Mechanism of Addition of 2-Ethylpyridine to Tricarbonyl(1—5-η-dienyl)iron(II) Cations (dienyl = C_6H_7, 2-$MeOC_6H_6$, or C_7H_9)

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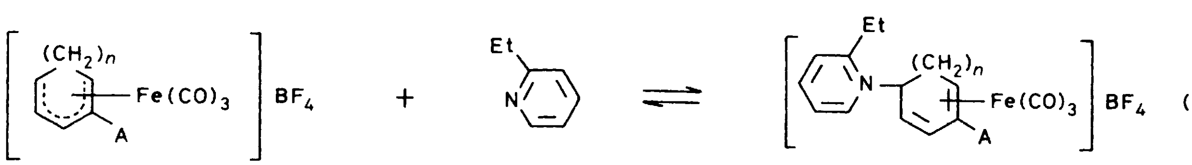
Detailed kinetic studies of the reactions between the complexes $[Fe(CO)_3(1—5\text{-}\eta\text{-dienyl})]BF_4$ (**1**; dienyl = C_6H_7, 2-$MeOC_6H_6$, or C_7H_9) and 2-ethylpyridine in MeCN reveal the rate law, rate = k_1[Fe][amine] + k_{-1}[Fe]. The observed rate trend C_6H_7 > 2-$MeOC_6H_6$ > C_7H_9 (*e.g.* 46:6.4:1 at 0 °C) and the low $\Delta H_1^\ddagger$ values and the large negative $\Delta S_1^\ddagger$ values are consistent with direct addition (k_1) to the dienyl rings of complexes (**1**). On the other hand, the relatively much higher $\Delta H_{-1}^\ddagger$ values are as expected for bond cleavage in dissociation (k_{-1}) as is the positive $\Delta S_{-1}^\ddagger$ of +41 ± 13 J K^{-1} mol^{-1} determined for the addition of 2-ethylpyridine to (**1**; dienyl = C_6H_7). A plot of $\Delta H_{-1}^\ddagger$ *versus* $\Delta S_{-1}^\ddagger$ is linear, the slope of which gives an isokinetic temperature of 208 ± 20 K, indicating entropy control over the dissociative process.

The addition of a wide variety of aromatic substrates to co-ordinated π-hydrocarbons to form new 1,3-diene organometallics is well known.[1-8]

Recently a study of the reactions between $[Fe(1—5\text{-}\eta\text{-}C_6H_7)(CO)_3]^+$ 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 MeCN was undertaken in order to demonstrate the importance of basicity and steric effects in controlling amine nucleophilicity towards co-ordinated π-hydrocarbons. These reactions afforded products of the type tricarbonyl(1—4-η-5-*exo*-*N*-pyridiniocyclohexa-1,3-diene)iron tetrafluoroborate in yields of 60—70%. However, apart from the reactions of pyridine and 2-methylpyridine with the dienyl complexes (**1**),[9] very little quantitative information is currently available concerning the thermodynamics of the reactions of pyridines with co-ordinated π-hydrocarbons.



(1)

	n	A
(**1a**)	1	H
(**1b**)	1	MeO
(**1c**)	2	H

(**2a**)
(**2b**)
(**2c**)

As an extension to these studies, this paper reports the results of a detailed kinetic study of the reaction of 2-ethylpyridine with the organometallics (**1a**)—(**1c**) in MeCN [equation (1)] designed to enrich our understanding of the mechanism and thermodynamics of such systems.

Experimental

Materials.—The complexes (**1a**)—(**1c**) were synthesized and purified as previously described.[10,11] 2-Ethylpyridine was freshly distilled over KOH pellets prior to use. Acetonitrile (BDH) was distilled in bulk and stored over molecular sieves (size 3 Å) under a dinitrogen atmosphere.

