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Significance of entropies and volumes of activation for the addition of 4-formylpyridine to tricarbonyl(1–5-η-dienyl)iron(II) complexes (dienyl = C_6H_7, 2-$MeOC_6H_6$ and C_7H_9)

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Abstract

The kinetics of the addition of 4-formylpyridine to the coordinated dienyl ligand in tricarbonyl(1–5-η-dienyl)iron(II) complexes (**1**; dienyl = C_6H_7, 2-$MeOC_6H_6$ and C_7H_9) has been studied as a function of temperature and pressure in acetonitrile by stopped-flow techniques. The observed rate law is $k_{obs} = k_1$ [amine] + k_{-1}, and low $\Delta H_1^{\#}$ values, large negative $\Delta S_1^{\#}$ and negative $\Delta V_1^{\#}$ values indicate that there is direct addition (k_1) to the dienyl rings of complexes **1**. On the other hand, the relatively higher $\Delta H^{\#}_{-1}$ values and positive $\Delta S^{\#}_{-1}$ values are as expected for bond cleavage (k_{-1}), as are the positive $\Delta V^{\#}_{-1}$ values determined for the dissociation of 4-formylpyridine from **1** (dienyl = C_6H_7 and 2-$MeOC_6H_6$). The large negative $\Delta S^{\#}_{-1}$ value of -150 ± 7 J K^{-1} mol^{-1} found for the dissociation of 4-formylpyridine from **1** (dienyl = C_7H_9) is consistent with the insensitivity of this reaction to pressure changes and so with operation of the previously suggested interchange/"ordered transition state" mechanism. A plot of $\Delta H^{\#}_{-1}$ *versus* $\Delta S^{\#}_{-1}$ yields an isokinetic temperature of 260 ± 3 K, indicating entropy control in the dissociative process.

Introduction

The addition of a wide range of aromatic substrates to coordinated π-hydrocarbons to form novel 1,3-diene organometallics is well known [1–17]. We recently studied the effect of temperature and pressure on the addition of 4-cyanopyridine [18] and 4-ethylpyridine [19] to $[Fe(1\text{–}5\text{-}\eta\text{-dienyl})(CO)_3]^+$ complexes (**1**; dienyl = C_6H_7, 2-$MeOC_6H_6$ and C_7H_9) in order to improve understanding of the intimate mechanism of such reactions, and in particular to demonstrate the value of high pressure studies for the interpretation of the mechanism of amine additions to

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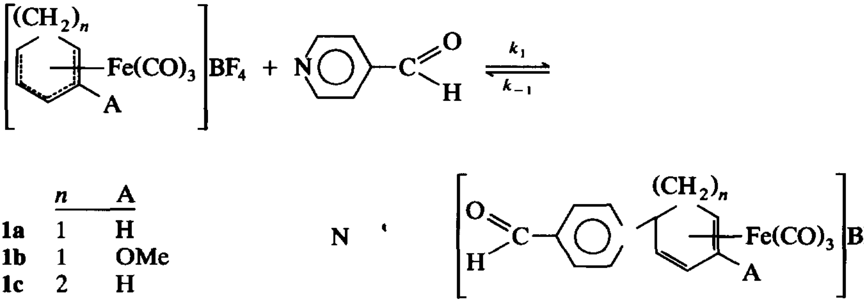
organometallics of type 1. These reactions afford products of the type tricarbonyl(1–4-η-5-exo-*N*-pyridiniocyclohexa- (or cyclohepta-)1,3-diene)iron tetrafluoroborate in 75–85% yields. The cyanopyridine reaction was insensitive to pressure changes, and this behaviour was rationalized in terms of an interchange/"ordered transition state" mechanism in which the volume changes associated with bond formation and bond breakage cancel out in the transition state [18]. On the other hand, the observed increase in rate with increasing pressure found for the 4-ethylpyridine reaction is as expected for an associative process in which direct addition occurs at the dienyl fragments of complexes 1 leading to C(diene)–N(4-Etpy) bond formation [19].

