Kinetics of Nucleophilic Attack on Co-ordinated Organic Moieties. Part 17.† Addition of Pyridines to $[Fe(1—5\text{-}\eta\text{-dienyl})(CO)_3]^+$ Cations (dienyl = C_6H_7, 2-$MeOC_6H_6$, or C_7H_9)

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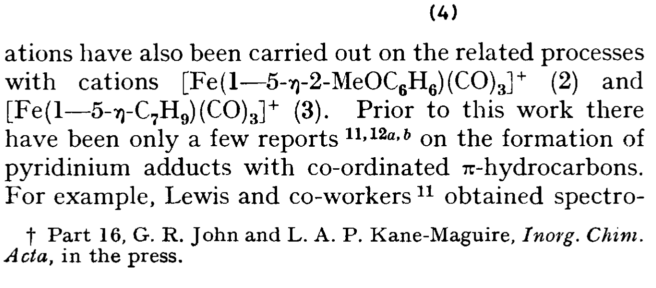
Synthetic and kinetic studies of the reactions between $[Fe(1—5\text{-}\eta\text{-}C_6H_7)(CO)_3]^+$ (1) and X-substituted pyridines (X = H, 2-Me, 3-Me, 4-Me, 4-Ph, 2-Cl, 3-CN, 2,5-Me_2, 2,6-Me_2, 3,5-Me_2, or 2,4,6-Me_3) in CH_3CN provide the first quantitative information on the importance of basicity and steric properties in controlling amine nucleophilicity towards co-ordinated π-hydrocarbons. The products are pyridinium adducts of tricarbonyl(hexa-1,3-diene)iron. Similar pyridinium adduct formation occurs with the cations $[Fe(1—5\text{-}\eta\text{-}2\text{-}MeOC_6H_6)(CO)_3]^+$ (2) and $[Fe(1—5\text{-}\eta\text{-}C_7H_9)(CO)_3][BF_4]$ (3). The general rate law rate = k_1[Fe][amine] is observed, except for the equilibrium reaction of (1) with 3-cyanopyridine which gives rate = k_1[Fe][amine] + k_{-1}[Fe]. The rate trend C_6H_7 > 2-$MeOC_6H_6$ > C_7H_9 found with several pyridines and the low $\Delta H_1^‡$ and large negative $\Delta S_1^‡$ values are consistent with direct addition to the dienyl rings. For attack of non-sterically crowded pyridines on (1), a Brönsted plot of log k_1 *versus* pK_a of the amine conjugate acid has a high slope α of 1.0, indicating a very marked dependence of rate on amine basicity. Successive blocking of the 2- and 6-positions of pyridine by methyl groups leads to marked non-additive steric retardation.

In previous papers we have examined how variations in the steric and electronic properties of co-ordinated π-hydrocarbons affect their reactivity towards common nucleophiles, *e.g.* tertiary phosphines.[1] Some progress has also been made in establishing the relative reactivity of a variety of $[M(\pi\text{-hydrocarbon})(CO)_3]^+$ cations (π-hydrocarbon = olefin, enyl, diene, dienyl, triene, trienyl) towards tertiary phosphines.[2-4] However, apart from some kinetic studies with β-diketones,[5] aromatic heterocycles,[6] activated arenes,[4,7] and phosphorus nucleophiles,[1-3] little quantitative information is currently available concerning nucleophilic reactivities. This situation contrasts with organic chemistry, where extensive studies have attempted to correlate nucleophilicity with a variety of parameters, *e.g.* the Swain-Scott,[8] Edwards,[9] and Ritchie [10] equations.

We now wish to report synthetic and kinetic studies of the addition of pyridines to the cation $[Fe(1—5\text{-}\eta\text{-}C_6H_7)(CO)_3]^+$ (1) in acetonitrile [equation (1); X = H, 2-Me, 3-Me, 4-Me, 4-Ph, 2-Cl, 3-CN, 2,5-Me_2, 2,6-Me_2, 3,5-Me_2, or 2,4,6-Me_3]. Similar, but less extensive, investigations have also been carried out on the related processes with cations $[Fe(1—5\text{-}\eta\text{-}2\text{-}MeOC_6H_6)(CO)_3]^+$ (2) and $[Fe(1—5\text{-}\eta\text{-}C_7H_9)(CO)_3]^+$ (3). Prior to this work there have been only a few reports [11,12a,b] on the formation of pyridinium adducts with co-ordinated π-hydrocarbons. For example, Lewis and co-workers [11] obtained spectroscopic evidence for adduct (4; X = H). The kinetic studies of reactions (1) provide the first quantitative information on the importance of basicity and steric properties in controlling amine nucleophilicity towards co-ordinated π-hydrocarbons. A preliminary report has appeared.[13]



EXPERIMENTAL

Materials.—The cations (1)—(3) were isolated as their BF_4^- salts and purified using published procedures.[14,15] The various pyridine nucleophiles were purchased in the purest form available and freshly distilled over K[OH] pellets prior to use. Acetonitrile (BDH) solvent was distilled in bulk and stored over molecular sieves (grade 3A) under a dinitrogen atmosphere.

