

Steric and electronic influences on the addition of pyridines to the tricarbonyl(2-methoxycyclohexadienyl)iron(II) cation

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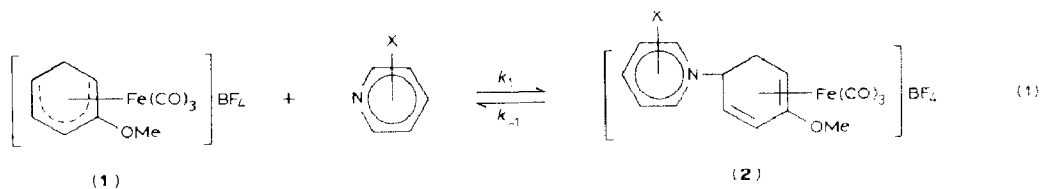
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Abstract

Kinetic studies of the reversible addition of pyridines to the cation $[\text{Fe}(1-5-\eta-2\text{-MeOC}_6\text{H}_6)(\text{CO})_3]^+$ (**1**) provide further support of the dependence of the rate on the steric and electronic nature of the attacking nucleophile. A comparison of plots of $\log k_1$ versus $\text{p}K_a$ for pyridine additions to **1** and to the cations $[\text{Fe}(1-5-\eta\text{-C}_6\text{H}_7)(\text{CO})_3]^+$ (**3**) and $[\text{Fe}(1-5-\eta\text{-C}_7\text{H}_9)(\text{CO})_3]^+$ (**4**) indicate that the accumulation of positive charge in the transition states of these systems decreases along the series $\text{C}_6\text{H}_7 > 2\text{-MeOC}_6\text{H}_6 > \text{C}_7\text{H}_9$ (i.e. **3** > **1** > **4**, in accordance with their decreasing electrophilicities.

Introduction

In previous reports we have examined the way in which the steric and electronic properties of coordinated organic molecules affect their reactivity towards a wide variety of aromatic substrates such as amines [1–7], amides [8], tertiary phosphines [9–12], activated arenes [13–15], and aryltrimethyl-silanes and -stannanes [16,17]. Recently a study of the reactions between the organometallic complexes $[\text{Fe}(1-5-\eta\text{-Dienyl})(\text{CO})_3]^+$ (Dienyl = C_6H_7 (**3**) or C_7H_9 (**4**)) and a wide variety of X-substituted pyridines (X = H, 2-Me, 3-Me, 4-Me, 4-Ph, 2-Cl, 3-CN, 2-CHO, 4-Ac, 2,4-Me₂, 2,5-Me₂, 2,6-Me₂, 3,4-Me₂, 3,5-Me₂ or 2,4,6-Me₃) [18,19] in MeCN was undertaken in order to throw some light on the importance of basicity and steric effects in controlling the nucleophilicity of amines towards coordinated organic molecules. These reactions afforded tricarbonyl (1-4- η -5-*exo-N*-pyridiniocyclohexa- (or cyclohepta-)1,3-diene)iron complexes in high yields. We have now carried out a kinetic study of the reaction between $[\text{Fe}(1-5-\eta-2\text{MeOC}_6\text{H}_6)(\text{CO})_3]^+$ (**1**) and X-substituted pyridines (X = H, 2-Me, 3-Me, 4-Me, 4-Ac, 4-CN, 2-Et, 2,4-Me₂, 2,5-Me₂, 2,6-Me₂, 3,4-Me₂, 3,5-Me₂ or 2,4,6-Me₃) in MeCN (eq. 1).



Comparison of the results with those reported earlier for pyridine additions to $[\text{Fe}(1\text{-}5\text{-}\eta\text{-Dienyl})(\text{CO})_3]^+$ complexes (Dienyl = C_6H_7 or C_7H_9) [18,19] provides the first quantitative information on the relationship between the nature of the coordinated organic substrates and the degree of positive charge in the transition states in their reactions with amines.

Experimental

Materials. Complex **1** was synthesized and purified as previously described [20]. The various pyridine nucleophiles were purchased (BDH or Aldrich) in the purest grade available and freshly distilled over KOH pellets before use, except for 4-cyanopyridine which was used as supplied. Acetonitrile (BDH) was distilled in bulk and stored over molecular sieves (size 3 Å) under nitrogen.

Product isolation and characterisation

For those with $\text{X} = \text{H}$ and Et see ref. 18 and 5, respectively.