Detailed studies of the temperature dependence of amine additions to organometallics of type 1 [8,12,13] have demonstrated that the forward reaction (k_1) is generally characterized by relatively low $\Delta H_1^{\#}$ and high negative $\Delta S_1^{\#}$ values, whereas the reverse dissociation process (k_{-1}) is usually associated with significantly higher $\Delta H^{\#}_{-1}$ values and predominantly negative $\Delta S^{\#}_{-1}$ values [13], or in some cases, positive $\Delta S^{\#}_{-1}$ values [8]. Our observation of the predominance of large negative entropies of activation for the dissociative processes led to the "ordered transition state mechanism" [13]. Detailed pressure dependence studies on these systems could be expected to shed more light on the intimate mechanism, as has been demonstrated in our laboratories to be the case for several organometallic reactions [20–28].

The results of a detailed temperature and pressure dependence study of the rate of addition of 4-formylpyridine to complexes (**1**) in MeCN (eq. (1)) are reported.



(1)

	n	A
1a	1	H
1b	1	OMe
1c	2	H

2a
2b
2c

We have also isolated the new 1,3-diene products (**2**) and determined the overall equilibrium constant for reaction 1.

Experimental section

Materials

The complexes **1a**–**1c** were made and purified as previously described [29,30]. 4-Formylpyridine (4-CHOpy) was freshly distilled under vacuum from KOH pellets prior to use. Acetonitrile was distilled and stored over 3 Å molecular sieves under dinitrogen.

Product isolation and characterization

Tricarbonyl [1–4-η-5-exo-(N-4-formylpyridinio)cyclohexa-1,3-diene]-iron tetrafluoroborate (2a). Solutions of [(1–5-η-C_6H_7)Fe(CO)$_3$]BF_4 (**1a**, 0.05 g, 0.164 mmol) in MeCN (10 cm^3) and 4-formylpyridine (160 μl, 1.68 mmol) in MeCN (10 cm^3) were mixed under dinitrogen in a 50 cm^3 flask. The mixture was kept at room temperature for 10 min then the solvent was removed by rotary evaporation under dinitrogen at 35°C to give a yellow residue, which upon washing with cold petroleum ether (b.p. 40–60°C) gave **2a** as a yellow solid. This complex was found to be air-sensitive, turning into a yellowish-brown sticky solid on exposure to air, so was stored under dinitrogen. IR ν(CO) in MeCN: 2055 and 1980 cm^{-1}. The appearance of a strong band at ~ 1060 cm^{-1} (Nujol mull) confirmed the presence of the BF_4^- anion.

Tricarbonyl [1–4-η-5-exo-(N-4-formylpyridinio)2-methoxy-cyclohexa-1,3-diene] iron tetrafluoroborate (2b). A similar procedure starting from [(1–5-η-2-$MeOC_6H_6$)Fe(CO)$_3$]BF_4 (**1b**, 0.05 g, 0.149 mmol) and 4-formylpyridine (145 μl, 1.52 mmol) in MeCN (20 cm^3), gave **2b** as a yellow solid, which was dried on a vacuum line for 4 h. This product was also air-sensitive, and so was stored under dinitrogen. IR ν(CO) in MeCN: 2055 and 1980 cm^{-1}; ν(BF_4^-) in Nujol mull: ~ 1060 cm^{-1}.

Tricarbonyl [1–4-η-5-exo-(N-4-formylpyridinio)cyclohepta-1,3-diene]iron tetrafluoroborate (2c). A similar procedure starting from [(1–5-η-C_7H_9)Fe(CO)$_3$]BF_4 (**1c**, 0.05 g, 0.156 mmol) and 4-formylpyridine (150 μl, 1.58 mmol) gave an intractable oil after the washing with cold petroleum (b.p. 40–60°C). However, shaking of this oil with deoxygenated diethyl ether gave **2c** as a crystalline yellow solid. This solid is highly air-sensitive, rapidly turning into a dark-brown solid mass on exposure to air, and so was stored under dinitrogen. IR ν(CO) in MeCN: 2055 and 1980 cm^{-1}; (BF_4^-) in Nujol mull: ~ 1060 cm^{-1}.