Isolation of New Pyridinium Adducts.—*Tricarbonyl*(1—4-η-5-*pyridiniocyclohexa*-1,3-*diene*)*iron tetrafluoroborate* (4a). Solutions of $[Fe(1—5\text{-}\eta\text{-}C_6H_7)(CO)_3][BF_4]$ (0.10 g, 0.327 mmol) in CH_3CN (10 cm^3) and freshly distilled pyridine (0.265 cm^3, 3.27 mmol) in CH_3CN (10 cm^3) were mixed under dinitrogen. After 10 min the resulting yellow solution was rotary evaporated to dryness under dinitrogen, yielding an oily solid. Addition of 20 cm^3 of light petroleum (b.p. 60—80 °C) gave the product as a pale yellow microcrystalline solid, which was collected on a frit and washed several times with further light petroleum. The yield after drying on a vacuum line for 2 h was 0.091 g (72%) (Found: 43.6; H, 3.2; N, 3.4. Calc. for $C_{14}H_{12}BF_4FeNO_3$: C, 43.7; H, 3.1; N, 3.6%). An acetonitrile solution exhibited strong i.r. carbonyl bands at 2 055 and 1 980 cm^{-1}. The presence of a strong band at *ca.* 1 060 cm^{-1} (Nujol mull) confirmed the presence of the BF_4^- anion. ^1H N.m.r. (CD_3COCD_3) τ 0.90 (d, 2 H, aromatic), 1.38 (t, 1 H, aromatic), 1.82 (t, 2 H, aromatic), 4.00 (overlapping multiplets, 2 H, H^2 and H^3), 4.45 (m, 1 H, $H^{5'}$), 6.65 (overlapping multiplets, 2 H, H^1 and H^4), 7.10 (m, 1 H, $H^{6'}$), 8.00 (m, 1 H, H^6).

Tricarbonyl(1—4-η-5-*pyridinio*-2-*methoxycyclohexa*-1,3-*diene*)*iron tetrafluoroborate* (4b). This adduct was prepared in an analogous manner to that described above, using $[Fe(2\text{-}MeOC_6H_6)(CO)_3][BF_4]$ (0.10 g) and pyridine (0.24 cm^3) in CH_3CN (20 cm^3). The yield of pale yellow solid product was 0.079 g (64%) (Found: C, 43.7; H, 3.3; N, 3.6. Calc. for $C_{15}H_{14}BF_4FeNO_4$: C, 43.4; H, 3.4; N, 3.4%).

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† Part 16, G. R. John and L. A. P. Kane-Maguire, *Inorg. Chim. Acta*, in the press.

I.r. ν(CO) (CH_3CN) 2 055 and 1 980 cm^{-1}, ν(BF_4^-) (Nujol mull) *ca.* 1 060br cm^{-1}. ^{1}H N.m.r. (CD_3COCD_3) τ 0.90 (m, 2 H, aromatic), 1.38 (m, 1 H, aromatic), 1.85 (m, 2 H, aromatic), 4.20 (m, 1 H, H^3), 4.60 (m, 1 H, H$^{5'}$), 6.16 (s, 3 H, OMe), 6.53 (overlapping multiplets, 2 H, H^1 and H^4), 6.9—8.2 (masked by acetone, H^6 and H$^{6'}$).

Tricarbonyl(1—4-η-5-*pyridiniocyclohepta*-1,3-*diene*)*iron tetrafluoroborate* (4c). A similar procedure employing [Fe(1—5-η-C_7H_9)(CO)$_3$][BF_4] (0.10 g, 0.313 mmol) and pyridine (0.26 cm^3, 3.22 mmol) gave 0.075 g (60% yield) of this cream-yellow product, m.p. 124—125 °C (decomp.) (Found: C, 45.4; H, 3.6; N, 3.2. Calc. for $C_{15}H_{14}BF_4FeNO_3$: C, 45.2; H, 3.5; N, 3.5%). I.r. ν(CO)(CH_3CN) 2 050 and 1 980 cm^{-1}, ν(BF_4^-) (Nujol mull) *ca.* 1 060br cm^{-1}. ^{1}H N.m.r. (CD_3CN) τ 1.18 (m, 2 H, aromatic), 1.55 (m, 1 H, aromatic), 2.01 (m, 2 H, aromatic), 4.32 (overlapping multiplets, 2 H, H^2 and H^3), 4.95 (m, 1 H, H$^{5'}$), 6.72 (m, 1 H, H^1), 7.15 (m, 1 H, H^4), 7.4—8.5 (overlapping resonances, 4 H, H^6, H^7, H$^{6'}$, and H$^{7'}$).

A field desorption (f.d.) mass spectrum revealed the following mass peaks (with relative intensities in parentheses): 79 (23), 127 (10), 128 (13), 149 (24), 205 (21), 233 (100). The base peak at *m/e* 233 corresponds to the cation minus the pyridinium group.

Tricarbonyl[1—4-η-5-(2-*methylpyridinio*)*cyclohepta*-1,3-*diene*]*iron tetrafluoroborate* (4d). This adduct was synthesised in a similar fashion from [Fe(1—5-η-C_7H_9)(CO)$_3$]-[BF_4] (0.10 g, 0.313 mmol) and 2-methylpyridine (0.31 cm^3, 3.13 mmol). It was obtained as an off-white powder (0.090 g, 70%), m.p. 120 °C (decomp.) (Found: C, 46.5; H, 3.9; N, 3.2. Calc. for $C_{16}H_{16}BF_4FeNO_3$: C, 46.5; H, 3.9; N, 3.4%). I.r. ν(CO) (CH_3CN) 2 045 and 1 975 cm^{-1}, ν(BF_4^-) (Nujol mull) *ca.* 1 060br cm^{-1}. ^{1}H N.m.r. (CD_3CN) τ 1.10—2.25 (aromatic), 4.30 (overlapping multiplets, 2 H, H^2 and H^3), 4.80 (m, 1 H, H$^{5'}$), 6.74 (overlapping multiplets, 2 H, H^1 and H^4), 7.0—8.4 (H^6, H^7, H$^{6'}$, and H$^{7'}$, overlapping with CH_3), 7.53 (s, CH_3).