Tricarbonyl(1-4-η-5-exo-N-4-methylpyridino-2-methoxycyclohexa-1,3-diene)iron tetrafluoroborate ($\text{X} = 4\text{-Me}$). Solutions of $[\text{Fe}(\eta^5\text{-2-MeOC}_6\text{H}_6)(\text{CO})_3][\text{BF}_4^-]$ (0.05 g, 0.149 mmol) in CH_3CN (10 cm^3) and 4-methyl pyridine (198 μl , 1.49 mmol) in CH_3CN (10 cm^3) were mixed under nitrogen and the mixture was kept at room temperature for 10 min. Rotary evaporation of the mixture under nitrogen at 35°C afforded an oil, which was shaken with 20 cm^3 of dry and deoxygenated petroleum spirit (60–80°C). Rotary evaporation of the solvent under nitrogen gave a yellow oil, which gradually turned brown on exposure to air. The yield was 0.039 g, 60%.

IR $\nu(\text{CO})$ in CH_3CN ; 2055 and 1980 cm^{-1} . IR $\nu(\text{BF}_4^-)$ in nujol mull: ca. 1060 cm^{-1} . $^1\text{H NMR}$ (τ) in acetonitrile- d_3 : 6.83 (2H, m, H(1,4)), 4.17 (1H, m, H(3)), 4.78 (1H, m, H(5')), 8.15 (1H, m, H(6)), 7.18 (1H, m, H(6')), 1.46 (2H, d, aromatic), 2.21 (2H, d, Aromatic), 7.42 (3H, s, CH_3) and 6.16 (3H, s, OCH_3).

Tricarbonyl(1-4-η-5-exo-N-2,4,6-trimethyl pyridino-2-methoxycyclohexa-1,3-diene)iron tetrafluoroborate ($\text{X} = 2,4,6\text{-}(\text{Me})_3$). A similar procedure to that above using $[\text{Fe}(\eta^5\text{-2-MeOC}_6\text{H}_6)(\text{CO})_3][\text{BF}_4^-]$ (0.05, 0.149 mmol) and 2,4,6-trimethylpyridine (198 μl , 1.49 mmol) in CH_3CN (20 cm^3) gave an intractible yellowish-brown solid. This was washed several times with deoxygenated sodium-dried diethyl ether and dried by suction on a glass frit to give a light brown solid (0.048 g, 71% yield). The product gradually darkened on exposure to air.

IR $\nu(\text{CO})$ in CH_3CN : 2055 and 1980 cm^{-1} . IR $\nu(\text{BF}_4^-)$ in nujol mull: ca. 1060 cm^{-1} . $^1\text{H NMR}$ (τ) in nitromethane- d_3 : 6.91 (2H, m, H(1,4)), 4.23 (1H, m, H(3)), 4.72 (1H, m, H(5')), 8.19 (1H, m, H(6)), 7.21 (1H, m, H(6')), 2.82 (2H, s, aromatic), 7.45 (6H, s, CH_3), 7.60 (3H, s, CH_3) and 6.18 (3H, s, OCH_3).

Kinetic studies. The reactions in CH_3CN were studied under pseudo-first-order conditions involving a large excess of the pyridine nucleophile ($[\text{Fe}] = 1.5 \times 10^{-3}$

mol dm⁻³, [amine] = 0.01–1.0 mol dm⁻³). The reactions were monitored at 390 nm by use of a thermostatted ($\pm 0.1^\circ\text{C}$) stopped-flow spectrophotometer; at this wavelength there was a large decrease in absorbance. The reaction traces were recorded and analysed with a rapid data-capture system purchased from Lombardi Scientific Ltd. and computer programs developed jointly with Lombardi (UK) Ltd. (see ref. 21). Pseudo-first-order rate constant, k_{obs} , were calculated from the slopes of plots of $\log(A_t - A_\infty)$ versus time which were linear for at least 75% completion of reaction. Each k_{obs} value is the average for at least six separate runs, with an average reproducibility of $\pm 3\%$. The second-order rate constants, k_1 , were derived by a least-squares fit to the k_{obs} versus [amine] plots, and the errors quoted are the standard deviations.

Results and discussion

(a) *Nature of the reactions.* The nature of the reactions between the organometallic complex **1** and a wide variety of pyridines has been established by the isolation and characterisation of the pyridinium adducts (**2**: X = H, 4-Me, 2-Et or 2,4,6-Me₃) and by in situ IR and ¹H NMR spectral studies of several other products [5,14,18]. Their IR spectra exhibited two strong carbonyl bands at ca. 2055 and 1980 cm⁻¹. The same two $\nu(\text{CO})$ bands were observed during the IR studies of reactions (1) when a large excess of the amine nucleophile was used, indicating the formation of the same tricarbonyl(1-4- η -5-*exo*-N-pyridinio-2-methoxycyclohexa-1,3-diene)iron complexes. In addition to the two strong $\nu(\text{CO})$ bands at 2055 and 1980 cm⁻¹, products **2** also exhibited the characteristic broad band at ca. 1060 cm⁻¹ attributed to the BF₄⁻ anion. For each of the reactions of complex **1** with equimolar amounts of the appropriate amine nucleophile, in situ IR studies showed the presence of $\nu(\text{CO})$ bands at 2120 and 2065 cm⁻¹ as well as those due to products **2**, indicating that reactions 1 are equilibrium processes.

