A Kinetic Study of the Lewis Base Promoted Migratory Insertion Reaction of *fac*-[(diars)Fe(CO)₃CH₃]⁺. Direct Observation of a Solvent Coordinated Intermediate

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A kinetic study of the trimethylphosphite promoted migratory carbonyl insertion of fac-[(diars)Fe(CO)₃Me]⁺ to give [(diars)Fe(CO)₂(C(O)-Me)(P(OMe)₃)]⁺ establishes that the insertion rate is first order in Fe–Me substrate and zero order in phosphite in a number of solvents. The rate law is consistent with a rate determining unimolecular insertion producing an acyl intermediate which is rapidly scavenged by phosphite. The pseudo first order rate constant, k_{obs}, is remarkably insensitive to both polarity and coordinating ability of a variety of solvents (methanol, methylene chloride, nitromethane, acetone and acetonitrile). A significant rate acceleration is observed in dimethylformamide. In acetonitrile, insertion proceeds in the absence of added trimethylphosphite to give an isolable solvent coordinated acyl, however k_{obs} is not measurably increased. Specific solvent assistance of migratory carbonyl insertion appears to be relatively unimportant for the Fe(II) case examined.

Introduction

Kinetic studies of Lewis base promoted migratory carbonyl insertion reactions on d^6 transition metal substrates are in accord with the mechanism presented in Scheme I [1–3].
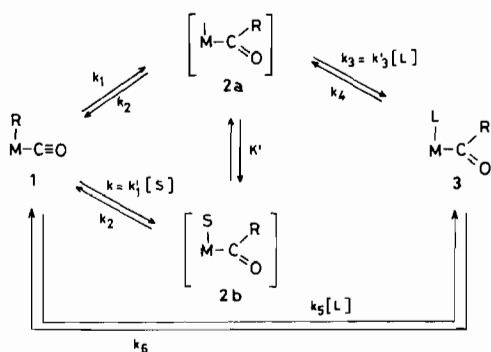
Scheme I

In nonpolar media a relatively slow second order rate law is obtained [4a, c, d, g, i] (Rate = $k_5[1][L]$) implying an apparent bimolecular reaction with the promoting base L to give the acyl product *3* directly. In most cases [4a, c, d, g, h, i] a concurrent unimolecular reaction (k_1) also occurs producing an intermediate *2a* which is rapidly scavenged by L. In more polar media the bimolecular route (k_5) is apparently suppressed [4a]. Insertion rates are then either independent of [L] [4c, d, g, h] or, given a sufficiently wide concentration range, approach a limiting value at high [L] [4b, c, d, e, f]. Collectively the kinetic results in polar media support the assumption of a rate determining formation of an intermediate *2* which either returns to reactant or is captured by L to give product ·(Scheme I). The extent of competition for the intermediate, given by the ratio $k_3'[L]/k_2$ determines the form of the rate law [1]. Intermediate *2* may arise from two kinetically indistinguishable paths: (i) via a unimolecular (k_1) path giving *2a* or (ii) via an associative (bimolecular) ($k_1 = k_1'[S]$) path where solvent, S, functions in a nucleophilic sense.

Several five coordinate Rh(III) acyls (serving as models for *2a*), have, in fact, been isolated and determined to be approximately square pyramidal with apical acyl [5]. Other examples of d^6 systems less prone toward five coordination appear to require an η^2 acyl bonding mode in order to maintain the coordination sphere [6].

'Solvent assistance' [1], wherein the rate of migratory carbonyl insertion increases with the polarity of the solvent, has been observed in a number of cases [4a, b, c, d, g, h]. It is not surprising, in light of the discussion above concerning the nature of the kinetically implicated intermediate (*2a, 2b*), that considerable discussion surrounds the actual mechanistic role of solvent in such reactions [1–4]. Evidence favouring direct nucleophilic participation (specific solvent interaction) which presumes the formation of a solvent coordinated intermediate *2b* derives primarily from qualitative results [7], observation of relatively large negative $\Delta S^{\ddagger}$ values [1] and correlations of rate with various

measures of solvent coordinating ability [1, 4a, c, d, e, g, h]. Other workers [4b, f, 8a] attribute solvent acceleration to nonspecific solvation effects related to general solvent polarity parameters and suggest that a coordinatively unsaturated intermediate is formed even in cases where a solvent coordinated acyl product can be detected [8].