In situ *Preparation of other Pyridinium Adducts*.—Several other pyridinium adducts (4e—g) have been obtained quantitatively *in situ*, and characterised by their ^{1}H n.m.r. spectra. With (4e) and (4f) equimolar concentrations (0.25 mol dm^{-3}) of the appropriate dienyl salt and amine were mixed in CD_3CN or CD_3NO_2 under dinitrogen. For (4g), a two-fold excess (0.50 mol dm^{-3}) of 2,4,6-trimethylpyridine was employed.

Tricarbonyl[1—4-η-5-(4-*methylpyridinio*)*cyclohexa*-1,3-*diene*]*iron tetrafluoroborate* (4e). ^{1}H N.m.r. (CD_3CN) τ 1.48 (d, 2 H, aromatic), 2.25 (d, 2 H, aromatic), 4.18 (overlapping multiplets, 2 H, H^2 and H^3), 4.80 (m, 1 H, H$^{5'}$), 6.85 (overlapping multiplets, 2 H, H^1 and H^4), 7.20 (m, 1 H, H$^{6'}$), 7.43 (s, 3 H, CH_3), 8.20 (m, 1 H, H^6).

Tricarbonyl[1—4-η-5-(2,6-*dimethylpyridinio*)*cyclohepta*-1,3-*diene*]*iron tetrafluoroborate* (4f). ^{1}H N.m.r. (CD_3NO_2) τ 2.00 (t, 1 H, aromatic), 2.60 (d, 2 H, aromatic), 4.0—5.0 (overlapping resonances, 3 H, H^2, H^3, and H$^{5'}$), *ca.* 6.7 (overlapping multiplets, 2 H, H^1 and H^4), 6.8—8.2 (H^6, H^7, H$^{6'}$, and H$^{7'}$, overlap with CH_3), 7.43 (s, CH_3).

Tricarbonyl[1—4-η-5-(2,4,6-*trimethylpyridinio*)*cyclohepta*-1,3-*diene*]*iron tetrafluoroborate* (4g). ^{1}H N.m.r. (CD_3NO_2) τ 2.83 (s, aromatic), 4.0—4.7 (overlapping multiplets, H^2 and H^3), 4.5—5.0 (m, H$^{5'}$), 6.4—7.1 (overlapping multiplets, H^1 and H^4), 6.8—8.3 (H^6, H^7, H$^{6'}$, and H$^{7'}$, overlap with CH_3), 7.48 (s, CH_3), 7.61 (s, CH_3).

Spectroscopic Studies.—Infrared spectra were recorded on a Perkin-Elmer 257 spectrophotometer, and ^{1}H n.m.r. (90 MHz) on a Perkin-Elmer R32 spectrophotometer. The field-desorption (f.d.) mass spectrum of adduct (4c) was measured using a Varian combined FD/FI/EI source on a CH5D mass spectrophotometer linked to a Varian 620 i data system. Acetone was employed as solvent.

Kinetic Studies.—All of the reactions (1) in CH_3CN were studied under pseudo-first-order conditions using a large excess of nucleophile ([Fe] = 1.5 × 10^{-3} mol dm^{-3}, [amine] = 0.01—2.0 mol dm^{-3}), except for the 3,5-dimethylpyridine case which was followed under equimolar conditions ([Fe] = [amine] = 1.5 × 10^{-3} mol dm^{-3}). Except for the reaction with 3-cyanopyridine, which was an equilibrium process, each addition proceeded to completion under the kinetic conditions employed.

All of the reactions were rapid and were studied using a thermostatted (±0.1 °C) stopped-flow spectrophotometer. Solutions of the dienyl cations (1)—(3) and the pyridine nucleophiles of appropriate concentrations were freshly prepared in CH_3CN prior to mixing. Incident light of the desired wavelength was provided by a Bausch and Lomb monochromator fitted with variable slits. Each of the additions was monitored at 390 nm, at which wavelength a large decrease in absorbance occurred. Reaction traces were stored on a Tektronic 564B storage oscilloscope fitted with a log converter, thus giving a direct record of absorbance changes.

TABLE 1

Rate constants for the reaction of [Fe(1—5-η-dienyl)(CO)$_3$]$^+$ cations with pyridine in CH_3CN. [Fe] = 1.5 × 10^{-3} mol dm^{-3}

Complex	θ_c/°C	10^2[pyridine]/ mol dm^{-3}	$k_{obs.}$/s^{-1}	k_1 */ dm^3 mol^{-1} s^{-1}
(1)	0.0	1.25	26.0	2 170(120)
		2.48	60.3	
		4.96	108	
	11.1	1.25	56.6	4 530
	17.9	1.25	77.7	6 210
(2)	0.0	1.00	4.27	425(11)
		2.00	8.42	
		4.01	17.3	
		5.03	22.7	
		8.01	33.6	
	12.1	2.0	17.9	895
	14.5	2.0	20.3	1 010
	19.4	2.0	26.4	1 320
	23.7	2.0	33.2	1 660
(3)	0.0	1.0	1.28	140(1)
		2.1	2.89	
		4.0	5.34	
		10.8	15.0	
	8.4	4.0	7.70	193
	9.5	4.0	8.43	211
	13.2	4.0	9.47	237
	18.0	4.0	11.9	298
	25.0	4.0	15.6	390

* Derived from equation (2). Estimated standard deviations are given in parentheses.