(b) *Kinetics and Mechanism.* Kinetic data for the addition of substituted pyridines to complex **1** are listed in Table 1. They reveal close adherence to the second order rate law (eq. 2), which is consistent with an equilibrium process. The

$$\text{Rate} = k_1[\text{Complex}][\text{amine}] + k_{-1}[\text{Complex}]$$

$$k_{\text{obs}} = k_1[\text{amine}] + k_{-1} \dots \dots \dots \quad (2)$$

values of k_{-1} for the substituted pyridines in Table 1 tend to zero because of the very low temperature, 0°C, at which they were studied. At higher temperatures (see ref. 5 and 19), the k_{-1} values are expected to increase gradually because of the reversibility. Thus plots of k_{obs} versus [amine] are linear with non-zero intercepts. The slopes of these plots give k_1 , the second-order rate constant for direct addition to the dienyl ring of **1**, while the intercept on the k_{obs} axis correspond to k_{-1} , the first-order-rate constant for the dissociation of the amine nucleophile from the pyridinium adducts **2**.

Influence of nucleophile basicity

A close look at the unhindered pyridines in Table 2 clearly demonstrates that reactivity decreases with decreasing basicity of the pyridine nucleophile. In general, the rate of addition of pyridines to complex **1** follows the sequence 3,5-Me₂ >

Table 1

Kinetic data for reaction of $[\text{Fe}(\text{CO})_3(1-5-\eta-2-\text{MeOC}_6\text{H}_6)]\text{BF}_4$ with substituted pyridines in CH_3CN at 0°C . $[\text{Fe}] = 1.5 \times 10^{-3} \text{ mol dm}^{-3}$

Nucleophile	$10^2[\text{Nucleophile}]$ (mol dm^{-3})	k_1 ($\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) ^a	k_{-1} (s^{-1}) ^a
$\text{NC}_5\text{H}_3\text{Me}_2-3,5$	1.0–4.0	1332 (10)	0.40 (0.30)
$\text{NC}_5\text{H}_3\text{Me}_2-3,4$	1.0–5.0	1257 (4)	0.22 (0.13)
$\text{NC}_5\text{H}_4\text{Me}-4$	1.0–6.0	1037 (4)	0.16 (0.34)
$\text{NC}_5\text{H}_4\text{Me}-3$	1.0–6.0	823 (2)	0.93 (0.12)
$\text{NC}_5\text{H}_3\text{Me}_2-2,4$	1.0–8.0	182 (4)	0.30 (0.21)
$\text{NC}_5\text{H}_3\text{Me}_2-2,5$	1.0–8.0	104 (8)	0.02 (0.38)
$\text{NC}_5\text{H}_4\text{Ac}-4$	2.5–20.0	76.5 (0.3)	0.04 (0.03)
$\text{NC}_5\text{H}_4\text{CN}-4$	5.0–100.0	20.2 (1.1)	16.2 (0.6)
$\text{NC}_5\text{H}_2\text{Me}_3-2,4,6$	10.0–50.0	11.4 (0.07)	0.03 (0.02)
$\text{NC}_5\text{H}_3\text{Me}_2-2,6$	10.0–80.0	10.4 (0.06)	0.36 (0.03)

^a Determined by a least squares fit to equation 2; figures in parentheses denote the standard deviation.