A further complication stems from the observation that increasing solvent polarity or coordinating ability does not guarantee an increase in the rate of migratory carbonyl insertion. A case in point is the *deceleration* of the measured insertion rate [9] for the Ir(III) complex *4* on changing solvent from 1,2-dichloroethane to tetrahydrofuran.

$$[Ir(CO)_2Cl_2Et(AsPh_3)] + AsPh_3 \rightarrow$$
$$\boldsymbol{4}$$

$$[Ir(CO)(C(O)Et)Cl_2(AsPh_3)_2] \qquad (1)$$
$$\boldsymbol{5}$$
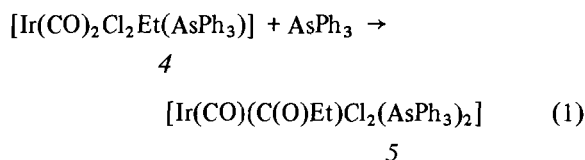
Clearly the origin of 'solvent assistance' of migratory carbonyl insertion remains controversial and there is a need to establish further examples in order to define the effect in more detail. In this paper we describe the results of a kinetic study of the trimethylphosphite promoted migratory carbonyl insertion of fac-[(diars)Fe(CO)$_3$Me]$^+$, [10] *6*, which proceeds to completion without complications to give a single *cis,trans* acyl complex, *7* [11], in a number of solvents of varying polarity and coordination ability.

$$\boldsymbol{6} \qquad\qquad \boldsymbol{7}$$
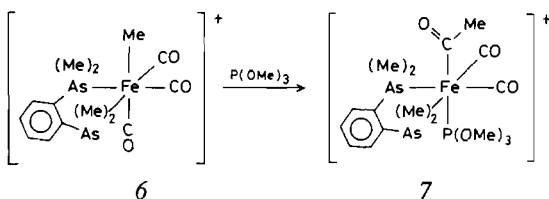
Results and Discussion

Excellent fits of nmr derived concentration time data (*cf.* Figs. 1 and 2) to the first order expression $[A]_t = [A]_0 \exp(-kt)$ ($[A]_t$ = concentration of *6* at time t; $[A]_0$ = initial concentration of *6*) indicate that the disappearance of fac-[(diars)Fe(CO)$_3$Me]$^+$-BF$_4^-$, *6*, on reaction with a large excess of P(OMe)$_3$ according to equation (2) is a clean first order process. Table I shows that the observed first order rate constants, k_{obs}, are independent of phosphite concentration over a fairly wide range thus establishing an overall first order rate law (Rate = $-d[6]/dt$ = $k[6]$). Careful examination of the ^{1}H nmr acyl region during the course of insertion failed to detect the presence of appreciable concentrations of any intermediate species. Spectroscopic (^{1}H nmr and ir)

examination of t = ∞ solutions indicate that the reaction is essentially complete.

The observed rate law is consistent with the insertion mechanism of Scheme I providing we assume that k$_4$ and the direct second order route (k$_5$) can be neglected and that k$_3'$[L] ≫ k$_2$. Application of the usual steady state assumptions for the intermediate [1] gives eqn. (3) which reduces to k_{obs} = k$_1$ under the restrictions described above.

$$k_{obs} = \frac{k_1 k_3'[L]}{k_2 + k_3'[L]} \qquad (3)$$

Trimethylphosphite appears to be a particularly good scavenger for the proposed intermediate of Scheme I and k_{obs} will thus provide a direct estimate of the insertion rate, k$_1$, uncomplicated by a parallel 2nd order route or by significant return to the reactant even at relatively low concentrations of added P(OMe)$_3$.