Pseudo-first-order rate constants, $k_{obs.}$, were calculated from the slopes of plots of log ($A_t - A_\infty$) *versus* time. Such plots were generally linear for at least two half-lives. Each $k_{obs.}$ is the average of at least three separate runs, with an average reproducibility of ±3%. Second-order rate constants, k_1, were calculated by least-squares analyses of $k_{obs.}$ *versus* [amine] plots, the errors quoted being the appropriate standard deviations.

The second-order rate constant, k_1, for the reaction of 3,5-dimethylpyridine with cation (1) was obtained directly from the slope of a plot of $x/a(a - x)$ *versus* time, where a is the initial concentration of dienyl salt and x is the concentration of adduct at time t. This run was carried out in quadruplicate, the plots generally being linear for at least 70% completion of reaction. The reproducibility of k_1 was *ca.* ±4%

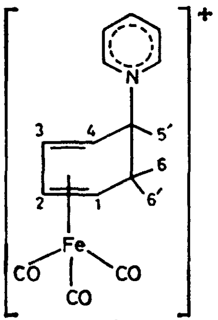
Activation enthalpies were obtained from the gradients of Arrhenius plots of log k_1 *versus* T^{-1}, calculated by a least-squares method. The errors quoted are the standard deviations derived from the least-squares analyses. Entropies of activation were calculated using the second-order rate constants, k_1.

RESULTS AND DISCUSSION

(*a*) *Nature of the Reactions.*—The nature of reactions (1) has been established from *in situ* i.r. and ^1H n.m.r. spectral studies, and by the isolation and characterisation of the pyridinium adducts in certain cases (4a—d). These latter products are stable for long periods in the solid state or in solution (CH_3CN, CH_3NO_2, or acetone) under dinitrogen, but solutions slowly decompose in the presence of air.

The i.r. spectra of (4a—d) in CH_3CN exhibit two strong carbonyl bands at *ca.* 2 055 and 1 980 cm^{-1}. The shift (*ca.* 10 cm^{-1}) of ν(CO) to higher frequency compared with related neutral complexes such as 1—4-η-5-*N*-anilinocyclohexa-1,3-diene(tricarbonyl)iron [16] is compatible with cationic species in which the positive charge is largely localised on the nitrogen atom of the pyridine substituent. Not surprisingly, the ν(CO) bands of adducts (4a—d) are very similar to those of the analogous phosphonium ions formed [1] *via* addition of tertiary phosphines and phosphites to cations (1)—(3).

The ^1H n.m.r. spectra of these isolated products (see Experimental section) are also fully consistent with their formulation as tricarbonyl(1—4-η-5-*N*-pyridinio-1,3-diene)iron derivatives. They show similar features to those reported [1] for the related phosphonium adducts. Although the ^1H n.m.r. spectra do not unequivocally establish the stereochemistry of the pyridine substituents in these pyridinium adducts, an *exo* configuration is assumed as shown below for (4a). Except for a few instances arising from serious steric problems, all other nucleophilic additions to cations (1)—(3) have been observed to occur in an *exo* fashion.[16b] Further support for *exo* addition of the pyridines to cations (1)—(3) comes from the general rate trend $C_6H_7 > 2\text{-}MeOC_6H_6 > C_7H_9$ observed for these reactions (see below).



(4a)

Interestingly, the f.d. mass spectrum of (4c) does not show the expected molecular $M^{\cdot+}$ ion, but instead gives a base peak at *m*/*e* 233 corresponding to $[M - \text{pyridine}]^{\cdot+}$. A medium intensity peak due to pyridine is also observed at *m*/*e* 79. Further peaks are seen at *m*/*e* 205 and *m*/*e* 149 which are attributed to the fragment ions $[M - \text{pyridine} - CO]^{\cdot+}$ and $[M - \text{pyridine} - 3CO]^{\cdot+}$. However, in common with the f.d. mass spectra of other $[M(\pi\text{-hydrocarbon})(CO)_3]^+$ cations, little other fragmentation is observed. Loss of pyridine from adduct (4c) in the f.d. mass spectrometer is particularly interesting since for most $[M(\pi\text{-hydrocarbon})(CO)_3]^+$ cations investigated to date [1,17,18] the base peaks correspond to the molecular $M^{\cdot+}$ ions. However, a related observation has been reported [1] for the phosphonium adducts $[Fe\{P(OBu)_3(C_6H_6X)\}(CO)_3][BF_4]$ (X = H or 2-OMe), which undergo Arbusov elimination in the mass spectrometer to give the corresponding phosphonates $[Fe\{PO(OBu)_2(C_6H_6X)\}(CO)_3]$.

