), 0.04—0.2 mmol l^{-1}; halide source NBu$_4$X or LiX, *ca.* 1—30 mmol l^{-1}, or as permitted by solubility restrictions] were introduced into two vertically oriented thermostatted drive syringes (2.5-ml Hamilton gas-tight) and left to equilibrate. A manually operated ram mixed the reagents at a Teflon chromatographic Y-fitting prior to injection into the glass/Teflon observation cell. The volume of reagents driven was *ca.* six times the volume of the cell and more than twice that required for efficient purging of the cell as determined from dye mixing experiments. The path length was *ca.* 1 cm. The temperature was monitored by a thermocouple connected to a digital multimeter (Keithley 177). Temperature drift was generally less than ±0.05 °C.

Rate constants, $k_{obs.}$, were determined by a direct, iterative, non-linear least-squares[22] fit of stored optical density *vs.* time data [*cf.* Figure 1(*a*)] to the first-order expression $A_t = A_\infty[1 - \exp(-kt)] + B$ with A_∞, k, and the instrumental offset, B, as parameters. The number of equally spaced points used in the regression was greater than 70 and in general *ca.* 200. The kinetic parameters were considered acceptable only if scatter plots of $A_{obs.} - A_{calc.}$ over the entire observation period showed no systematic deviations [*cf.* Figure 1(*b*)]. Rate determinations were carried out in duplicate for the slower reactions, but more typically in triplicate. In favourable cases, rate constants were reproducible to within 2%.

Some difficulty was encountered with the reproducibility of the results in methylene chloride when solvents of different lot numbers were used. The data reported were determined using methylene chloride samples with the same lot number.

Results and Discussion

Kinetic Studies.—^{1}H N.m.r. analysis showed that reaction (2) proceeded to completion without complications from side reactions in all the solvents examined. The electronic spectra of reactant and product are characterized by featureless charge-transfer bands which differ only slightly in absorption coefficient. To allow both for the largest possible change in promoting halide concentration and to access the critical very low concentration region, the reaction rate was monitored spectrophotometrically at wavelengths chosen for maximum change in absorbance [350 nm (iodide), 340 nm (bromide)]. In all cases excellent pseudo-first-order behaviour was observed in the presence of a large excess (10—50 fold) of added NBu$_4$X salts. The pseudo-first-order rate constants, $k_{obs.}$ listed in Table 1, were extracted from non-linear least-squares fits[22] of the

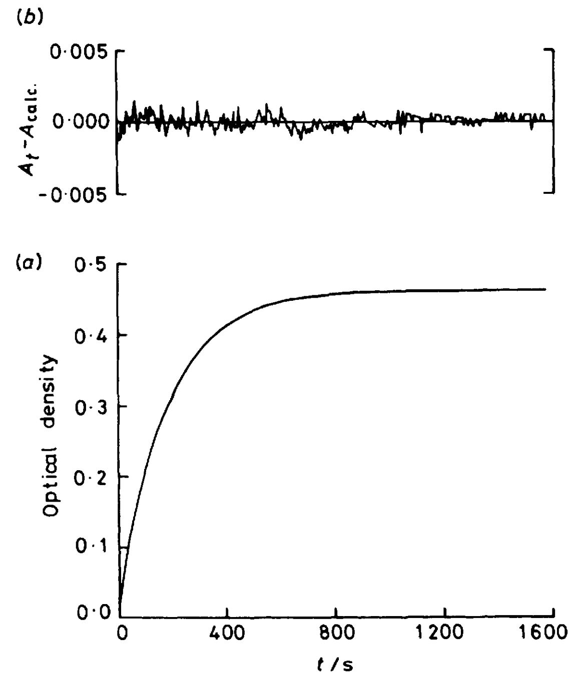


Figure 1. (*a*) Typical optical density *vs.* time profile at 350 nm for equation (2), $X^- = I^-$ at +10 °C in acetone. (*b*) Error plot ($A_{obs.} - \{A_\infty[1 - \exp(-kt)] + B\}$) for the same data set