Solutions of *6* in acetonitrile were found to undergo a slow insertion reaction with the concomitant formation of a bright yellow colour even in the absence of added trimethylphosphite. Although solutions of *6* in dimethylformamide, dimethylsulfoxide or methanol also develop a similar yellow colour, no acyl products could be detected in the ^{1}H nmr spectrum of solutions equilibrated for several hours at 273 K.

Two isomeric acyl products were observed in acetonitrile. ^{1}H nmr spectra showed characteristic acyl absorptions at 2.34 and 2.84 ppm (*cf.* Fig. 3) identifying the *cis,trans*, *8*, and *cis,cis* isomers, *9a* or *9b*, respectively. Stereochemical assignments are based on correlation of ^{1}H nmr chemical shifts of related compounds [10, 11] in conjunction with

$$\boldsymbol{8} \qquad\qquad \boldsymbol{9a} \qquad\qquad \boldsymbol{9b}$$
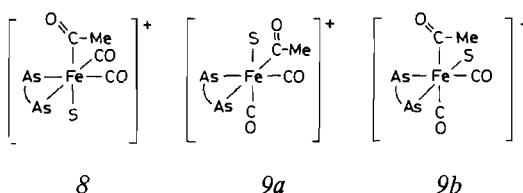
the presence of two magnetically nonequivalent arsenic methyl signals (1.81, 1.65 ppm) for *8* and four magnetically nonequivalent arsenic methyl signals (1.86, 1.75, 1.74, 173 ppm) for *9a* or *9b*.

Conversion to the acyls *8* and *9* was incomplete in acetonitrile even after equilibration for extended periods of time indicating the establishment of a dynamic equilibrium. Equilibrium constants (K = ([*8*] + [*9*])/[*6*], *cf.* Table II) were determined by integration of ^{1}H spectra. The temperature dependence of K reveals an exothermic reaction (ΔH = −20.0 kJ mol^{-1}, ΔS = −52 J K^{-1} mol^{-1}) and conversion to the acyl was >96% only after extended reaction (several weeks) at low temperature (256 K).