TABLE 2

Rate constants for reaction of $[Fe(1\text{—}5\text{-}\eta\text{-dienyl})(CO)_3]^+$ cations with 2-methylpyridine in CH_3CN. $[Fe] = 1.5 \times 10^{-3}$ mol dm^{-3}

Complex	θ_c/°C	$10^2[NC_5H_4Me\text{-}2]$/ mol dm^{-3}	$k_{obs.}/s^{-1}$	k_1 */dm^3 mol^{-1} s^{-1}
(1)	0.0	2.03	14.4	766(7)
		4.05	29.1	
		6.08	44.5	
		10.0	75.3	
	10.4	1.00	12.3	1 230
	15.5	1.00	16.6	1 660
	20.0	1.00	21.5	2 150
	25.4	1.00	26.3	2 630
	30.0	1.00	32.8	3 280
(2)	0.0	2.19	2.42	96(1)
		4.05	4.21	
		6.08	6.14	
		8.10	8.05	
		10.1	10.0	
	8.9	4.00	6.99	175
	14.2	4.00	9.08	227
	20.1	4.00	13.9	348
	25.0	4.00	18.1	453
(3)	0.0	2.03	0.415	22.2(0.3)
		4.05	0.848	
		6.08	1.40	
		10.0	2.17	
		20.0	4.42	
	10.4	4.00	1.53	38.3
	15.2	4.00	1.96	49.0
	20.1	4.00	2.45	61.3

* Derived from equation (2). Estimated standard deviations are given in parentheses.

In situ ^1H n.m.r. experiments also confirm the quantitative formation of pyridinium adducts in the reactions of (1) with 4-methylpyridine and of (3) with the sterically hindered amines 2,6-dimethylpyridine and 2,4,6-trimethylpyridine (see Experimental section). Products have not been isolated from the other reactions (1) studied here. However, the appearance in all cases of only two strong product carbonyl bands at *ca.* 2 055 and 1 980 cm^{-1} in CH_3CN indicates that reaction (1) is a general process. These latter i.r. studies also established that all of the reactions (1) proceeded to completion under the kinetic conditions employed, except for the addition of 3-cyanopyridine to cation (1) which was an equilibrium process ($K_{eq.} = ca.\ 3$ dm^3 mol^{-1} at 20 °C).

(*b*) *Kinetics and Mechanism.*—Kinetic results for the reactions of cations (1)—(3) with pyridine and 2-methylpyridine are collected in Tables 1 and 2. Similar results for 2,6-dimethylpyridine with cations (1) and (3) are given in Table 3. For each of these three pyridines plots of $k_{obs.}$ *versus* [amine] are linear and pass through the origin, indicating the general rate law (2).

TABLE 3

Rate constants for reaction of $[Fe(1—5\text{-}\eta\text{-dienyl})(CO)_3]^+$ cations with 2,6-dimethylpyridine in CH_3CN. [Fe] = 1.5×10^{-3} mol dm^{-3}

Complex	θ_c/°C	10[$NC_5H_3Me_2$-2,6]/ mol dm^{-3}	$k_{obs.}$/s^{-1}	k_1 */dm^3 mol^{-1} s^{-1}
(1)	0.0	5.0	3.33	6.66
	10.0	5.0	6.99	14.0
	21.8	5.0	15.6	31.2
	28.0	5.0	23.1	46.2
	37.3	2.0	17.7	88.3(0.2)
		4.0	35.6	
		8.0	70.7	
(3)	0.0	5.0	0.212	0.424
	10.0	5.0	0.500	1.00
	21.8	5.0	0.876	1.75
	28.0	5.0	1.60	3.20
	37.3	4.0	2.06	5.32(0.1)
		8.0	4.37	
		20.0	10.6	

* Derived from equation (2). Estimated standard deviations are given in parentheses.

$$\begin{aligned} \text{Rate} &= k_{obs.}\,[\text{complex}] \\ k_{obs.} &= k_1\,[\text{amine}] \qquad (2) \end{aligned}$$

Less extensive kinetic results for other substituted pyridines are summarised in Table 4. Equation (2) is seen to be again obeyed in the reactions of cation (1) with 4-methylpyridine and 2-chloropyridine.

TABLE 4

Rate constants for reaction of $[Fe(1—5\text{-}\eta\text{-dienyl})(CO)_3]^+$ cations with other pyridines in CH_3CN at 0 °C. [Fe] = 1.5×10^{-3} mol dm^{-3}

Complex	Nucleophile	10^2[Nucleophile]/ mol dm^{-3}	$k_{obs.}$/s^{-1}	k_1 [a]/dm^3 mol^{-1} s^{-1}
(1)	$NC_5H_3Me_2$-3,5	0.15		10 400 [b]
	NC_5H_4Me-4	1.00	84.9	8 340(230)
		1.50	123.0	
	NC_5H_4Me-3	1.50	105.0	6 980
	NC_5H_4Ph-4	2.0	41.0	2 050
	$NC_5H_3Me_2$-2,5	5.0	66.0	1 320
	$NC_5H_2Me_3$-2,4,6	10.0	6.72	67.2
	NC_5H_4Cl-2	10.0	2.21	22.1
		20.2	5.64	27.9
		40.3	11.7	29.0
	NC_5H_4CN-3	20.0	2.90	8.4(0.3) [c]
		40.0	4.47	
		50.0	5.43	
(3)	$NC_5H_3Me_2$-2,4	10.0	2.76	27.6
	$NC_5H_2Me_3$-2,4,6	10.0	0.424	4.24