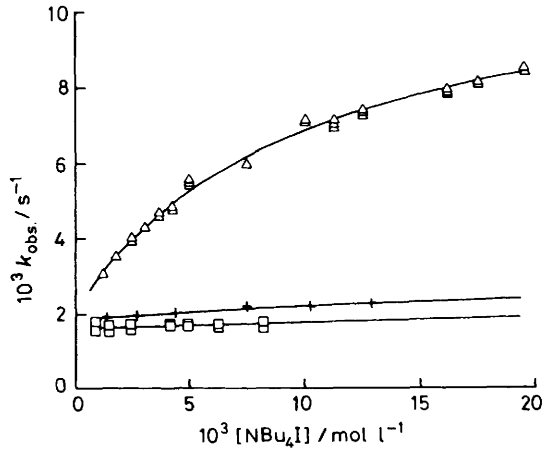


Figure 2. $k_{obs.}$ *vs.* [NBu$_4$I] plots for reaction (2) in acetone (△), acetone–water (80:20) (+), and acetone–water (60:40) (□) at +10 °C

Table 1. Pseudo-first-order rate constants for equation (2) at +10 °C

Solvent	MX	10^3c_{MX}	10^3c_{Fe}	$10^3[X^-]$	$f_\pm$[a]	$10^3k_{obs.}$[b]/s^{-1}
			mol l^{-1}			
Acetone	NBu_4I	4.96	0.20	3.96[c]	0.664[c]	5.49(0.07)
		10.01		7.23	0.597	7.13(0.04)
		16.13		10.94	0.550	7.93(0.07)
		2.51		2.16	0.727	3.95(0.07)
		7.44		5.65	0.625	6.01(0.01)
		12.47		8.80	0.575	7.37(0.07)
		11.24		8.06	0.585	7.06(0.11)
		17.45		11.69	0.543	8.15(0.04)
		19.46		12.81	0.532	8.50(0.08)
		1.26	0.07	1.14	0.784	3.07(0.02)
		1.83		1.62	0.754	3.57(0.03)
		2.44		2.10	0.729	3.98(0.02)
		3.06		2.58	0.709	4.31(0.02)
		3.70		3.06	0.692	4.63(0.07)
		4.26		3.47	0.678	4.83(0.04)
Acetone–water (80:20, wt.%)	NBu_4I	1.39	0.09	1.34[d]	0.860[d]	1.91(0.02)
		2.75		2.57	0.818	1.97[e]
		4.39		3.98	0.786	2.04[e]
		7.49		6.50	0.746	2.20[e]
		10.28		8.65	0.721	2.21[e]
		12.94		10.61	0.703	2.27[e]
Acetone–water (60:40, wt.%)	NBu_4I	0.91	0.04	0.89[f]	0.929[f]	1.68(0.11)
		1.51		1.48	0.912	1.64(0.05)
		2.44		2.36	0.892	1.68(0.04)
		4.14		3.94	0.868	1.71(0.04)
		4.93		4.65	0.859	1.70(0.02)
		6.27		5.85	0.847	1.70(0.05)
		8.22		7.54	0.832	1.71(0.07)
CH_2Cl_2	NBu_4I	0.729	0.08	0.144[g]	0.715[g]	12.4(0.04)
		1.43		0.223	0.664	14.7(0.2)
		2.17		0.294	0.628	16.0(0.1)
		2.89		0.356	0.603	16.7(0.2)
		3.68		0.420	0.580	17.3(0.3)
		4.40		0.476	0.562	17.6(0.2)
		5.12		0.529	0.547	17.7(0.1)
		5.75		0.574	0.535	18.1(0.1)
		6.58		0.632	0.521	18.2(0.2)
		7.23		0.676	0.511	18.5(0.1)
		11.2		0.934	0.463	18.8(0.2)
		14.6		1.14	0.432	19.1(0.3)
		18.8		1.39	0.403	19.2(0.2)
		0.244		0.0713	0.786	9.52(0.01)
		0.503		0.114	0.741	11.5(0.3)
		0.768		0.149	0.712	13.1(0.5)
		1.06		0.184	0.687	13.9(0.2)
		1.60		0.241	0.654	15.2(0.06)
		2.14		0.292	0.630	16.2(0.1)
		2.72		0.342	0.608	16.8(0.3)
		5.40		0.549	0.542	18.0(0.1)
		8.21		0.742	0.497	18.5(0.2)
Acetone	LiI	0.716	0.12	0.672[h]	0.823[h]	2.65(0.03)
		1.39		1.25	0.773	3.37(0.03)
		3.20		2.69	0.699	4.58(0.03)
		4.02		3.29	0.677	5.03(0.02)
		4.65		3.75	0.663	5.29(0.02)
		6.28		4.89	0.633	5.94(0.04)
		7.86		5.95	0.610	6.47(0.03)
		11.19		8.51	0.567	7.45(0.02)
		15.89		10.91	0.537	8.24(0.04)
		23.88		15.41	0.496	9.38(0.05)
		32.19		19.81	0.466	10.26(0.05)