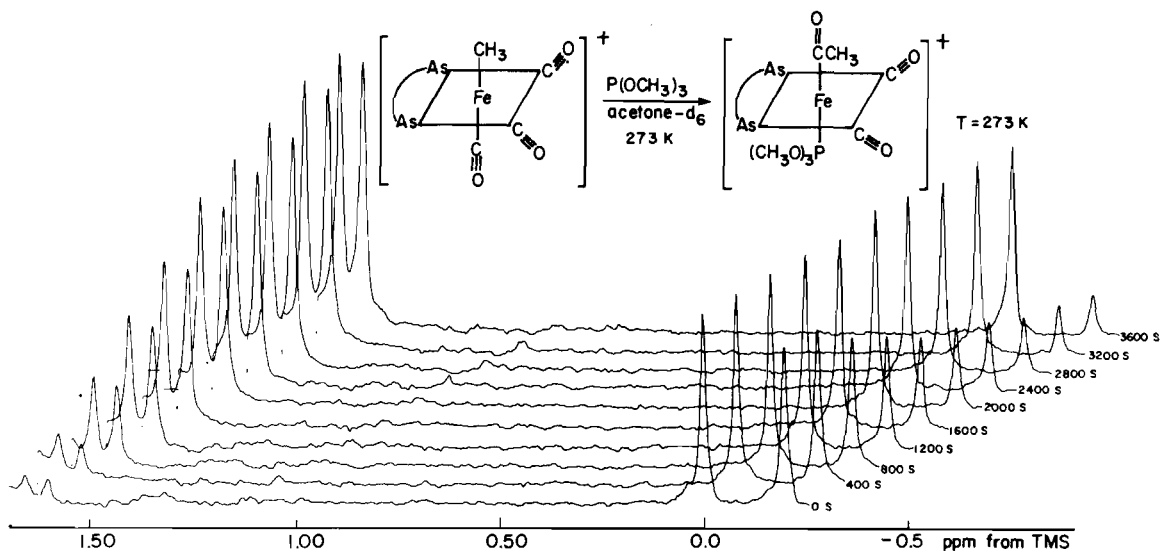Fig. 1. Sequential 80 MHz ^{1}H nmr spectrum of fac-[(diars)Fe(CO)$_3$Me]$^+$BF$_4$$^-$ in the presence of excess P(OMe)$_3$ in acetone-d$_6$.
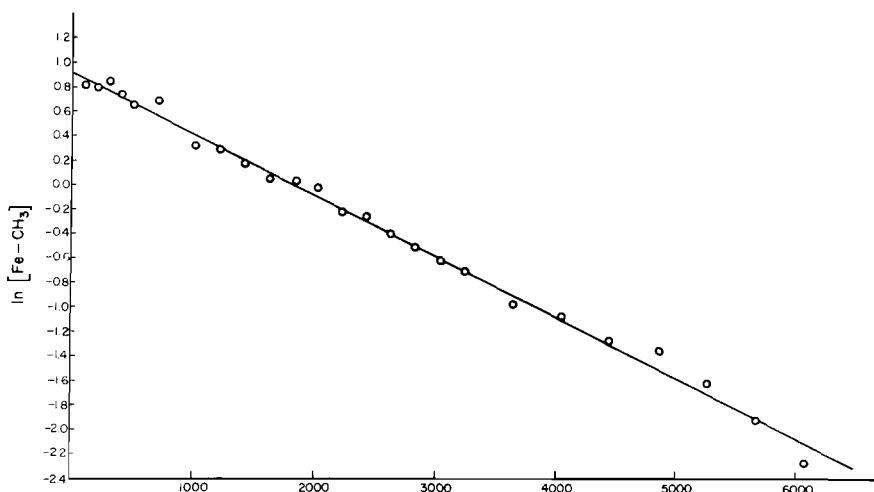

Fig. 2. Typical pseudo first order plot for the reaction 6 → 7 in acetone-d$_6$ at 273 K.

Addition of ether to solutions of *6* equilibrated in acetonitrile at 256 K precipitated an off white solid which showed infrared absorptions at 2260 cm^{-1}(w) and 1626 cm^{-1}(s) assigned to coordinated acetonitrile [12] and ν_{CO}(acyl) respectively [10, 11]. Additional bands at 2097(s), 2030(s) and 1983(s) cm^{-1} (ν_{CO}) as well as 1453, 1290, 770, 620, 585, 523, 441, 370 and 278 cm^{-1} characteristic of coordinated diars [10] were also observed. The isolated solid acyl (*8 + 9*) readily dissociates acetonitrile at room temperature *in vacuo* or merely by evaporation of the solution in a nitrogen stream to give back the methyl complex *6*.

The approach to equilibrium was monitored by following the decrease in intensity of the ^{1}H nmr signal assigned to the Fe–Me group of *6*. Good fits to the integrated rate expression (A − A$_\infty$) = KA$_\infty$exp(Qt), derived from Scheme I assuming a steady state concentration for the intermediate *2* and neglecting the direct reaction (k$_5$), were obtained (*cf.* Table II and experimental). A simple

reversible first order reaction $1\underset{k_2}{\overset{k_1''}{\rightleftarrows}} 3$, leads to a

rate expression of identical form (K = k$_1''$/k$_2''$, Q = −(k$_1''$ + k$_2''$)) however, since the phosphite

TABLE I. Pseudo First Order Rate Constants (k_{obs}) for Eqn. (2).

