Effects of Temperature and Pressure on the Addition of 4-Ethylpyridine to Tricarbonyl(η^5-dienyl)iron(II) Complexes

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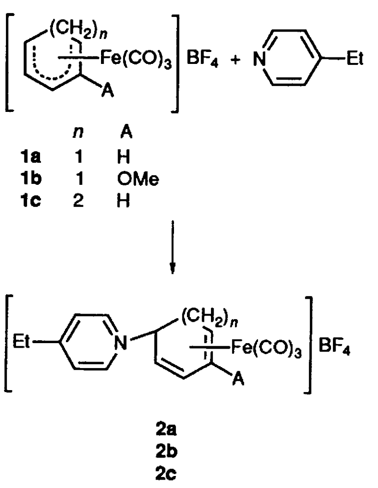
Detailed kinetic studies of the reaction between $[Fe(CO)_3(\eta^5\text{-dienyl})]BF_4$ **1** (dienyl = C_6H_7, 2-$MeOC_6H_6$ or C_7H_9) and 4-ethylpyridine in MeCN have been performed as a function of temperature and pressure using stopped-flow techniques. The reactions proceed to completion under pseudo-first-order conditions, *i.e.* $k_{obs} = k_1[\text{4Et-py}]$. The observed rate sequence $C_6H_7 >$ 2-$MeOC_6H_6 > C_7H_9$ (*e.g.* 25:4:1 at 10 °C and 0.1 MPa) and the low $\Delta H^‡$ and large negative $\Delta S^‡$ and $\Delta V^‡$ values are consistent with direct addition (k_1) to the dienyl fragments of complexes **1**. The results contrast sharply with a recent report on the reversible addition of 4-cyanopyridine to complexes **1** (dienyl = C_6H_7 or C_7H_9) where application of pressure had no effect on the forward (k_1) and reverse (k_{-1}) steps. These results provide the first quantitative information on the applicability of pressure dependences in the mechanistic interpretation of amine additions to dienylium organometallics of type **1**.

In previous work we have investigated the influence of nucleophile basicity and of the steric and electronic nature of the co-ordinated organic group in the reactions of amines,[1–9] amides,[10] activated arenes,[11–14] tertiary phosphines[15–18] and aryltrimethyl-silanes and -stannanes[19,20] with organometallics of the type $[Fe(CO)_3(\eta^5\text{-dienyl})]BF_4$ **1** (dienyl = C_6H_7, 2-$MeOC_6H_6$ or C_7H_9). Detailed studies have also been made of the influence of temperature on the rates and mechanisms of these reactions (*e.g.* refs. 5 and 9), thus allowing mechanistic assignments based on the nature and magnitude of the $\Delta H^‡$ and $\Delta S^‡$ values. In such studies, associative processes have been characterized by low $\Delta H^‡$ and large negative $\Delta S^‡$ values, whereas dissociative processes are associated with high $\Delta H^‡$ and positive $\Delta S^‡$ values. However, pressure-dependent studies of inorganic, bioinorganic and organometallic reactions[21–23] have produced a wealth of information on bond-formation and -breakage processes in such systems, and high-pressure kinetic techniques have now become an important tool in the elucidation of reaction mechanisms.[24] The mechanistic utility of this technique in organometallic systems has recently been demonstrated in our laboratories.[25–34]

Recently, a study of the effect of temperature on the reaction of 2-ethylpyridine[5] with complexes **1** and of the effects of temperature and pressure on the reaction of 4-cyanopyridine with **1** (dienyl = C_6H_7 or C_7H_9)[34] was undertaken in order to throw more light on the intimate nature of the mechanism of amine additions to co-ordinated organic molecules. These reactions afforded products of the type tricarbonyl[η-5-*exo*-pyridiniocyclohexa (or cyclohepta)-1,3-diene]iron tetrafluoroborate in high yields. However, apart from the temperature-dependence studies of the reactions of pyridine,[2] 2-methyl-,[2] 2-ethyl-[5] and 4-cyano-pyridine[34] with the dienyl complexes **1** and of the pressure-dependence study of the reaction of 4-cyanopyridine with **1** (dienyl = C_6H_7 or C_7H_9),[34] little information is still available on the intimate mechanism of the reactions of pyridines with co-ordinated organic molecules.