Instrumentation

Reaction 1 is accompanied by significant UV–VIS spectral changes, involving an increase in absorbance at 410 nm (**1a** and **1c**) or 400 nm (**1b**), which were monitored with a Shimadzu UV 250 spectrophotometer. The spectral measurements were also used to estimate the equilibrium constant for reaction 1. Infrared studies were performed on a Perkin–Elmer 397 spectrophotometer. The kinetics of reaction 1 were studied under pseudo-first-order conditions, involving use of a large excess of 4-CHOpy. The addition reactions are fast, and were followed by use of a thermostatted (±0.1°C) Durrum D110 stopped-flow instrument coupled to an on-line data acquisition and analysis system [31]. Rate measurements at pressures of up to 150 MPa were performed with a home-made high pressure stopped-flow instrument [32]. Under all experimental conditions, plots of $\ln(A_\infty - A_t)$ *versus* t were linear for at least 2–3 half-lives, and yielded values of the observed first-order rate constants k_{obs}. Each k_{obs} value is the average from 5–6 separate runs. All rate and activation parameters were calculated by linear least-squares analysis.

Results and discussion

The 1,3-diene products **2** formed from the addition of 4-CHOpy to the dienyl complexes as shown in reaction 1, were isolated and shown by IR studies to be tricarbonyl[1-4-η-5-exo-N-pyridiniocyclohexa- (or cyclohepta-)1,3-diene]iron tetrafluoroborates (**2**). Their IR spectra showed two strong carbonyl bands at ~ 2055 and 1980 cm^{-1} and a strong $\nu(BF_4^-)$ band at ~ 1060 cm^{-1}, as previously established [3,8] for cationic 1,3-diene iron complexes derived from the addition of pyridines to the dienyl complexes **1**. All three products (**2a**–**2c**) are yellow solids when pure but are very air-sensitive, forming unidentified dark-brown materials. They are unstable in solutions (CH_2Cl_2, CH_3NO_2, $CHCl_3$ or acetone) that have not been purged with nitrogen, particularly in $CHCl_3$, in which decomposition is fastest. Since the reactions are very rapid and were studied kinetically by monitoring the large increase in absorbance due to the disappearance of the starting organometallics **1** to form products **2**, there was no interference from product decomposition. For each of the reactions of complexes **1** with equimolar amounts of 4-formylpyridine, *in situ* IR studies showed the presence of $\nu(CO)$ bands at 2120 and 2065 cm^{-1} as well as from the products **2**, indicating that reactions 1 are equilibrium processes.

The observed pseudo-first-order rate constant, k_{obs}, for reaction 1 depends linearly on the concentration of the nucleophile, as can be seen from the data summarized in Table 1. There is close adherence to the second-order rate law (eq. (2)), which is consistent with a reversible process.

$$k_{obs} = k_1[\text{4-CHOpy}] + k_{-1} \tag{2}$$

Thus plots of k_{obs} versus [4-CHOpy] are linear with non-zero intercepts. The slopes of these plots afford k_1 (the forward rate constant), and the intercepts on the k_{obs} axis give k_{-1} (the rate constant for the reverse process) for reaction 1. Values of k_1 and k_{-1} at various temperatures are included in Table 1, and the corresponding activation parameters are listed in Table 2.

The spectral changes associated with reaction 1 were employed to determine the overall equilibrium constant K_1. A plot of the absorbance at 410 nm (**1a** and **1c**) or 400 nm (**1b**) versus [4-CHOpy] is curved and attains a limiting value at high values of [4-CHOpy]. K_1 can be expressed by eq. (3), where A_0, A and A_∞ are the absorbances in the absence of added 4-CHOpy and the presence of low and high concentrations of 4-CHOpy, respectively.

$$K_1 = (A - A_0)/(A_\infty - A) \times [\text{4-CHOpy}] \tag{3}$$

Thus a plot of $(A - A_0)/[\text{4-CHOpy}]$ versus A was linear, with a slope of K_1. The K_1 values of 106 ± 5, 20.7 ± 1.1 and 101 ± 6 M^{-1} determined for reaction 1 in MeCN at 20.3°C (dienyl = C_6H_7, 2-MeOC_6H_6 and C_7H_9, respectively) are in reasonable agreement with the corresponding values of 157 ± 3, 22.2 ± 0.2 and 134 ± 12 M^{-1} calculated ($K_1 = k_1/k_{-1}$) from the kinetic data in Table 1 under the same conditions (see Table 3). These results further confirm the equilibrium nature of reaction 1 when account is taken of the fact that equilibrium constants determined from spectroscopic data are usually subject to significantly larger errors than those obtained from the ratio of two rate constants.