Solvent	Temp. (K ± 0.3)	[P(OMe)$_3$][a] mol dm^{-3}	k_{obs} ($\times 10^4$ (σ))[b]	Activation Parameters[c]	
				$\Delta H^{\ddagger}$ (kJ mol^{-1} (σ))	$\Delta S^{\ddagger}$ (JK^{-1} mol^{-1} (σ))
methylene chloride	252.3	0.458	0.133(0.003)	81.3(1.3)	−15(5)
	272.9	0.218	2.75(0.08)		
	272.9	0.303	2.63(0.05)[d]		
	272.9	0.607	2.91(0.06)		
	272.9	0.830	2.48(0.09)[d]		
	272.9	1.23	2.47(0.08)[d]		
	272.9	1.64	2.62(0.06)[d]		
	272.9	2.32	2.80(0.09)[d]		
	293.4	0.458	35.2(0.5)		
methanol	273.0	0.150	2.29(0.03)		
	273.0	0.290	2.32(0.03)		
	273.0	0.520	2.21(0.03)		
acetonitrile	252.0	0.458	0.271(0.008)	78.8(1.2)	−19(4.5)
	273.0	0.458	5.20(0.1)		
	293.0	0.458	65.6(4)[d]		
acetone	253.0	0.758	0.256(0.01)	82.9(1.4)	−4(5)
	273.0	0.106	3.66(0.2)[d]		
	273.0	0.304	4.15(0.1)		
	273.0	0.419	3.93(0.1)		
	273.0	0.508	4.14(0.1)[d]		
	273.0	0.630	3.96(0.1)		
	273.0	0.758	4.19(0.2)		
	293.0	0.758	64.7(5)		
nitromethane	253.6	0.459	0.164(0.01)	82.3(1.5)	−11(6)
	273.8	0.459	3.14(0.07)		
	289.1	0.459	22.5(0.4)		
dimethylformamide	243.8	0.459	0.336(0.008)	74.9(1.7)	−21(7)
	258.7	0.459	5.09(0.8)		
	268.9	0.459	10.9(0.1)		

[a]P(OMe)$_3$ present in at least 10 fold excess.   [b]Obtained using Wentworth algorithm, *cf.* experimental and ref. 23, σ = standard error.   [c]Best fit of Eyring equation using Wentworth algorithm, *cf.* ref. 23, σ = standard error.   [d]Average of duplicate runs.

promoted insertions were zero order in P(OMe)$_3$, Scheme I and the presence of an intermediate may be safely assumed [13].

Values of Q and K obtained in acetonitrile in conjunction with k_1 values measured in the same solvent in the presence of excess trimethylphosphite allow calculation of k_3'/k_2 ratios for L = acetonitrile (*cf.* Scheme I). The k_3'/k_2 values (*cf.* Table II), which indicate the ratio of intermediate proceeding to product and returning to reactant, are quite small (<1) but nevertheless establish the ability of acetonitrile to function as an effective nucleophile with respect to Fe(II) in the compounds under consideration [4b, d].

Table III shows the dependence of the pseudo first order rate constant for trimethylphosphite promoted insertion (k_{obs}) on solvent. Unlike carbonyl

insertion for the related d^6 MeMn(CO)$_5$ [4a, f, h], changes in bulk solvent dielectric or polarity (Z value [14, 15], E$_T$ [16]) appear to have little effect on k_{obs}. Presumably in the present case the degree of charge separation is not significantly altered as 6 approaches the transition state for carbon monoxide insertion.