[a] Calculated by the method of successive approximations using the extended Debye–Huckel expression.[32] [b] Standard deviations in parentheses. [c] Calculated with $a = 6.31$ A (A = absorbance) and $K_A = 143$.[26] [d] Calculated with $a = 6.31$ A and $K_A = 42$.[30] [e] Average of duplicate runs. [f] Calculated with $a = 6.31$ A and $K_A = 17.3$.[30] [g] Calculated with $a = 6.31$ A and $K_A = 54\,900$.[30] [h] Calculated with $a = 5.5$ A and $K_A = 145$.[25] [i] Calculated with $a = 4$ A and $K_A = 264$.[26]

Table 1 (*continued*)

Solvent	MX	10^3c_{MX}	10^3c_{Fe}	$10^3[X^-]$	$f_\pm$ [a]	$10^3k_{obs.}$ [b]/s^{-1}
			mol l^{-1}			
Acetone	NBu_4Br	1.01	0.085	0.883 [i]	0.798 [i]	24.2(0.1)
		1.53		1.28	0.765	30.8(0.3)
		2.04		1.65	0.740	35.8(0.4)
		2.58		2.02	0.719	40.9(0.3)
		3.10		2.37	0.702	43.9(0.2)
		3.61		2.70	0.688	47.8(0.2)
		4.17		3.05	0.673	50.5(0.1)
		4.61		3.33	0.663	53.3(0.5)
		2.57		2.01	0.720	41.2(0.1)
		3.33		2.52	0.695	46.3(0.2)
		4.17		3.05	0.673	51.7(0.1)
		5.15		3.65	0.652	55.4(0.07)
		7.13		4.80	0.619	62.5(0.15)
		8.88		5.77	0.595	67.3(0.3)
		13.26		8.05	0.551	77.2(0.3)
		17.72		10.27	0.519	83.4(0.4)
		22.28		12.39	0.494	88.2(0.4)
		0.823		0.729	0.813	21.9(0.09)
		0.977		0.854	0.801	23.5(0.3)
		1.17		1.00	0.787	26.4(0.2)
		1.31		1.11	0.778	28.2(0.1)
		1.67		1.38	0.758	32.1(0.2)
		2.33		1.85	0.728	38.3(0.1)
		3.38		2.56	0.694	45.7(0.3)
		5.07		3.60	0.654	54.9(0.2)
		6.77		4.60	0.624	61.7(0.4)
		8.46		5.54	0.600	67.7(0.3)
		10.75		6.77	0.574	72.8(0.3)
		14.48		8.66	0.542	78.8(0.5)
		21.45		12.01	0.498	87.8(0.6)

Table 2. Kinetic and thermodynamic parameters for reaction (2) at +10 °C, with standard deviations in parantheses

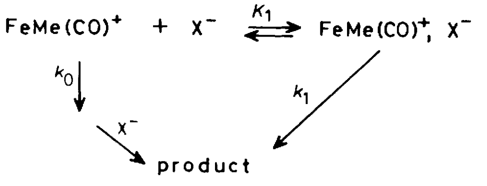
Solvent	ε (10 °C)	Halide source	$10^{-2}K_A$	$10^{-2}K_1$ [a]	$10^3k_0(\sigma)$ [a]	$10^3k_1(\sigma)$ [a]
			dm^3 mol^{-1}		s^{-1}	
CH_2Cl_2	9.49 [b]	NBu_4I	549 [c]	113(3) 115(6) [e]	1.01 [d] 1.01 [d,e]	22.8(0.4) 26.9(1) [e]
Acetone	22.22 [f]	NBu_4I	1.43 [g]	0.86(0.1) 0.77(0.4) [e]	1.73(0.1) 1.39(0.2) [e]	17.5(1) 34.1(5) [e]
Acetone–water (80:20)	31.85 [h]	NBu_4I	0.420 [c]	0.76(1.2) 0.80(1.8) [e]	1.80(0.07) 1.79(0.09) [e]	2.94(3.5) 3.4(5) [e]
Acetone–water (60:40)	45.00 [h]	NBu_4I	0.173 [c]	0.75(4) 0.56(5) [e]	1.65 [i] 1.65 [e,i]	1.9(10) 1.9(9) [e]
Acetone	22.22 [f]	LiI	1.45 [j]	0.77(0.05) 0.50(0.02) [e]	1.86(0.05) 1.57(0.09) [e]	19.4(0.6) 50.7(3) [e]
		NBu_4Br	2.64 [g]	1.87(0.08) 1.70(0.2) [e]	5.18(0.5) 2.2(1) [e]	148(3) 257(11) [e]