The effect of pressure on k_{obs} for reaction 1 was initially studied at both low and high 4-CHOpy concentrations in order to distinguish between the pressure dependence of the reverse dissociation step (k_{-1}) and the forward addition step (k_1). The results are summarized in Table 4 and show that the rate of the forward step increases with increasing pressure (C_6H_7 and 2-MeOC_6H_6 reactions) and

Table 1

Values of k_{obs} at various nucleophile concentrations and temperatures for the addition of 4-CHOpy to **1a**–**1c** in MeCN ([Fe] = 1.5×10^{-3} M)

Complex	Temperature (°C)	10^2 [4-CHOpy] (M)	k_{obs} (s^{-1})^a	k_1 (M^{-1} s^{-1})^b	k_{-1} (s^{-1})^b
1a	10.2	1.0	12.8 ± 0.4	1040 ± 4	2.37 ± 0.15
		2.0	23.1 ± 0.6		
		3.0	33.6 ± 0.6		
		4.0	44.2 ± 0.8		
		5.0	54.3 ± 1.1		
	15.3	1.0	17.5 ± 0.5	1310 ± 6	4.55 ± 0.21
		2.0	31.0 ± 0.6		
		3.0	44.1 ± 0.8		
		4.0	56.9 ± 1.5		
		5.0	70.2 ± 1.6		
	20.3	1.0	24.5 ± 0.5	1490 ± 6	9.50 ± 0.19
		2.0	39.3 ± 0.3		
		3.0	54.1 ± 0.5		
		4.0	68.9 ± 0.6		
		5.0	84.2 ± 2.1		
	25.1	1.0	35.5 ± 0.3	1780 ± 17	18.1 ± 0.6
		2.0	54.4 ± 0.8		
		3.0	71.0 ± 1.0		
		4.0	89.1 ± 2.4		
		5.0	107 ± 3		
	30.1	1.0	51.1 ± 1.4	2280 ± 29	28.2 ± 0.8
		2.0	73.2 ± 1.6		
		3.0	97.2 ± 1.5		
		4.0	119 ± 4		
1b	10.4	1.0	6.50 ± 0.31	259 ± 1	3.94 ± 0.06
		2.0	9.11 ± 0.32		
		4.0	14.3 ± 0.4		
		6.0	19.6 ± 0.5		
		10.0	29.8 ± 0.6		
	15.2	1.0	10.6 ± 0.4	311 ± 2	7.40 ± 0.09
		2.0	13.5 ± 0.3		
		4.0	19.8 ± 0.4		
		6.0	26.2 ± 0.6		
		10.0	38.5 ± 0.8		
	20.3	1.0	20.2 ± 0.4	368 ± 2	16.6 ± 0.1
		2.0	23.9 ± 0.4		
		4.0	31.5 ± 0.4		
		6.0	38.6 ± 0.6		
		10.0	53.4 ± 0.8		
	25.2	1.0	30.5 ± 0.5	439 ± 2	26.2 ± 0.1
		2.0	35.2 ± 0.8		
		4.0	43.7 ± 0.8		
		6.0	52.4 ± 1.1		
		10.0	70.2 ± 1.2		
	30.3	1.0	55.0 ± 0.6	498 ± 3	50.0 ± 0.2
		2.0	60.2 ± 0.5		
		4.0	70.1 ± 1.8		
		6.0	79.6 ± 1.9		
		10.0	100 ± 3		

Table 1 (continued)

Complex	Temperature (°C)	10^2 [4-CHOpy] (M)	k_{obs} (s^{-1}) [a]	k_1 (M^{-1} s^{-1}) [b]	k_{-1} (s^{-1}) [b]
1c	10.1	1.0	0.701 ± 0.007	40.0 ± 0.1	0.306 ± 0.008
		2.0	1.12 ± 0.02		
		4.0	1.90 ± 0.02		
		6.0	2.70 ± 0.06		
		10.0	4.31 ± 0.08		
	15.4	1.0	0.901 ± 0.022	49.9 ± 0.1	0.407 ± 0.004
		2.0	1.41 ± 0.01		
		4.0	2.41 ± 0.02		
		6.0	3.40 ± 0.01		
		10.0	5.40 ± 0.10		
	20.2	1.0	1.15 ± 0.03	65.6 ± 0.8	0.491 ± 0.045
		2.0	1.81 ± 0.01		
		4.0	3.05 ± 0.04		
		6.0	4.50 ± 0.06		
		10.0	7.03 ± 0.05		
	25.2	1.0	1.40 ± 0.03	80.1 ± 0.7	0.579 ± 0.042
		2.0	2.21 ± 0.02		
		4.0	3.70 ± 0.03		
		6.0	5.40 ± 0.06		
		10.0	8.60 ± 0.10		
	30.1	1.0	1.81 ± 0.02	98.5 ± 1.3	0.782 ± 0.071
		2.0	2.70 ± 0.02		
		4.0	4.65 ± 0.03		
		6.0	6.81 ± 0.05		
		10.0	10.6 ± 0.1		