Rate acceleration of migratory carbonyl insertion by specific nucleophilic solvent participation prior to the transition state predicts a correlation of k_{obs} with the relative ability of solvent to function as a nucleophile. Table III presents k_{obs} for reaction (2) along with several measures of solvent coordinating ability (donor number (DN) [17] and relative base strength [18]). The detection and isolation of the solvent coordinated acyls 8 and 9 confirms the affinity of acetonitrile for Fe(II) and suggests that
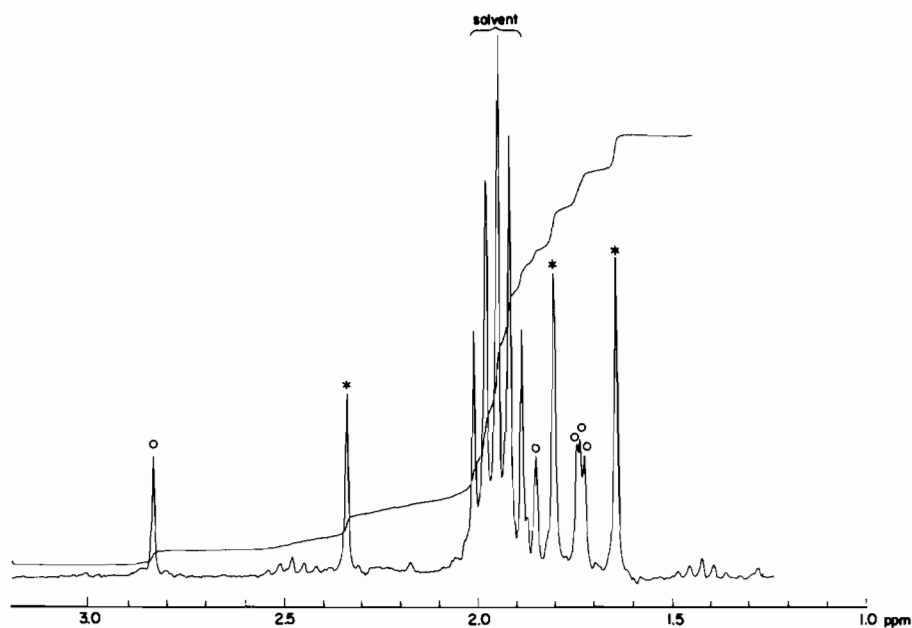
Fig. 3. Partial 80 MHz ^{1}H nmr spectrum of fac-[(diars)Fe(CO)$_3$Me]$^+$ in CD$_3$CN showing >96% conversion to isomeric acyls $8 + 9$. * = *cis,trans* [(diars)Fe(CO)$_2$(C(O)Me)CD$_3$CN]$^+$, 8, ○ = *cis,cis* [(diars)Fe(CO)$_2$(C(O)MeCD$_3$CN]$^+$ $9a$ or $9b$.

TABLE II. Rate and Equilibrium Data for Acetonitrile Promoted Insertion.

T(K)	K( )^a	$-Q \times 10^4$ s$^{-1\,b}$	$k_1 \times 10^4$ s$^{-1\,c}$	k_3/k_2^{d}	k_3'/k_2 mol^{-1} dm$^{3\,e}$
293.0	6.8(8.3)	51.5	60.3	2.9	0.15
272.9	14(18.8)	5.07	5.19	10	0.52
253	25( )^f	_^{f}	—	_^{f}	_^{f}

^{a}K = [(diars)Fe(CO)$_2$Ac(CD$_3$CN$^+$)]/[(diars)Fe(CO)$_3$Me$^+$] determined from ^{1}H nmr spectra of equilibrated samples; value in ( ) calculated as best fit value from the equation (A − A$_\infty$) = KA$_\infty$ exp(Qt), *cf.* experimental. ^{b}Q = −(k$_1$k$_3$ + k$_2$k$_4$)/(k$_2$ + k$_3$), *cf.* experimental and Scheme I. ^{c}Extrapolated from the data in Table I. ^{d}k$_2$/k$_3$ = −(k$_1$(1 + 1/K)/Q + 1); k$_1$, k$_2$, k$_3$ refer to the rate constants in Scheme I. ^{e}k$_3'$ = k$_3$/[CD$_3$CN] = k$_3$/19.09. ^{f}Rate data not obtained.

TABLE III. Solvent Dependence of k$_{obs}$ at 273 K.