$3,4-\text{Me}_2 > 4-\text{Me} > 3-\text{Me} > \text{H} > 2,4-\text{Me}_2 > 2,5-\text{Me}_2 > 2-\text{Me} > 4-\text{Ac} > 2-\text{Et} > 4-\text{CN} > 2,4,6-\text{Me}_3 > 2,6-\text{Me}_2$, with a reactivity range of ca. 10^2 . This is demonstrated quantitatively by the linear free-energy relationship obtained on plotting $\log k_1$ against the $\text{p}K_a$ of the amine conjugate acid in water [22] (Fig. 1). Thus reaction 1 obeys the Bronsted relationship (eq. 3), with slope, α of 0.43 ± 0.01 .

$$\log k_1 = \text{p}K_a + \text{constant} \dots \dots \dots (3)$$

It is noteworthy that this slope is very similar to the α value of ca. 0.5 found for amine addition to free carbonium ions [23], indicating a strong dependence of rate on amine basicity and suggesting, by the reasoning of Pearson et al. [24], that cation 1 is a 'hard' species. Similar plots for addition of such unhindered pyridines to $[\text{Fe}(1-5-\eta-\text{C}_6\text{H}_7)(\text{CO})_3]^+$ (3) and $[\text{Fe}(1-5-\eta-\text{C}_7\text{H}_9)(\text{CO})_3]^+$ (4) gave α values of 0.97 ± 0.04 and 0.39 ± 0.03 respectively [18,19], indicating that the electrophilicities

Table 2

Variation of rates with amine basicity for the reactions of pyridines with $[\text{Fe}(\text{CO})_3(1-5-\eta-2-\text{MeOC}_6\text{H}_6)]\text{BF}_4$ in CH_3CN at 0°C

Amine	k_1 ($\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$)	$\text{p}K_a$ (H_2O) ^a
$\text{NC}_5\text{H}_3\text{Me}_2-3,5$	1332	6.55
$\text{NC}_5\text{H}_3\text{Me}_2-3,4$	1257	6.52
$\text{NC}_5\text{H}_4\text{Me}-4$	1037	6.50
$\text{NC}_5\text{H}_4\text{Me}-3$	823	6.02
NC_5H_5 ^b	425	5.60
$\text{NC}_5\text{H}_3\text{Me}_2-2,4$	182	7.14
$\text{NC}_5\text{H}_3\text{Me}_2-2,5$	104	6.63
$\text{NC}_5\text{H}_4\text{Me}-2$ ^b	96.0	6.41
$\text{NC}_5\text{H}_4\text{Ac}-4$	76.5	3.70
$\text{NC}_5\text{H}_4\text{Et}-2$ ^b	42.1	5.89
$\text{NC}_5\text{H}_4\text{CN}-4$	20.2	2.38
$\text{NC}_5\text{H}_2\text{Me}_3-2,4,6$	11.4	7.43
$\text{NC}_5\text{H}_3\text{Me}_2-2,6$	10.4	7.35

^a From ref. 22a, except for $\text{NC}_5\text{H}_2(\text{Me})_3-2,4,6$ [22b]. ^b Rate constants from ref. 5 and 18.

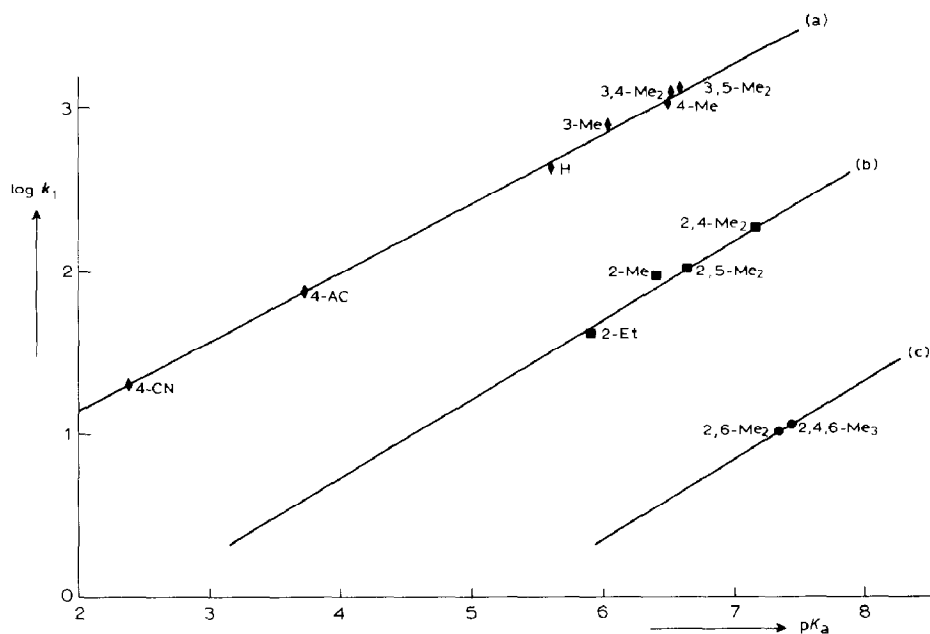


Fig. 1. Brønsted plots for the reaction of $[\text{Fe}(\text{CO})_3(1-5-\eta-2\text{-MeOC}_6\text{H}_6)]\text{BF}_4$ in CH_3CN at 0°C with (a) non-sterically hindered pyridines; (b) Pyridines with 2-Me or 2-Et groups and (c) Pyridines with 2,6-Me₂ groups.