Kinetic Studies.—All of the reactions (1) in MeCN were studied under pseudo-first-order conditions using a large excess of 2-ethylpyridine ([Fe] = 1.5 × 10^{-3}, [2-EtC_5H_4N] = 0.01—0.10 mol dm^{-3}). The reactions were rapid and were studied using a thermostatted (±0.1 °C) stopped-flow spectrophotometer at a wavelength of 390 nm where a large decrease in absorbance was observed. The reaction traces were recorded and analysed using a rapid data-capture system (Lombardi Scientific Ltd.), employing computer programs developed jointly with Lombardi (U.K.) Ltd. and described elsewhere.[12] Pseudo-first-order rate constants, $k_{obs.}$, 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 $k_{obs.}$ is the average from at least six separate runs, with an average reproducibility of ±3%. Second-order rate constants, k_1, were calculated by least-squares analysis of plots of $k_{obs.}$ *versus* [2-EtC_5H_4N], the errors quoted being the appropriate standard deviations. Activation enthalpies were obtained from the slopes of Arrhenius plots of log k_1 or log k_{-1} *versus* T^{-1}, calculated by a least-squares method. The errors quoted are the standard errors of estimation from these analyses. Entropies of activation were calculated using the second- and first-order rate constants, k_1 and k_{-1} respectively.

Results and Discussion

Nature of the Reactions.—The nature of the reactions between the organometallic complexes (**1**) and a wide variety of pyridines has been established by the isolation and characterisation of the pyridinium adducts and by *in situ* i.r. and ^1H n.m.r. spectral studies.[2,9] Their i.r. spectra exhibited two strong carbonyl bands at *ca.* 2 055 and 1 980 cm^{-1}. The same two ν(CO) bands were observed during the i.r. studies of reactions (1) using a large excess of 2-ethylpyridine, indicating the formation of the same tricarbonyl[1—4-η-5-*exo*-*N*-pyridiniocyclohexa-(or cyclohepta-)1,3-diene]iron complexes. Products (**2a**) and (**2b**) are yellow crystalline solids while (**2c**)

Table 1. Kinetic results for reactions of $[Fe(CO)_3(1—5\text{-}\eta\text{-dienyl})]BF_4$ (1.5×10^{-3} mol dm^{-3}) with 2-ethylpyridine in MeCN

Dienyl	θ_c/°C	$10^2[2\text{-}EtC_5H_4N]$/ mol dm^{-3}	$k_{obs.}$/s^{-1}	k_1*/dm^3 mol^{-1} s^{-1}	k_{-1}*/s^{-1}
C_6H_7	0.0	1.0	4.18	300 ± 5	1.17 ± 0.03
	0.0	2.0	7.17		
	0.0	4.0	13.1		
	0.0	8.0	25.2		
	0.0	10.0	31.1		
	5.4	1.0	6.19	357 ± 2	2.55 ± 0.10
	5.4	2.0	9.58		
	5.4	4.0	16.8		
	5.4	8.0	31.3		
	5.4	10.0	38.1		
$2\text{-}MeOC_6H_6$	0.0	1.0	2.34	42.1 ± 0.4	1.91 ± 0.02
	0.0	2.0	2.78		
	0.0	4.0	3.55		
	0.0	8.0	5.26		
	0.0	10.0	6.15		
	8.5	1.0	4.10		
	8.5	2.0	5.30	87.3 ± 2	4.03 ± 0.07
	8.5	4.0	7.50		
	8.5	8.0	11.0		
C_7H_9	0.0	1.0	0.097	6.54 ± 0.04	0.035 ± 0.002
	0.0	2.0	0.165		
	0.0	4.0	0.301		
	0.0	8.0	0.560		
	0.0	10.0	0.686		
	8.5	1.0	0.180	11.5 ± 0.03	0.063 ± 0.001
	8.5	2.0	0.291		
	8.5	4.0	0.520		
	8.5	8.0	0.981		
C_6H_7	10.5	1.0	8.50	406 ± 4	4.51 ± 0.26
	10.5	2.0	13.1		
	10.5	4.0	20.2		
	10.5	8.0	37.0		
	10.5	10.0	45.2		
	15.4	1.0	12.0	482 ± 3	7.60 ± 0.20
	15.4	2.0	17.3		
	15.4	4.0	27.2		
	15.4	8.0	46.0		
	15.4	10.0	55.6		
$2\text{-}MeOC_6H_6$	15.4	1.0	9.26	178 ± 1	7.55 ± 0.04
	15.4	2.0	11.2		
	15.4	4.0	14.7		
	15.4	8.0	21.8		
	15.4	10.0	25.4		
	20.2	1.0	15.2		
	20.2	2.0	18.1	262 ± 2	12.7 ± 0.10
	20.2	4.0	23.0		
	20.2	8.0	33.6		
	20.2	10.0	38.9		
C_7H_9	15.8	1.0	0.291	17.5 ± 0.08	0.125 ± 0.005
	15.8	2.0	0.485		
	15.8	4.0	0.820		
	15.8	8.0	1.52		
	15.8	10.0	1.87		
	22.2	1.0	0.423		
	22.2	2.0	0.678	24.7 ± 0.10	0.175 ± 0.006
	22.2	4.0	1.15		
	22.2	8.0	2.15		
	22.2	10.0	2.65		