[a] Mean value of 5–6 kinetic runs. [b] Estimated by a least-squares fit to eq. (2).

Table 2

Rate constants and activation parameters for the addition of 4-CHOpy to **1a**, **1b** and **1c** in MeCN [a]

Complex	k_1 at 15°C (M^{-1} s^{-1})	k_1 (rel.)	$\Delta H_1^{\neq}$ (kJ mol^{-1})	$\Delta S_1^{\neq}$ (J K^{-1} mol^{-1})	k_{-1} at 15°C (s^{-1})	k_{-1} (rel.)	$\Delta H_{-1}^{\neq}$ (kJ mol^{-1})	$\Delta S_{-1}^{\neq}$ (J K^{-1} mol^{-1})
1a	1310	26	24.6 ± 1.7	−100 ± 6	4.55	11	88.9 ± 3.5	+77 ± 12
1b	311	6	21.3 ± 0.7	−123 ± 2	7.40	18	88.8 ± 3.4	+80 ± 12
1c	49.9	1	30.2 ± 1.0	−107 ± 3	0.407	1	29.5 ± 1.9	−150 ± 7

[a] Activation parameters calculated using the second-order (k_1) and first-order (k_{-1}) rate constants in Table 1.

Table 3

Equilibrium constants determined kinetically (K_{kin}) and spectroscopically (K_{spec}) for the reaction of 4-CHOpy with [Fe(1–5-η-dienyl)(CO)$_3$]BF$_4$ in CH$_3$CN at 20.3°C

Dienyl	K_{kin} (M^{-1})	K_{spec} (M^{-1})
C_6H_7	157 ± 3	106 ± 5
2-MeOC$_6$H$_6$	22.2 ± 0.2	20.7 ± 1.1
C_7H_9	134 ± 12	101 ± 6

Table 4

Effect of pressure on the rate of addition of 4-CHOpy to **1a**, **1b** and **1c** in MeCN [a]

Complex	Temperature (°C)	$10^2 \times$[4-CHOpy] (M)	Pressure (MPa)	k_{obs} (s^{-1}) [b]	$\Delta V^{\neq}$ (cm^3 mol^{-1})
1a	14.2	1.0	10	17.6 ±0.3	+5.6±0.4
			50	16.4 ±0.4	
			100	14.6 ±0.4	
			150	12.7 ±0.3	
		5.0	10	64.8 ±0.7	−2.9±0.1
			50	68.4 ±0.9	
			100	72.2 ±0.5	
			150	77.1 ±0.7	
1b	14.2	2.0	10	16.6 ±0.4	+5.9±0.3
			50	15.1 ±0.3	
			100	13.6 ±0.4	
			150	11.7 ±0.4	
		4.0	10	21.2 ±0.4	+1.2±0.1
			50	20.6 ±0.4	
			100	20.2 ±0.3	
			150	19.8 ±0.3	
		8.0	10	29.2 ±0.4	−2.9±0.3
			50	31.2 ±0.5	
			100	33.0 ±0.5	
			150	34.4 ±0.5	
		10.0	10	33.8 ±0.4	−3.8±0.2
			50	36.5 ±0.4	
			100	39.4 ±0.5	
			150	42.4 ±0.5	
1c	25.1	1.0	0.1	1.40±0.03	+0.4±1.1
			10	1.26±0.03	
			50	1.24±0.05	
			100	1.28±0.03	
			150	1.31±0.03	
		10.0	0.1	8.60±0.10	+0.1±0.1
			10	8.58±0.06	
			50	8.62±0.05	
			100	8.49±0.08	
			150	8.58±0.06	