[a] Second-order rate constants derived from equation (2), except where otherwise stated. Estimated standard deviations are given in parentheses. [mean $k_{-1} = 1.2(0.1)$ s^{-1}]. [b] Derived from equimolar rate run. [c] Derived from equation (3)

This rate law (2) is most readily explained by a one-step mechanism in which the second-order rate constants, k_1, refer to direct addition by the pyridine nucleophiles to the dienyl rings. Strong support for such direct attack comes from the relative rates found for the reactions of these pyridines with each of the cations (1)—(3). The k_1 values are seen from Tables 1 and 2 to decrease in the order $C_6H_7 > 2\text{-}MeOC_6H_6 > C_7H_9$. For example, at 0 °C the relative rates for addition of pyridine and 2-methylpyridine to these cations are 15.5 : 3 : 1 and 34 : 4 : 1, respectively. The lower reactivity of $[Fe(1—5\text{-}\eta\text{-}2\text{-}MeOC_6H_6)(CO)_3][BF_4]$ (2) compared with the parent cation $[Fe(1—5\text{-}\eta\text{-}C_6H_7)(CO)_3][BF_4]$ (1) is in accordance with the mesomeric influence of the methoxide group, which has been shown from INDO molecular-orbital calculations [19] to decrease the positive charge on the dienyl C(5) atom, the site of nucleophilic addition. The more pronounced rate difference between the parent cation (1) and $[Fe(1—5\text{-}\eta\text{-}C_7H_9)(CO)_3][BF_4]$ (3) is readily explained by the increased steric hindrance caused by the extra methylene group in (3) if one assumes approach of the pyridines from above the dienyl rings.

Added support for this direct mechanism comes from the observation [20] that the iodide ion reacts with each of the complexes (1)—(3) at a similar rate. In these latter reactions, leading ultimately to $[Fe(1—5\text{-}\eta\text{-dienyl})(CO)_2I]$ products, the rate-determining step is believed to be attack at the metal or a carbonyl carbon. Thus, not surprisingly, for nucleophilic attack at a carbonyl ligand (or metal) similar steric effects are expected for each of the cations (1)—(3).

The low $\Delta H_1^\ddagger$ values and the large negative $\Delta S_1^\ddagger$ values found for reactions (1) (Table 5) are also consistent with simple addition to the dienyl rings. The activation parameters indicate entropy control over the relative rates for additions of pyridine and 2,6-dimethylpyridine to the various cations. For example, the rate trend $C_6H_7 > 2\text{-}MeOC_6H_6 > C_7H_9$ for the pyridine reactions is associated with increasingly negative $\Delta S_1^\ddagger$ values (−45, −63, and −107 J K^{-1} mol^{-1}, respectively). On the other hand, $\Delta H_1^\ddagger$ values decrease significantly in

TABLE 5

Summary of activation parameters for addition of pyridines to $[Fe(1—5\text{-}\eta\text{-dienyl})(CO)_3]^+$ cations in CH_3CN

Nucleophile	Complex	Relative rate (0 °C)	$\Delta H_1^\ddagger$/ kJ mol^{-1}	$\Delta S_1^\ddagger$/ J K^{-1} mol^{-1}
NC_5H_5	(1)	15.5	36.9 (1.5)	−45(6)
	(2)	3	35.8 (0.3)	−63(1)
	(3)	1	26.3 (0.6)	−107(2)
NC_5H_4Me-2	(1)	34	31.3 (0.8)	−74(3)
	(2)	4	39.8 (0.9)	−60(3)
	(3)	1	31.4 (0.2)	−103(2)
$NC_5H_3Me_2$-2,6	(1)	15.7	45.8 (0.6)	−61(2)
	(3)	1	44.6 (1.9)	−88(7)

the order $C_6H_7 \geqslant 2\text{-}MeOC_6H_6 > C_7H_9$. Further support for entropy control in these pyridine reactions comes from a plot of $\Delta H_1^{\ddagger}$ *versus* $\Delta S_1^{\ddagger}$, the slope of which gives an isokinetic temperature of 179(20) K. This value is much lower than the temperature range (273—298 K) employed in these studies, indicating entropy control at the latter temperatures.

However, for the reactions of 2-methylpyridine with each of the complexes (1)—(3) the relative rates are seen from Table 5 to arise from a play-off between enthalpy and entropy effects. Thus, while the slower rate for the C_7H_9 cation compared with C_6H_7 is again associated with a more negative $\Delta S_1^{\ddagger}$ value of -103 J K^{-1} mol^{-1} compared with -74 J K^{-1} mol^{-1}, the intermediate rate for the $2\text{-}MeOC_6H_6$ cation is associated with both the largest $\Delta H_1^{\ddagger}$ value and the least negative $\Delta S_1^{\ddagger}$ value of -60 J K^{-1} mol^{-1}.