[a] Parameters (K_1, k_0, k_1) extracted from an iterative, non-linear least-squares fit[22] of the equation $k_{obs.} = \{2K_Ak_0 + k_1K_1[(1 + 4K_Ac_{MX})^{\frac{1}{2}} - 1]\}/\{2K_A + K_1[(1 + 4K_Ac_{MX})^{\frac{1}{2}} - 1)]\}$, where K_A = association constant for halide source; K_1 = association constant for FeMe,X; c_{MX} = total halide concentration. [b] $\varepsilon = (3\,320/T) - 2.24$ (CRC Handbook of Chemistry and Physics, 64th edn., CRC Press Inc., West Palm Beach, 1984). [c] Calculated from the data of ref. 30; $\log K_A = 0.300\,86 + 1.192 \times 10^4 T\varepsilon$. [d] Obtained from a two parameter (K_1, k_1) fit of the expression in footnote *a* with a k_0 value extrapolated from the data of Jablonski and Wang.[11] [e] Corrected for salt effects, see text. [f] Extrapolated from 25 °C data (see ref. in footnote *b*); $d\varepsilon/dT = 0.205 \times 10^{-2}$. [g] Taken from the 25 °C data of Kay and co-workers.[26] [h] From the data of (G. Akerhoef, *J. Am. Chem. Soc.*, 1932, **54**, 4125); 80:20, $\ln \varepsilon = 4.851\,4 - 4.913T$; 60:40, $\ln \varepsilon = 5.190\,7 - 4.890T$. [i] Obtained from a two parameter (K_1, k_1) fit of the equation in footnote *a* with a k_0 value extrapolated from a linear fit of the c_{MX} *vs.* $k_{obs.}$ data. [j] Taken from the data of Savedoff.[25]

expression $A_t = A_\infty[1 - \exp(-kt)] + B$ (*cf.* Experimental section). Figure 1(*a*) and (*b*) show a typical optical density *versus* time profile and the accompanying error plot.

Effect of X^- *Concentration on* $k_{obs.}$.—Plots of the pseudo-first-order rate constants, $k_{obs.}$ *vs.* the total analytical concentration (c_{MX}) of added halide source MX (M = NBu_4 or Li), showed distinct non-zero intercepts and tended to reach a limiting value at high c_{MX} (*cf.* Figure 2).

The qualitative nature of the $k_{obs.}$ *vs.* halide concentration plots, combined with the charge type of the substrates and the known propensity of the NBu_4X halide sources to aggregate in low dielectric organic media,[23–26] suggested a reaction mechanism involving a concurrent halide independent channel (k_0) and a halide dependent channel (k_1) which forms a reactive ion pair[27,28] in a pre-equilibrium step. A generalized mechanism which leads to saturation kinetics under the conditions of the present study (*cf.* following discussion) is shown schematically in Scheme 2.



Scheme 2.

The thermodynamic equilibrium ion-association constant for the formation of the ion paired substrate (FeMe,X) is given by equation (3) which omits the activity coefficients of electrically neutral species.

$$K_1 = [\mathrm{FeMe,X}]/[\mathrm{FeMe}^+][\mathrm{X}^-](f_{\mathrm{FeMe}^+})(f_{\mathrm{X}^-}) \qquad (3)$$

Substitution of [FeMe,X], derived from expression (3), into the transition state theory rate expression (4), derived from Scheme 2,[29] yields equation (5) after the assumption of equivalent activities for species of identical charge type ($f_{\mathrm{FeMe}^+} = f_{\mathrm{FeMe}^{+*}}$ and $f_{\mathrm{FeMe,X}} = f_{\mathrm{FeMe,X}^*}$, where * refers to the transition state).

$$\mathrm{Rate} = k_0[\mathrm{FeMe}^+](f_{\mathrm{FeMe}^+})/(f_{\mathrm{FeMe}^{+*}}) + k_1[\mathrm{FeMe,X}](f_{\mathrm{FeMe,X}})/(f_{\mathrm{FeMe,X}^*}) \qquad (4)$$

$$\mathrm{Rate} = [\mathrm{FeMe}^+]\{k_0 + k_1K_1[\mathrm{X}^-](f_{\mathrm{FeMe}^+})(f_{\mathrm{X}^-})\} \qquad (5)$$