Solvent	k$_{obs}$^{a} (relative)	ϵ	Relative coordinating ability		Empirical solvent polarity		Relative acceptor ability^b
			Donor number^b	Rel. base strength^c	Z value^d	E$_T$ value^e	
methanol	0.838	32.6	20.0	0.5	83.6	55.5	41.3
methylene chloride	1.00	9.08	<2(est.)	>5(est.)	64.2	41.1	20.4
nitromethane	1.04	35.9	2.7	—	71.5	46.3	20.5
acetone	1.69	20.7	17.0	~1.9(est.)	65.7	42.2	12.5
acetonitrile	1.94	36.2	14.1	3.5	71.3	46.0	19.3
dimethylformamide	8.15	37	26.6	−2.9	68.5	43.8	16.0

^{a}Calculated relative to methylene chloride (k$_{obs}$ = 2.71 × 10^{-4} s^{-1}) using data extrapolated from Table I. ^{b}DN = −ΔH for B + SbCl$_5$ ⇌ SbCl$_5$·B in 1,2-dichloroethane, *cf.* ref. 17. ^{c}Base strength = ΔG° for B + UO$_2$[(CF$_3$CO)$_2$CH]$_2$·THF ⇌ THF + UO$_2$[(CF$_3$CO)$_2$CH]$_2$·B, *cf.* ref. 18. ^{d}Z = 2.859 × 10^5/λ$_{(max)}$ for charge transfer band of MeO$_2$C —⟨○⟩— Et$^+$I$^-$, *cf.* ref. 14.

^{e}Based on solvatochromic shifts (λ$_{max}$) for charge transfer band of pyridinium phenol betaines, *cf.* ref. 14, 16.

both scales of solvent coordinating ability used in Table III underestimate the position of acetonitrile [19]. Although the solvents examined appear to span a wide range of coordinating ability, changes in k_{obs} are nominal with a spread of less than a factor of two except for dimethylformamide. Cases where nucleophilic solvent participation is proposed generally show rate enhancements of 2–3 orders of magnitude in coordinating vs. noncoordinating media [4a, d]. We conclude that specific nucleophilic solvent participation does not occur for reaction (2).

Values of $\Delta S^{\ddagger}$ for equation (2) lie in the range of -5 to -20 J K^{-1} mol^{-1}, substantially smaller than the range of -71 to -138 J K^{-1} mol^{-1} which appear to accompany specific solvent participation [1]. Significantly, solvent exerts a negligible effect on $\Delta S^{\ddagger}$ for reaction (2) and all the determined values are nearly identical within the (rather large) error limits. A relatively constant and negative $\Delta S^{\ddagger}$ in markedly different media can be ascribed to a similar loss of internal rotational entropy as 6 approaches the transition state of appropriate conformation for methyl migration [10, 11] without benefit of solvent assistance.

The rate acceleration for reaction (2) in dimethylformamide, although enthalphy controlled, is perplexing. We note however that other workers have observed the same phenomenon with both manganese [4a] and molybdenum [4d] substrates. In view of the above discussion significant solvent stabilization of the transition state leading to insertion in the case of dimethylformamide seems unlikely and clues regarding the origin of the effect must be sought elsewhere.

Recent work by Shriver [20] provides experimental proof for the theoretical prediction [21] of Lewis acid catalysis of methyl migration and suggests that a similar role might be played by solvents having appreciable acceptor character. In connection with this point it might be argued that the yellow colour which develops when 6 is dissolved in dimethylformamide derives from a bathochromic shift of metal-to-ligand charge transfer bands in response to excited state stabilization resulting from the donor–acceptor interaction 10. Table III shows,

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   |   /
   |  /
---Fe--- C≡O ----► DMF
  /|
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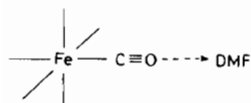
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however, that the acceptor character of dimethylformamide is quite low and thus cannot account for the observed rate enhancement.