In order to improve our understanding of these novel reactions, we have made detailed temperature- and pressure-dependence studies of the reaction of 4-ethylpyridine with the organometallics **1a**–**1c** in MeCN [equation (1)]. The products **2a**–**2c** have also been isolated for the first time and characterized on the basis of their IR and ^1H NMR spectra, and in the case of **2b** by microanalysis.



(1)

Experimental

Materials.—Complexes **1a**–**1c** were synthesised and purified as previously described.[35,36] 4-Ethylpyridine (4Et-py) was freshly distilled over KOH pellets prior to use. Acetonitrile (MeCN) was distilled in bulk and stored over molecular sieves (3 Å) under a dinitrogen atmosphere.

Product Isolation and Characterization.—*Tricarbonyl*[η-5-exo-(4-*ethylpyridinio*)*cyclohexa*-1,3-*diene*]*iron tetrafluoroborate* **2a**. Solutions of $[Fe(CO)_3(\eta^5\text{-}C_6H_7)]BF_4$ **1a** (0.05 g, 0.164 mmol) in MeCN (10 cm^3) and 4Et-py (186 μl, 1.63 mmol) in MeCN (10 cm^3) were mixed under dinitrogen in a flask (50 cm^3) and allowed to stand at room temperature for 10 min. Rotary evaporation of the mixture under dinitrogen at 35 °C afforded a yellow oil. On washing with cold light petroleum (b.p. 40–60 °C) the product **2a** was obtained as a yellow oil which could not be crystallized; yield, after drying on a vacuum line for 4 h, 0.054 g (80%). IR (MeCN): ν(CO) 2055 and 1980 cm^{-1}. The presence of a strong band at *ca.* 1060 cm^{-1} (Nujol mull) confirmed the presence of the BF_4^- anion. ^1H NMR ($CDCl_3$): δ 8.67 (2 H, d, aromatic), 7.76 (2 H, d, aromatic), 5.80 (1 H, m, H^3), 5.70 (1 H,

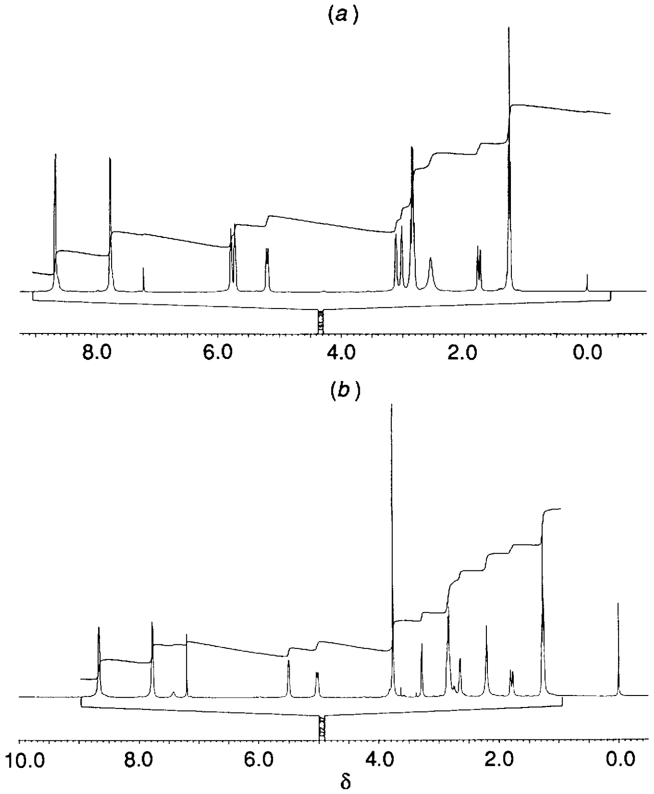


Fig. 1 Proton NMR spectra of products **2a** (*a*) and **2b** (*b*) in $CDCl_3$

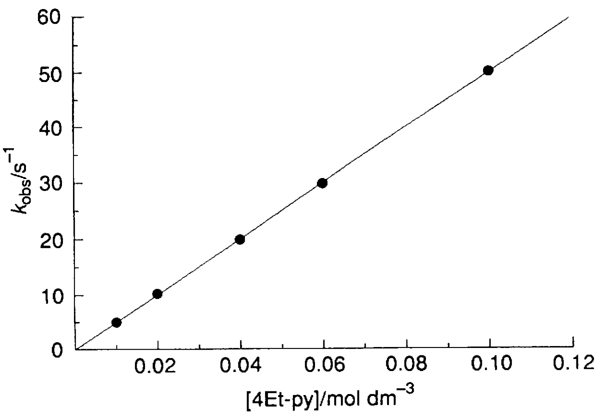


Fig. 2 Plot of k_{obs} *versus* [4Et-py] for the reaction of complex **1c** with 4Et-py in MeCN at 10.3 °C