Equation (5) shows that the rate of reaction (2) is subject to salt effects *via* the ion association equilibrium defined by K_1. Recasting (5) into a more convenient form, using the degree of dissociation of FeMe,X ($\alpha_{\mathrm{FeMe,X}} = [\mathrm{FeMe}^+]/c_{\mathrm{Fe}}$) and equations (6), yields the rate in terms of the total iron substrate concentration, c_{Fe} [*cf.* equations (7) and (8)].

$$[\mathrm{FeMe}^+] = \alpha_{\mathrm{FeMe,X}}c_{\mathrm{Fe}} \qquad (6a)$$

$$[\mathrm{FeMe,X}] = c_{\mathrm{Fe}}(1 - \alpha_{\mathrm{FeMe,X}}) \qquad (6b)$$

$$\mathrm{Rate} = c_{\mathrm{Fe}}\alpha_{\mathrm{FeMe,X}}\{k_0 + k_1K_1[\mathrm{X}^-](f_{\mathrm{FeMe}^+})(f_{\mathrm{X}^-})\} \qquad (7)$$

$$k_{\mathrm{obs.}} = \{k_0 + k_1K_1[\mathrm{X}^-](f_{\mathrm{FeMe}^+})(f_{\mathrm{X}^-})\}/\{1 + K_1[\mathrm{X}^-](f_{\mathrm{FeMe}^+})(f_{\mathrm{X}^-})\} \qquad (8)$$

The ion association constant, K_A, for the halide source is expressed in terms of the degree of dissociation ($\alpha_{\mathrm{MX}} = [\mathrm{X}^-]/c_{\mathrm{MX}}$) and the total analytical halide concentration, c_{MX}, by equation (9), which is derived assuming all the free halide originates from MX which is always present in large excess.

$$K_\mathrm{A} = (1 - \alpha_{\mathrm{MX}})/[c_{\mathrm{MX}}\alpha_{\mathrm{MX}}^2(f_{\mathrm{M}^+})(f_{\mathrm{X}^-})] \qquad (9)$$

Solving (9) for $c_{\mathrm{MX}}\alpha_{\mathrm{MX}} = [\mathrm{X}^-]$ and substituting into equation (8) gives an expression [*cf.* equation (10)] for the observed pseudo-first-order rate constants, $k_{\mathrm{obs.}}$, obtained when $c_{\mathrm{MX}} \gg c_{\mathrm{Fe}}$.[†] Values for the association constant of the halide source, K_A, were taken from the literature or determined from log K_A *vs.* reciprocal solvent dielectric constant plots using the data of Hirsch and Fuoss.[30] These were generally found to be more reliable than values calculated from extended Debye–Huckel and related theories.[31,32] The latter method, which can be very sensitive to the 'distance of closest approach', *a*, was found to underestimate K_A in very low dielectric media.[‡]

$$k_{\mathrm{obs.}} = \{2K_\mathrm{A}k_0 + k_1K_1[(1 + 4K_\mathrm{A}c_{\mathrm{MX}}f_\pm{}^2)^{\frac{1}{2}} - 1]\}/\{2K_\mathrm{A} + K_1[(1 + 4K_\mathrm{A}c_{\mathrm{MX}}f_\pm{}^2)^{\frac{1}{2}} - 1]\} \qquad (10)$$

As a first approximation, salt effects were neglected in the data analysis. The dependence of $k_{\mathrm{obs.}}$ on added halide concentration was fitted to equation (10) using the Wentworth[22] method with k_0, k_1K_1, and K_1 as parameters and activity coefficients set to unity. In several cases difficulties arising from the limited experimentally accessible concentration range, coupled with insufficient curvature, resulted in ill defined values of k_0 and K_1 or complete convergence failure. In such cases the $k_{\mathrm{obs.}}$ *vs.* added halide concentration data were analyzed according to equation (10) using a two-parameter (k_1K_1, K_1) Wentworth fit with the value of k_0 introduced as a constant estimated from the literature.[11]

In most cases the variation in c_{MX} was sufficiently large as to give an order of magnitude change in the ionic strength. An attempt was therefore made to correct[§] for the attendant salt effects by calculating for ionic activity coefficients and free halide concentrations and fitting $k_{\mathrm{obs.}}$ obtained from equation (8) with $[\mathrm{X}^-](f_{\mathrm{FeMe}^+})(f_{\mathrm{X}^-})$ as the independent variable. Activity coefficients[¶] where estimated from extended Debye–Huckel theory using the method of successive approximations.[32,35] The activity coefficients and free halide concentrations used in the data analysis are presented in Table 1. Inspection of the parameters in Table 2 determined for both methods of analysis shows that in general the corrections for salt effects produced only minor changes in the relevant extracted parameters.