For the other substituted pyridines for which i.r. studies showed that reactions (1) proceeded to completion, the simple rate law (2) was assumed, allowing calculation of the second-order rate constants, k_1, given in Table 4. However, for the equilibrium reaction of cation (1) with the relatively non-basic 3-cyanopyridine a plot of $k_{obs.}$ *versus* [amine] has a non-zero intercept (Figure 1), indicating a two-term expression of the form (3) for $k_{obs.}$. Equation (3) is consistent with an equilibrium process, where k_a refers to k_1 (the second-order rate constant for attack on the dienyl ring) and k_b refers to k_{-1}, the first-order rate constant for the dissociation of 3-cyanopyridine from the pyridinium adduct. The results in Table 4 for this latter reaction at 0 °C lead to a k_1 value of 8.4(0.3) dm^3 mol^{-1} s^{-1} and a reverse dissociation constant (k_{-1}) of 1.2(0.1) s^{-1}. The equilibrium constant, K_1 ($= k_1/k_{-1}$), is thus estimated as 7.0(0.6) dm^3 mol^{-1} at 0 °C. This compares favourably with a K_1 value of *ca.* 3 dm^3 mol^{-1} estimated independently from i.r. studies at 20 °C.

$$k_{obs.} = k_a\,[\text{amine}] + k_b \qquad (3)$$

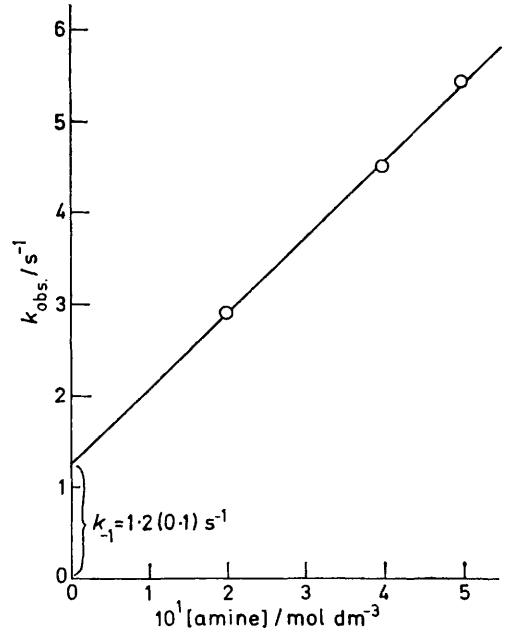


FIGURE 1 Dependence of $k_{obs.}$ on [amine] for the reaction of $[Fe(1—5\text{-}\eta\text{-}C_6H_7)(CO)_3][BF_4]$ with 3-cyanopyridine in CH_3CN at 0 °C. Mean k_1 = 8.4(0.3) dm^3 mol^{-1} s^{-1}

Some limited kinetic studies have also been carried out on the reactions of pyridine with cations (1)—(3) in CH_3NO_2 to examine the influence of changing the solvent. *In situ* i.r. studies in CH_3NO_2 ([Fe] = 1.5 × 10^{-3} mol dm^{-3}, [pyridine] = 1.5 × 10^{-2} mol dm^{-3}) again showed the presence of only two strong carbonyl bands at *ca.* 2 055 and 1 980 cm^{-1} as expected for the complete formation of products (4) under the kinetic conditions employed. The k_1 values obtained at 0 °C of 4 810(230), 518(9), and 128(9) dm^3 mol^{-1} s^{-1} respectively for complexes (1)—(3) compare with the corresponding values of 2 170(120), 425(11), and 140(1) dm^3 mol^{-1} s^{-1} respectively found above in CH_3CN (Table 1). The very similar k_1 (CH_3NO_2) and k_1 (CH_3CN) values indicate similar solvation effects on the dienyl cations and their corresponding transition states in both solvents.

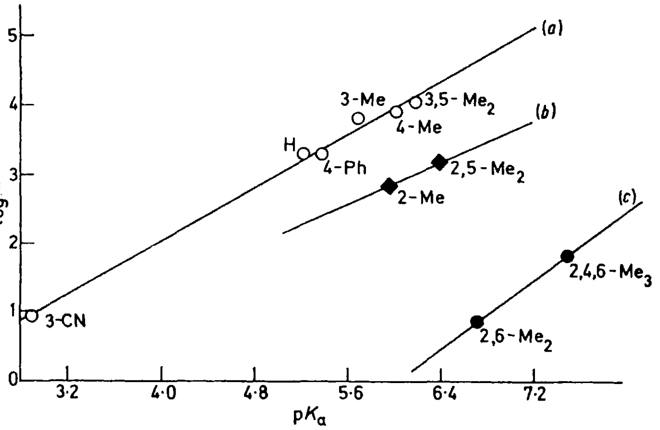


FIGURE 2 Brönsted plots for the reactions of $[Fe(1—5\text{-}\eta\text{-}C_6H_7)(CO)_3]^+$ in CH_3CN at 0 °C with (*a*) non-sterically crowded pyridines; (*b*) pyridines with 2-Me groups; and (*c*) pyridines with 2,6-Me$_2$ groups

Influence of nucleophile basicity. For the pyridine nucleophiles without substituents in the 2- or 6-positions (which will give rise to complicating steric effects, see below) the influence of nucleophile basicity on the rates of reactions (1) can be readily examined. The k_1 values summarised in Table 6 for addition of various pyridines (X = 3,5-Me$_2$, 4-Me, 3-Me, 4-Ph, H, or 3-CN) to cation (1) reveal a very strong dependence on the basicity of the amine. This is demonstrated quantitatively by the linear free-energy relationship obtained on plotting log k_1 *versus* pK_a of the amine conjugate acid (in water) [Figure 2(*a*)]. Thus, reaction (1) obeys the Brönsted relationship (4), with a slope, α, of about 1.0. The high slope of 1.0 indicates a very marked dependence of k_1 on nucleophile basicity. Unfortunately, compre-

$$\log k_1 = pK_a + \text{constant} \qquad (4)$$

hensive pK_a values for pyridines are unavailable in CH_3CN. However, studies by Hall [21] with other amines indicate that basicities in water and CH_3CN generally show parallel trends.