* Estimated by a least-squares fit to equation (2); with standard errors of estimate.

Table 2. Rate and activation parameters for reactions of $[Fe(CO)_3(1-5-\eta\text{-dienyl})]BF_4$ with 2-ethylpyridine in MeCN

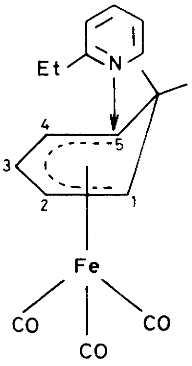
Dienyl	k_1 relative (0 °C)	$\Delta H_1^{\ddagger}$/ kJ mol^{-1}	$\Delta S_1^{\ddagger}$/ J K^{-1} mol^{-1}	$\Delta H_{-1}^{\ddagger}$/ kJ mol^{-1}	$\Delta S_{-1}^{\ddagger}$/ J K^{-1} mol^{-1}
C_6H_7	46.0	17.5 ± 0.54	−133 ± 2	77.4 ± 3.6	+41 ± 13
2-MeOC_6H_6	6.4	58.8 ± 0.80	−2.6 ± 2.7	60.0 ± 0.83	−20 ± 3
C_7H_9	1.0	37.8 ± 0.54	−90 ± 2	48.0 ± 2.2	−97 ± 8

was isolated as a yellow oil. All three are sensitive to air in their pure state and gave poor microanalyses. For example, the yellow crystalline solids (**2a**) and (**2b**) turned dark brown within minutes of exposure to air and showed the absence of nitrogen in their microanalyses, indicating loss of the pyridinium group during the decomposition process. However, the two strong ν(CO) bands at 2 055 and 1 980 cm^{-1} as well as the broad band at *ca.* 1 060 cm^{-1} (BF_4^-) found for products (**2**) immediately after isolation are characteristic of cationic 1,3-diene-substituted iron complexes.[2,9,13] Since the reactions are very rapid and were studied kinetically by monitoring the large decrease in absorbance due to the disappearance of the starting organometallics (**1**), no interference is expected from the product decomposition. For each of the reactions of complexes (**1**) with equimolar amounts of 2-ethylpyridine, *in situ* i.r. studies showed the presence of ν(CO) bands at 2 120 and 2 065 cm^{-1} as well as those due to the products (**2**), indicating that reactions (1) are equilibrium processes.

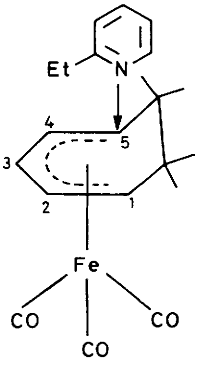
Kinetics and Mechanism.—Kinetic results for the addition of 2-ethylpyridine to each of the dienyl complexes (**1**) in MeCN are collected in Table 1. These results show close adherence to the second-order rate law (2) which is consistent with an

$$\text{Rate} = k_1[\text{complex}][2\text{-EtC}_5H_4N] + k_{-1}[\text{complex}]$$
$$k_{\text{obs.}} = k_1[2\text{-EtC}_5H_4N] + k_{-1} \qquad (2)$$