Effect of Solvent.—Changing the solvent exhibited a strong effect on the curvature but a less significant effect on the intercept and limiting of the $k_{\mathrm{obs.}}$ *vs.* c_{MX} plots for $\mathrm{NBu_4I}$ as halide source. Although limited somewhat by decreased solubility in aqueous acetone, increasing the solvent dielectric constant along the solvent series methylene chloride < acetone < 80:20 (wt.%) acetone–water < 60:40 (wt.%) acetone–water resulted in a marked decrease in curvature (*cf.* Figure 2).

Table 3 compares values of the ion association constant, K_1, determined from the kinetic data of this study with those projected using the Yokoyama–Yamatera equation.[31] Allowing for the fact that the Yokoyama–Yamatera expression omits

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[†] Positive roots for $(1 + 4K_\mathrm{A}c_{\mathrm{MX}}f_\pm{}^2)$ were selected and activities for ions of identical charge were taken as equivalent. The individual ion activity coefficients are replaced by the mean ionic activity coefficient, $f_\pm{}^2 = (f_{\mathrm{FeMe}^+})(f_{\mathrm{X}^-})$.

[‡] The association constant for $\mathrm{NBu_4I}$, using $a = 6.31$ Å,[30] was estimated as 54 900 l mol^{-1} from the data of Hirsch and Fuoss[30] but was calculated as 7 324 l mol^{-1} using the Yamatera equation[31] with the same value of *a*. The former is in accord with conductometric values reported for related $\mathrm{NBu_4}^+$ salts measured in low dielectric solvents.[33]

[§] Attempts to conduct experiments at 'constant ionic strength' using $\mathrm{LiClO_4}$ introduced complications due to extensive ion pairing with the added salt. Owing to the possibility of extensive specific ion–ion interactions in low dielectric media, the validity of adding background electrolytes to maintain constant high ionic strength is questionable, see ref. 34.

[¶] $(f_{\mathrm{MeMe}^+})(f_{\mathrm{X}^-})$ was approximated as $f_\pm{}^2$ with the *a* value equivalent to that of the MX salt used.[30]

Table 3. Comparison of K_1 values ($dm^3\ mol^{-1}$) for $FeMe(CO)^+ + X^- \rightleftharpoons FeMe(CO),X$

Solvent	X^-	$10^{-2}K_1$[a]	$10^{-2}K_1$ (calc.)[b]
CH_2Cl_2	I^c	114 (5)	128
Acetone	I^c	0.81 (0.4)	0.72
	I^d	0.64 (0.03)	0.72
	Br^e	1.78 (0.1)	0.77
Acetone–water (80:20)	I^c	0.78 (0.9)	0.15
Acetone–water (60:40)	I^c	0.65 (3)	0.04

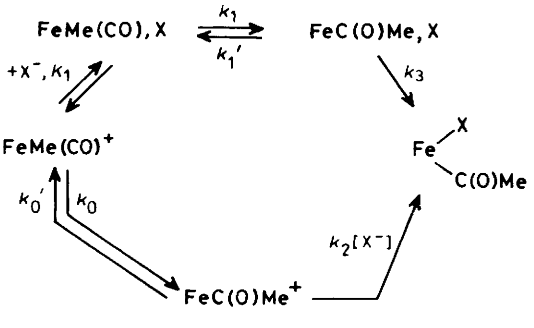
[a] Mean value of Table 2; standard deviations in parentheses. [b] Calculated[31] with $a_{FeMe,I} = 5.7$ *A* and $a_{FeMe,Br} = 5.5$ *A* estimated from crystallographic radii (C. R. Jablonski and N. J. Taylor, *Inorg. Chim. Acta*, 1985, **96**, L17). [c] Halide source NBu_4I. [d] Halide source LiI. [e] Halide source NBu_4Br.

ion–dipole interactions between electrically unsymmetrical ions and that crystallographic radii are used in the calculation, the agreement found is reasonable and supports the kinetic analysis according to Scheme 2. As expected on the basis of charge considerations, the ion association constants, K_1, decrease with increasing solvent dielectric constant, and increase with decreasing anion radius.