[a] For complexes **1a** and **1c** [Fe] = 1.5×10^{-3} M and for complex **1b** [Fe] = 3.0×10^{-3} M. [b] Mean value of 5–6 kinetic runs.

that of the reverse process falls. However, the rates for the C_7H_9 reaction were found to be independent of pressure up to 150 MPa. A systematic pressure dependence study was performed for **1b** at various 4-CHOpy concentrations, and this revealed the dependence of k_1 and k_{-1} on the pressure. From the data, it was possible to derive values of $\Delta V^{\neq}$ (k_1), -9.8 ± 0.9, and $\Delta V^{\neq}$ (k_{-1}), $+18.0 \pm 1.9$ cm^3 mol^{-1}, which demonstrates that the pressure dependence of k_1 and k_{-1} is more marked than that revealed by experiments performed at low and high nucleophile concentrations only. Furthermore, these results indicate an overall reaction volume $\Delta \bar{V} = \Delta V^{\neq}(k_1) - \Delta V(k_{-1}) = -28 \pm 3$ cm^3 mol^{-1} associated with the binding of 4-CHOpy to **1b**. Similar activation and reaction volumes are expected for the reaction with **1a**, but the high rate of this reaction prevented a detailed concentration dependence study such as was made for **1b**.

Strong support for the direct addition of 4-CHOpy to complexes **1** comes from the relative rates found for reaction 1. Thus the k_1 values follow the sequence $C_6H_7 > 2\text{-}MeOC_6H_6 > C_7H_9$ (e.g. 26:6:1 at 15°C, Table 2). The lower reactivity of $[Fe(1\text{–}5\text{-}\eta\text{-}2\text{-}MeOC_6H_6)(CO)_3]BF_4$ (**1b**) than of the parent complex $[Fe(1\text{–}5\text{-}\eta\text{-}C_6H_7)(CO)_3]BF_4$ (**1a**) is attributed to the mesomeric effect of the methoxide group, which has been shown from INDO molecular-orbital calculations [33] to lower the positive charge on the dienyl C(5) atom, the site of nucleophilic addition. This mesomeric effect may account for the high rate of dissociation of 4-CHOpy from **2b** (k_{-1} step) compared with that from **2a** and **2c** (eq. (1)). Thus Table 2 also reveals that the rates of dissociation of 4-CHOpy from **2a**–**2c** follow the sequence $2\text{-}MeOC_6H_6 > C_6H_7 > C_7H_9$, the relative rates at 15°C being 18:11:1. The more pronounced increase in rate (k_1) on going from the parent complex (**1a**) to $[Fe(1\text{–}5\text{-}\eta\text{-}C_7H_9)(CO)_3]BF_4$ (**1c**) is readily accounted for in terms of the steric hindrance by the additional methylene group (**1c**) if it is assumed that 4-CHOpy approaches from above the dienyl fragments of complexes **1a**–**1c**. The low $\Delta H_1^{\#}$ and large negative $\Delta S_1^{\#}$ values found for reactions 1 are also consistent with an associative process (Table 2). The observed rate sequence $C_6H_7 > 2\text{-}MeOC_6H_6 > C_7H_9$ can be attributed to a balance of enthalpy and entropy effects. Thus, the high rate of reaction of the C_6H_7 complex compared with that of C_7H_9 arises from a much smaller $\Delta H_1^{\#}$, while the intermediate rate for the $2\text{-}MeOC_6H_6$ complex is associated with the smallest $\Delta H_1^{\#}$ and the most negative $\Delta S_1^{\#}$ values. On the other hand, the much larger $\Delta H_{-1}^{\#}$ values found for the C_6H_7 and $2\text{-}MeOC_6H_6$ reactions are as expected for bond cleavage during dissociation (k_{-1}), as is the positive $\Delta S_{-1}^{\#}$ value obtained for these processes (Table 2). The large negative $\Delta S_{-1}^{\#}$ value of -150 ± 7 J K^{-1} mol^{-1} found for the C_7H_9 reaction suggests that product **2c** (eq. (1)) is formed through a highly ordered transition state. In addition, a plot of $\Delta H_{-1}^{\#}$ versus $\Delta S_{-1}^{\#}$ for reaction 1 provides an isokinetic temperature of 260 ± 3 K (which is much lower than the temperature range of 283–303 K in which reactions 1 were studied), indicating entropy control of the dissociative process.