of these organometallics decrease in the series $\text{C}_6\text{H}_7 > 2\text{-MeOC}_6\text{H}_6 > \text{C}_7\text{H}_9$ (i.e. $3 > 1 > 4$) (Table 3). The results also reveal that the accumulation of positive charge in the transition states of these pyridine reactions increases with increasing electrophilicities of the organometallics being attacked; that is, in the sequence $3 > 1 > 4$. Thus, the nature of the coordinated organometallics has a strong influence on the degree of positive charge formation in the transition states formed in their reactions with amines. The assignment of a 'hard' character to the dienyl rings of complexes **1**, **3**, and **4** is consistent with their frequent representation as stabilised carbonium ions, and with the high positive charges shown by calculations [25] to reside on the ring carbons.

Steric influence of nucleophile

The steric influence in pyridine additions to cation **1** is clearly demonstrated in Fig. 1 and in Table 4 (the rates fall in the sequence $\text{NC}_5\text{H}_5 > \text{NC}_5\text{H}_4\text{Me-2} > \text{NC}_5\text{H}_4\text{Et-2} > \text{NC}_5\text{H}_3\text{Me}_2,2,6$; relative rates 41/9/4/1). The three straight lines shown in the figure are plots of $\log k_1$ against the $\text{p}K_a$ of the amine conjugate acid

Table 3

Summary of α values for pyridine additions to $[\text{Fe}(\text{CO})_3(1-5-\eta\text{-Dienyl})]\text{BF}_4$ complexes in CH_3CN

Dienyl	α
C_6H_7	0.97 ± 0.04
2-MeOC ₆ H ₆	0.43 ± 0.01
C_7H_9	0.39 ± 0.03

Table 4

Steric effects on rates for addition of substituted pyridines to $[\text{Fe}(\text{CO})_3(1-5-\eta-2-\text{MeOC}_6\text{H}_6)]\text{BF}_4$ in CH_3CN at 0°C

Amine	k_1 ($\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$)	Relative k_1
NC_5H_5 ^a	425	41
$\text{NC}_5\text{H}_4\text{Me-2}$ ^a	96.0	9
$\text{NC}_5\text{H}_4\text{Et-2}$ ^a	42.1	4
$\text{NC}_5\text{H}_3\text{Me}_2\text{-2,6}$	10.4	1

^a Rate constants from ref. 5 and 18.

for (a) non-sterically hindered pyridines, (b) pyridines with a methyl or ethyl group at the 2-position, and (c) pyridines with methyl groups at both 2- and 6-positions. The difference of ca. 1 log unit between lines (a) and (b) corresponds with a 10-fold rate decrease due to the steric effect of groups in the 2-position of the pyridine nucleophile. This same 10-fold rate decrease has been reported for pyridine additions to complexes **3** [18] and **4** [19]. Thus there is a 10-fold rate decrease caused by the steric effect of successively introducing methyl (or ethyl) groups in the 2-position of pyridine for nucleophilic attack on organometallics of the type $[(\text{dienyl})\text{M}(\text{CO})_3]^+$ ($\text{M} = \text{Fe}, \text{Ru}$ or Os), and this may be general for pyridine additions to coordinated organic molecules. The difference of ca. 2.4 log units between lines (a) and (c) indicates that a ca. 250-fold rate decrease is caused by steric effects of methyl groups at the 2- and 6-positions. These results confirm the importance of steric effects in reactions 1, and the difference of ca. 1.3 log units between graphs (b) and (c) demonstrates that the steric effects of successive addition of methyl groups to pyridine (2-Me; 2,6-(Me)₂) are not additive. This value of ca. 1.3 is very similar to the values of ca. 1.6 and 1.5 found for the analogous reactions of pyridine with complexes **3** [18] and **4** [19], respectively, and confirms that, as expected, steric hindrance by methyl groups at the 2,6-positions of the pyridine nitrogen has a more pronounced effect on the entropy of the transition state than that by only one methyl group. With complexes **3** and **4**, steric hindrance by methyl groups at the 2- and 6-positions of the pyridine caused 10 000-fold and 1 000-fold rate decreases, respectively [18,19]. The greater steric influence for pyridine additions to complex **3** than to those for complex **4** is in keeping with the fact that more reactive cationic complex is expected to exhibit much greater variations in rate for attack by nucleophiles [26].

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