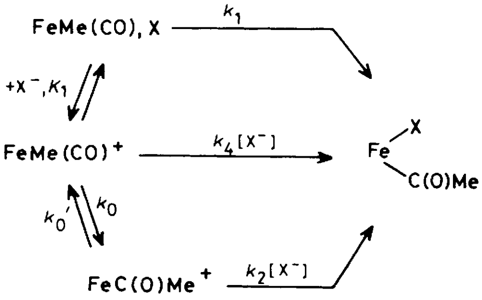
Values of the halide-independent rate constant, k_0, determined from three parameter fits of iodide data to equation (10) in different solvents compare favourably with each other and with the literature values of the unimolecular rate constants determined from reaction of (3) with neutral promoting bases.[11] In contrast, considerable variation of k_1 occurs on changing from non-aqueous media.

Effect of Halide Source.—The kinetics of the insertion reaction (2) were examined with NBu_4I, NBu_4Br, and LiI as halide sources in acetone solvent (*cf.* Table 2). Plots of $k_{obs.}$ *vs.* c_{MX} were in each case qualitatively the same. No significant differences in K_1, k_0, k_1 were apparent regardless of the source of iodide. The value of k_1 determined for bromide (NBu_4Br as halide source) was, however, significantly larger than the corresponding value obtained using iodide (NBu_4I as halide source).

Mechanism.—The observed rate law (10) derived from Scheme 2 can be accounted for more specifically in terms of the mechanisms shown in Schemes 3 and 4. Scheme 3 leads to the observed $k_{obs.}$ expression (10) following the assumptions that (*i*) the steady-state approximation applies to the reactive intermediates $FeC(O)Me^+$ and $FeC(O)Me,X$, (*ii*) $k_2[X^-] \gg k_0'$, and (*iii*) $k_3 \gg k_1'$. Similar assumptions apply for Scheme 4. The k_0 channel of both Schemes represents a unimolecular insertion of the free ion, $FeMe^+$. The relative insensitivity of this parameter to solvent and halide as well as the agreement with k_0 values of 1.01×10^{-3} and 1.58×10^{-3} s^{-1} in methylene chloride and acetone respectively, extrapolated from an earlier kinetic study[11] of the same reaction with neutral promoters, support this hypothesis. The k_1 channel of Scheme 3 is essentially a unimolecular insertion of the ion-paired species FeMe(CO),X.



Scheme 3.



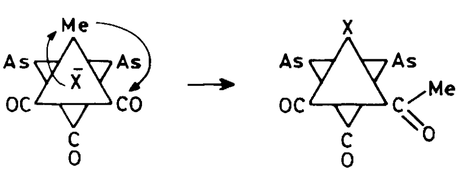
Scheme 4.

Scheme 4 differs in that there is significant associative character (*i.e.* bond making between $FeMe^+$ and X^-) assumed as the analogous ion-paired species approaches the transition state leading to the product. In the absence of any associative interactions k_0 and k_1 might be expected to be approximately equal. Thus it might be argued that the apparent increased rate of product formation *via* the ion-pair route (k_1/k_0 = *ca.* 20—30) in methylene chloride or acetone solvent is, in itself, evidence for the importance of bond making between X^- and Fe. However, the effect could be attributed to changes in ground and transition-state solvation for the two concurrent paths of Scheme 3.[35] More convincing support for an associative activation of the k_1 reaction channel follows from the NBu_4Br data. In this case the significant increase in the k_1/k_0 ratio (*ca.* 150) can be attributed to the increased nucleophilicity of bromide compared to iodide established in acetone media.[23] Finally, the observed decrease in the calculated values of k_1 for NBu_4I in acetone on addition of water is also in accord with associative activation. Although the effect is smaller for iodide than for the corresponding bromide or chloride salts, it has been established that the free energy of transfer of dissociated or ion-paired tetra-alkylammonium iodides from the aprotic dipolar solvent acetone to water is generally negative[36] (−3.7 kcal mol^{-1} for dissociated $NEt_4^+\ I^-$; −1.8 kcal mol^{-1} for ion paired NEt_4^+,I^-) due, at least in part, to increased anion solvation in the hydrogen-bonding solvent.[37] Tighter halide-ion solvation can reasonably be expected to correlate with decreased nucleophilicity and hence smaller k_1 values.[38] The order of nucleophilicities in aqueous media has in fact been determined to be $I^- > Br^- > Cl^-$.[39]

We add here that the form of the $k_{obs.}$ expression (3) permits an *additional* bimolecular route involving direct attack of X^- on the free ionic substrate $FeMe^+$ in Schemes 3 and 4. In such an event k_1 becomes an inseparable rate constant composite. The direct bimolecular attack is shown schematically as k_4 for the essentially associative Scheme 4 but is omitted for the unimolecular Scheme 3.