The relative insensitivity of the insertion reaction (2) to changes in the coordinating ability of the solvent are in accord with theoretical results [21] which indicate that nucleophilic participation at the metal centre prior to the transition state is destabilizing. In the case of acetonitrile, specific coordination of solvent must occur subsequent to the transition state for insertion and hence does not affect k_{obs}. Migratory carbonyl insertion is thus essentially a unimolecular process and the initial intermediate 2 (cf. Scheme I) is thus unlikely to be specifically solvated. It is probably best regarded as a coordinatively unsaturated η^1-acyl 2a with either square pyramidal or trigonal pyramidal geometry [23]. Although there is ample literature precedence [2, 3, 6] for 'side on' or η^2 acyls which retain an effective 18e$^-$ structure, it is difficult to see how such an intermediate could lead to the stereospecifically trans product formed in reaction (2) [11].

Experimental

Deuterated solvents were dried over activated 4A molecular sieves and transferred to dried, nitrogen filled, serum capped nmr tubes or volumetric flasks using a gas-tight syringe fitted with a 23 cm (24 G) flexible needle. Trimethylphosphite (Strem Chemicals) was distilled from Na before use. The complex fac[(diars)Fe(CO)$_3$Me]$^+$BF$_4^-$ was prepared as described previously [10]. Proton nmr spectra were measured on a Bruker WP-80 spectrometer equipped with a B-VT 1000 temperature controller. Temperature drift, measured by a thermocouple inserted in a dummy sample, was generally $< \pm 0.15$ K, however an appreciable temperature gradient along the long axis of the sample was apparent. Overall temperature reliability was judged to be ca. ± 0.3 K.

Kinetic Measurements

Standard solutions of 6 and of P(OMe)$_3$ were prepared in 1.0 ml volumetric flasks fitted with rubber septum caps. Aliquots were transferred by syringe to a nitrogen filled, septum capped 5 mm nmr tube chilled to -78 °C in a dry ice/acetone bath. Final concentrations were calculated assuming that volumes were additive. The [6] ranged from 0.02 to 0.05 mol dm^{-3} allowing reasonable signal to noise without excessive accumulation. Four to eight transients (8 K) were generally collected at computer determined time intervals. The [P(OMe)$_3$] was held constant in at least a ten-fold excess in all runs. Samples were mixed at low temperature using a Vortex Genie and quickly transferred to the equilibrated nmr probe to start a run. The rate of disappearance of 6 was followed by observing the decrease in intensity of the ^{1}H nmr singlet assigned

to Fe—Me [10] at *ca.* —0.23 ppm. Plots of $\ln(A_t)$ where A_t = normalized intensity (relative to internal TMS standard) of the Fe—Me resonance of *6 vs.* time were linear with no detectable curvature to three half lines (*cf.* Fig. 2). The pseudo first order rate constants, k_{obs}, were extracted from the normalized intensity *vs.* time plots using an iterative weighted non-linear least squares fit of the function $A_t = A_0 \exp(-k_{obs}t)$ based on the Wentworth algorithm [23]. Overall reproducibility for duplicate determinations of k_{obs} was generally *ca.* ±5%. Rate constants for the insertion of *6* in acetonitrile in the absence of added trimethylphosphite were obtained by following the approach to equilibrium determined by the rate of decrease of the Fe—Me ¹H nmr signal of *6*. Rate constants were extracted by curve fitting the equation $(A - A_\infty) = KA_\infty \exp(Qt)$ (where $Q = -(k_1k_3 + k_2k_4)/(k_2 + k_3)$ and $K = k_1k_3/k_2k_4$) which derives from Scheme I neglecting k_5, assuming a steady state condition for *2*, L = acetonitrile and appreciable k_4. Values of the equilbrium constant K extracted from the above expression were in good agreement with those obtained by integration of nmr spectra of equilibrated solutions.

Acknowledgement

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