Added support for the associative mechanism demonstrated above for the k_1 step in reaction 1 comes from the negative $\Delta V^{\#}$ values of -2.9 and -3.8 cm^3 mol^{-1} found for the addition of 4-CHOpy to the C_6H_7 and $2\text{-}MeOC_6H_6$ complexes, respectively, at the highest concentrations of nucleophile (Table 4). The rates of addition are increased, and the volume decrease associated with bond formation, i.e. $\{4\text{-}CHOC_5H_4N\text{–}C(diene)\}$, is reflected in the negative volumes of activation for addition of the nucleophile 4-CHOpy to the C(5) atom of the dienyl fragments in complexes **1a** and **1b**. On the other hand, the positive $\Delta V^{\#}$ values of $+5.6 \pm 0.4$ and $+5.9 \pm 0.3$ cm^3 mol^{-1} found for these reactions (C_6H_7 and $2\text{-}MeOC_6H_6$, respectively) at the lowest concentrations of nucleophile (Table 4) are as expected for the reverse dissociation of 4-CHOpy from products **2a** and **2b** to give the initial reactants (k_{-1} step). The rates of dissociation fall with increasing pressure, and the volume increase associated with $\{C(diene)\text{–}N(C_5H_4CHO\text{-}4)\}$ bond breakage is reflected in the positive $\Delta V^{\#}$ values. This is also consistent with the positive $\Delta S_{-1}^{\#}$ values found for these reactions (Table 2) and with the isokinetic temperature of 260 ± 3 K, which suggests entropy control over the dissociative processes of reaction 1. The more complete study performed for the addition to **1b** clearly reveals that the absolute values of the quoted activation volumes are too low, and that the overall reaction volume is significantly more negative than expected from these values. The reaction volume of -28 ± 3 cm^3 mol^{-1} seems to be very reasonable for the addition of 4-CHOpy, which has a partial molar volume of ~ 95 cm^3 mol^{-1} (as estimated from its density of 1.126 g cm^{-3}).

In the reaction of 4-CHOpy with the C_7H_9 complex there was no significant effect on k_{obs} (and so on k_1 and k_{-1}) with increase in pressures up to 150 MPa (Table 4). We recently observed a similar behaviour for 4-cyanopyridine (dienyl = C_6H_7 or C_7H_9) [18], and explained it in terms of the interchange/"ordered transition state" concept. It is noteworthy that a negative $\Delta S^{\#}_{-1}$ value of -150 ± 7 J K^{-1} mol^{-1} was found (Table 2) for the reverse dissociation step of the reaction of 4-CHOpy with the C_7H_9 complex. We also recently reported [18] a negative $\Delta S^{\#}_{-1}$ value of -16 ± 8 J K^{-1} mol^{-1} for the reverse dissociation step in the reaction of 4-cyanopyridine with the C_7H_9 complex, and large negative $\Delta S^{\#}_{-1}$ values for the reverse dissociation step of 2-ethylpyridine [8] in its reaction with the 2-$MeOC_6H_6$ and the C_7H_9 complexes ($\Delta S^{\#}_{-1}$ for 2-$MeOC_6H_6 = -20 \pm 3$ and $\Delta S^{\#}_{-1}$ for $C_7H_9 = -97 \pm 8$ J K^{-1} mol^{-1}). Such negative entropies of activation are common for the dissociation of amine from organometallics of type **2**, and have been rationalized in terms of the "ordered transition state mechanism" [13]. Our observation of the insensitivity of such processes to pressure changes (i.e. zero volume of activation) is clearly consistent with the "ordered transition state" concept in which the volume decrease associated with Fe–C(diene) bond formation is cancelled out by the volume increase associated with C(diene)–N(amine) bond breakage. Furthermore, for this reaction the overall reaction volume must be close to zero ($\Delta V^{\#}$ (k_1) and $\Delta V^{\#}$ (k_{-1}) are both close to zero), and thus significantly more positive than those for the reactions with **1a** and **1b**. This can only mean that bond formation with the amine must involve significant bond breakage with the diene ligand in the case of the C_7H_9, ligand, and thus can be attributed to the steric hindrance by the additional methylene group referred to above.