Stereochemistry.—Previously[17] we reported that the acyl product isomer distribution obtained from equation (2) was, unlike the reaction of (3) with uncharged Lewis bases,[40] quite strongly dependent on solvent. Changing solvent along the series methanol, acetone, methylene chloride resulted in a steady increase in the relative proportion of an all *cis* acyl product.† Although complicated by problems relating to crystal disorder, a preliminary single-crystal *X*-ray structure[41] of the acyl obtained as the major product in methylene chloride at 0 °C[40] or from the oxidative addition of methyl iodide to [Fe(pdma)(CO)$_3$][17,‡] in the same solvent, unequivocally established (**4b**), with iodide *cis* to both arsenic atoms, as the correct geometry.

Consideration of the mechanisms represented in Schemes 3 and 4 offers an interpretation of the stereochemical results in terms of a regiospecific site preference for ion-pair formation.[43] We propose that the stereochemical outcome of insertion by the k_0 (unimolecular) route and by the k_1 (ion pair) route is different. The former produces predominantly *trans* X–Fe–C(O)Me geometry (**4a**) consistent with the formation of a relatively long lived intermediate and a demonstrably strong *trans* directing effect of acyl.[17] The latter produces predominantly *cis* X–Fe–C(O)Me as a result of the distinctly anisotropic cation (**3**) which presents the halide ion with octahedral faces of different steric and electronic repulsions. If we assume that an energy minimum for the ion-paired species FeMe,X is reached on closest cation/anion approach consistent with steric and electronic factors, it is reasonable to expect that the anion will preferentially reside opposite the pdma group in (**3**). Scheme 5 shows the stereochemical result of a methyl migration in an ion-paired species with iodide positioned on the octahedral face defined by the ligands Me–CO–CO. Whether or not associative interactions are important, it follows that a least motion attack of halide on methyl migration will favour the all *cis* isomer (**4b**). Further, the relative proportion of (**4b**) formed will be related to the extent and 'tightness' of ion-pairing. Thus, in high dielectric media where the majority of reaction occurs *via* the free cation FeMe$^+$, the stereochemistry closely resembles that obtained for neutral promoting ligands.[40] Positioning of X$^-$ on the octahedral face determined by CO–CO–CO, although favourable in terms of closest approach distance, suffers from unfavourable electrostatic interaction with three negative oxygen dipoles and incurs problems with the principle of least motion unless a CO migration is assumed.



(**4b**)

Scheme 5.

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† An assignment error leading to an incorrect kinetic product distribution exists in Table 4 of our earlier paper.[17] These experiments have been repeated under more carefully controlled conditions using LiI as halide source. The correct kinetic product ratio (**4b**)/(**4a**) for reaction (2) is solvent dependent {at 263 K, [(**3**)] = 1 × 10^{-2} mmol cm^{-3}, [LiI] = 7.7 × 10^{-2} mmol cm^{-3}, (**4b**)/(**4a**) was determined to be: 2.3 (acetone), 0.30 (80:20 acetone–water), 0.16 (60:40 acetone–water)} and, to a lesser extent, [X$^-$] dependent {at 263 K, [(**3**)] = 2.6 × 10^{-2} mmol cm^{-3}, 60:40 acetone–water, (**4b**)/(**4a**) was determined to be: 0.16 ([LiI] = 7.7 × 10^{-2} mmol cm^{-3}), 0.24 (1.94 × 10^{-1} mmol cm^{-3}), 0.29 (3.9 × 10^{-1} mmol cm^{-3}), and 0.30 (7.8 × 10^{-1} mmol cm^{-3})}.

‡ The oxidation addition of methyl iodide to [M(PMe$_3$)$_2$(CO)$_3$] (M = Fe or Ru) proceeds stereospecifically in neat methyl iodide, see ref. 42.