TABLE 6

Variation of rates with amine basicity for the reactions of pyridines with $[Fe(1\text{—}5\text{-}\eta\text{-}C_6H_7)(CO)_3][BF_4]$ in CH_3CN at 0 °C

Amine	k_1/dm^3 mol^{-1} s^{-1}	$pK_a(H_2O)$ *
$NC_5H_3Me_2$-3,5	10 400	6.17
NC_5H_4Me-4	8 340	6.02
NC_5H_4Me-3	6 980	5.68
NC_5H_5	2 170	5.23
NC_5H_4Ph-4	2 050	5.38
NC_5H_4CN-3	8.4	2.90

* From R. M. Smith and A. E. Martell, ' Critical Stability Constants,' Plenum Press, New York, 1975, vol. 2.

This high slope contrasts sharply with the very low α values of *ca.* 0.05 reported for attack by pyridines (py) and other amines on the very ' soft ' Platinum(II) centre in complexes such as *trans*-$[Pt(py)_2Cl_2]$.[22] Amine attack on moderately ' soft ' substrates such as alkyl halides has been reported [23] to give α values of *ca.* 0.2. Interestingly, the slope is also somewhat larger than the α values of *ca.* 0.5 found for amine addition to free carbonium ions.[10] Following the reasoning of Pearson *et al.*[24] this suggests that the dienyl rings in cations (1)—(3) are ' hard ' species.

Assignment of a ' hard ' character to the dienyl groups of cations (1)—(3) is consistent with their frequent representation as stabilised carbonium ions, and with the relatively high positive charges calculated [25] to reside on the ring carbons. It is also significant that we have recently observed a similar strong dependence of k_1 on nucleophile basicity for the related additions of anilines [13] and phosphines and phosphites [1] to cations (1) and (2), as expected for ' hard ' dienyl substrates.

Steric influence of nucleophile. The steric effect of introducing methyl groups in the 2- or 6-position of the pyridine nucleophile is dramatically illustrated in Table 7 for attack on cation (1). The k_1 values decrease in the order pyridine > 2-methylpyridine > 2,6-dimethylpyridine (relative rates 330 : 110 : 1). A similar decrease is observed for the analogous reactions with cation (3). These rate trends compare with the much smaller decrease (40 : 3 : 1) previously found for attack on methyl iodide [26] by the same amines. This indicates that steric effects are more important in reactions (1) than for analogous attack on methyl iodide.

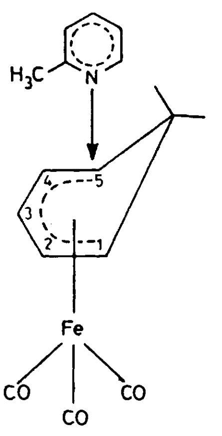
TABLE 7

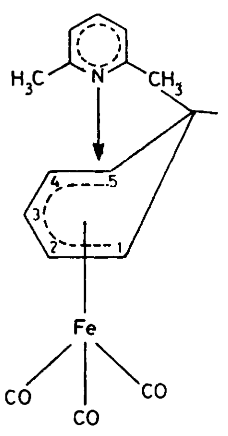
Steric effects on rates for addition of substituted pyridines to $[Fe(1\text{—}5\text{-}\eta\text{-}C_6H_7)(CO)_3][BF_4]$ in CH_3CN

Amine	k_1 (0 °C)/ dm^3 mol^{-1} s^{-1}	Relative k_1
NC_5H_5	2 170(120)	330
NC_5H_4Me-2	766(7)	110
$NC_5H_3Me_2$-2,6	6.66	1

Quantitative interpretation of the results in Table 7 is complicated by the concomitant electronic influence of the blocking methyl substituents. However, a direct measure of the steric influence of the pyridine nucleophiles in reactions (1) can be obtained from an examination of all the Brönsted plots in Figure 2 for attack of pyridines on cation (1). Three roughly parallel lines are obtained: (*a*) is for the non-sterically crowded pyridines discussed above, (*b*) is for pyridines containing a methyl group in the 2-position, and (*c*) is for pyridines with methyl groups in the 2- and 6-positions. The separation between each line, Δ, reflects the steric effect of successively introducing methyl groups in the 2- and 6-positions of pyridine, without any interference from basicity variations. It is seen that the introduction of a 2-Me group in pyridine leads to a Δ value of *ca.* 1, while two methyl groups gives Δ *ca.* 4. That is, successive blocking of the N reaction site by methyl groups causes approximately 10-fold and 10 000-fold decreases in rate when compared with the non-sterically hindered pyridines.

These results confirm the importance of steric effects in reactions (1). They also show that the steric effects of successive addition of methyl groups to pyridine (2-Me, 2,6-Me_2) are non-additive. This observation contrasts with the previous findings [22] for the reactions of substituted pyridines with square-planar platinum(II) and gold(III) complexes, where methyl-blocking was found to be additive. Our observation that 2,6-Me_2 groups cause very much more steric congestion than a 2-Me substituent is not surprising if one envisages approach of the pyridine nucleophile from above (or at an angle to) the dienyl ring towards the C(5) atom, as shown above.





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