For ease of comparison, a summary of the available rate and activation parameters for systems in which systematic temperature and pressure dependence studies have been performed, is given in Table 5. The variations of k_1 as the dienyl ligand is changed show similar trends for all the amines. They also correlate well with the pK_a values, i.e. the basicity, of the amines. As the basicity of the amines increases, the increase in k_1 due to the increasing nucleophilicity is accompanied by a decrease in k_{-1}, up to the point where no significant reverse reaction can be detected (4-Etpy). The increase in basicity along the series of amines also seems to correlate with the observed effect of pressure on the system, i.e. no effect for 4-CNpy and a significant effect for 4-Etpy. It has been suggested [19] that this feature may be related to the location of the transition state, namely an early transition state for the stronger nucleophile in which bond formation plays an important role (negative $\Delta V^{\#}$), and a late transition state for the slower reactions, in which bond formation will be partially cancelled by bond breaking in determining the associated volume changes. The latter behaviour seems to apply in the addition of 4-CNpy, and an interchange of bonds with a late, product-like transi-

Table 5

Rate and activation parameters for additions of a series of amines to complexes **1a**–**1c** in MeCN at 25°C

Amine	Dienyl	k_1 (M^{-1} s^{-1})	$\Delta H_1^{\neq}$ (kJ mol^{-1})	$\Delta S_1^{\neq}$ (J K^{-1} mol^{-1})	$\Delta V_1^{\neq}$ (cm^3 mol^{-1})	k_{-1} (s^{-1})	$\Delta H_{-1}^{\neq}$ (kJ mol^{-1})	$\Delta S_{-1}^{\neq}$ (J K^{-1} mol^{-1})	$\Delta V_{-1}^{\neq}$ (cm^3 mol^{-1})
4-CNpy [a]	C_6H_7	1.2×10^3	42 ± 2	-46 ± 6	≈ 0	53	81 ± 6	$+60 \pm 20$	≈ 0
	C_7H_9	30	38 ± 1	-89 ± 5	≈ 0	3.4	65 ± 2	-16 ± 8	≈ 0
4-CHOpy [b]	C_6H_7	1.8×10^3	25 ± 2	-100 ± 6	-2.9 ± 0.2 [d]	18.1	89 ± 3	$+77 \pm 12$	$+5.6 \pm 0.4$ [d]
	2-MeOC_6H_6	4.4×10^2	21 ± 1	-123 ± 2	-9.8 ± 0.9 [e]	26.2	89 ± 3	$+80 \pm 12$	$+18.0 \pm 1.9$ [e]
	C_7H_9	80	30 ± 1	-107 ± 3	≈ 0	0.58	29 ± 2	-150 ± 7	≈ 0
4-Etpy [c]	C_6H_7	1.9×10^4	16.9 ± 0.3	-106 ± 1	[f]	≈ 0			
	2-MeOC_6H_6	3.1×10^3	15.5 ± 0.4	-126 ± 1	-7.8 ± 0.2	≈ 0			
	C_7H_9	8.4×10^2	26 ± 2	-102 ± 6	-6.4 ± 0.2	≈ 0			

[a] Data from ref. 18, $pK_a = 1.9$. [b] This work, $pK_a = 4.9$. [c] Data from ref. 19, $pK_a = 5.9$. [d] Data measured at low and high nucleophile concentrations. [e] Data obtained from a detailed nucleophile concentration dependence study (see Table 4). [f] Reaction is too fast for the high-pressure stopped-flow system.

tion state would account for the pressure independence of the process. In the case of the 4-CHOpy system investigated in this study, the pK_a value suggests that the reaction is located between the two extremes (4-CNpy and 4-Etpy), and indeed both the forward and reverse reactions exhibit significant pressure dependence for C_6H_7 and 2-MeOC_6H_6. In these cases, the bond formation with the amine is followed by bond breaking (ring slippage of the dienyl ligand) after the transition state, and vice versa for the reverse process. In the case of C_7H_9, the reactions are significantly slower, and the transition state probably later on a volume basis, with no significant $\Delta V^{\#}$ values for either the forward or reverse reactions. We thus conclude that amine basicity and steric hindrance in the dienyl ligand are the crucial parameters that control the location of the transition state during such additions. The mechanism can therefore vary from a pure interchange of bonds (zero $\Delta V^{\#}$) to a highly associative bond formation process (negative $\Delta V^{\#}$). It is apparent that, as expected, the pressure dependence studies have revealed important information about the details of the reaction mechanism [34].

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