equilibrium process. Thus plots of $k_{\text{obs.}}$ *versus* $[2\text{-EtC}_5H_4N]$ are linear with non-zero intercepts. The slopes of these plots afford k_1, the second-order rate constant for attack on the dienyl rings of (**1**), while the intercepts on the $k_{\text{obs.}}$ axis refer to k_{-1}, the first-order rate constant for the dissociation of 2-ethylpyridine from the pyridinium adducts (**2**). The k_1 values in Tables 1 and 2 are seen 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 2-ethylpyridine to these complexes are 46:6.4:1 (Table 2), indicating direct addition to the dienyl rings of (**1**). Similar rate trends have been found for the addition of a wide variety of nucleophiles to complexes (**1**),[5–8] processes known to involve direct addition to the dienyl rings. The greater reactivity of the parent complex $[Fe(1-5-\eta\text{-}C_6H_7)(CO)_3]BF_4$ (**1a**) compared with $[Fe(1-5-\eta\text{-}2\text{-MeOC}_6H_6)(CO)_3]BF_4$ (**1b**) is due to the mesomeric influence of the methoxide group which has been demonstrated[14] from INDO molecular-orbital calculations to decrease the positive charge on the dienyl C(5) atom, the site of nucleophilic addition. The more pronounced increase in rate between the parent complex (**1a**) and $[Fe(1-5-\eta\text{-}C_7H_9)(CO)_3]BF_4$ (**1c**) is readily attributed to the steric hindrance caused by the additional methylene group in the latter if one assumes approach of 2-ethylpyridine from above the dienyl rings.



(**1a**)



(**1c**)

The low $\Delta H_1^{\ddagger}$ values and large negative $\Delta S_1^{\ddagger}$ values found for reactions (1) (Table 2) are also as expected for direct addition to the dienyl rings. The observed rate trend in the order $C_6H_7 > 2\text{-MeOC}_6H_6 > C_7H_9$ can be seen to arise from a play-off between enthalpy and entropy effects. Thus, the rapidity of the reaction of the C_6H_7 complex compared with that of C_7H_9 arises from a much smaller $\Delta H_1^{\ddagger}$ (despite a much higher $\Delta S_1^{\ddagger}$) (Table 2), while the intermediate rate for the 2-MeOC_6H_6 complex is associated with the least negative $\Delta S_1^{\ddagger}$ and the highest $\Delta H_1^{\ddagger}$ value. On the other hand, the much larger $\Delta H_{-1}^{\ddagger}$ values are as expected for bond cleavage in dissociation (k_{-1}), as is the positive $\Delta S_{-1}^{\ddagger}$ of +41 ± 13 J K^{-1} mol^{-1} determined for the addition of 2-ethylpyridine to complex (**1a**). The negative $\Delta S_{-1}^{\ddagger}$ values found for the reactions of 2-ethylpyridine with (**1b**) and (**1c**) (Table 2) may suggest solvation effects in these reactions. Thus MeCN–C(dienyl) bond making with the resultant formation of an *endo*-MeCN intermediate could lead to a negative entropy of activation. On the other hand, the possibility of an internal S_N2 reaction in which Fe–C(diene) bond making accompanies C(diene)–amine bond breaking cannot be excluded as this also would lead to a negative activation entropy due to a tightly bonded transition state. Both the $\Delta H_{-1}^{\ddagger}$ and $\Delta S_{-1}^{\ddagger}$ values decrease in the order $C_6H_7 > 2\text{-MeOC}_6H_6 > C_7H_9$. However a plot of $\Delta H_{-1}^{\ddagger}$ *versus* $\Delta S_{-1}^{\ddagger}$ is linear, the slope of which gives an isokinetic temperature of 208 ± 20 K [which is much lower than the temperature range of 273—295 K in which reactions (1) were studied], indicating entropy control over the dissociative process.

It is possible that the reversibility of reactions (1) demonstrated here with 2-ethylpyridine is a general phenomenon in the reaction of pyridines with complexes (**1**). An earlier work[9] had indicated that such reactions proceed to completion as indeed is observed at 0 °C (the temperature at which most of the earlier work was carried out) where k_{-1} tended to zero. At higher temperatures, k_{-1} is expected to increase gradually as demonstrated here and in the reactions of other substituted pyridines[15] with complexes (**1**).

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