m, H^2), 5.20 (1 H, m, $H^{5'}$), 3.12 (1 H, m, H^1), 3.04 (1 H, m, H^4), 2.84 (2 H, q, CH_2), 2.54 (1 H, m, $H^{6'}$), 1.76 (1 H, m, H^6) and 1.25 (3 H, t, CH_3) [see Fig. 1(*a*)].

Tricarbonyl[η-5-exo-(4-*ethylpyridinio*)-2-*methoxycyclohexa*-1,3-*diene*]*iron tetrafluoroborate* **2b**. An analogous reaction of $[Fe(CO)_3(\eta^5\text{-}2\text{-}MeOC_6H_6)]BF_4$ **1b** (0.05 g, 0.149 mmol) with 4Et-py (170 μl, 1.49 mmol) in MeCN (20 cm^3), followed by similar work-up to that described above for **2a**, gave **2b** as a pale yellow solid (0.056 g, 85% yield) after drying on a vacuum line for 4 h (Found: C, 46.2; H, 4.10; N, 3.15. Calc. for $C_{17}H_{18}BF_4FeNO_4$: C, 46.1; H, 4.10; N, 3.15%). IR (MeCN): ν(CO) 2055 and 1980 cm^{-1}. $\nu(BF_4^-)$ in Nujol mull: *ca.* 1060 (br) cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.67 (2 H, d, aromatic), 7.80 (2 H, d, aromatic), 5.50 (1 H, m, H^3), 5.06 (1 H, m, $H^{5'}$), 3.78 (3 H, s, OCH_3), 3.25 (1 H, m, H^1), 2.83 (2 H, q, CH_2), 2.63 (1 H, m, H^4), 2.20 (1 H, m, $H^{6'}$), 1.80 (1 H, m, H^6) and 1.25 (3 H, t, CH_3) [see Fig. 1(*b*)].

Tricarbonyl[η-5-exo-(4-*ethylpyridinio*)*cyclohepta*-1,3-*diene*]-*iron tetrafluoroborate* **2c**. An analogous reaction of $[Fe(CO)_3(\eta^5\text{-}C_7H_9)]BF_4$ **1c** (0.05 g, 0.156 mmol) with 4Et-py (180 μl, 1.58 mmol), followed by similar work-up to that of **2a** above, gave product **2c** as a yellow oil which could not be crystallized; yield, after drying on a vacuum line for 4 h, 0.05 g (75%). IR (MeCN): ν(CO) 2055 and 1980 cm^{-1}. $\nu(BF_4^-)$ in Nujol mull: *ca.* 1060 (br) cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.80 (2 H, d, aromatic), 7.80 (2 H, d, aromatic), 5.80 (1 H, m, H^3), 5.43 (1 H, m, H^2), 4.98 (1 H, m, $H^{5'}$), 3.13 (1 H, m, H^1), 2.85 (2 H, q, CH_2), 2.64 (1 H, m, H^4), 2.30 (2 H, m, $H^{7,7'}$), 1.80 (1 H, m, $H^{6'}$), 1.50 (1 H, m, H^6) and 1.25 (3 H, t, CH_3).

Instrumentation.—Reactions (1) in MeCN are characterized by significant UV/VIS spectral changes; the absorbance decreases at 420 nm, which was studied on a Shimadzu UV 250 spectrophotometer. Infrared studies of the products **2a**–**2c** were performed on a Perkin-Elmer 397 spectrophotometer and ^1H NMR (400 MHz) on a Bruker AM spectrometer. The kinetics of reaction (1) was studied under pseudo-first-order conditions using a large excess of 4Et-py. The addition reactions are fast and were followed using a thermostatted (±0.1 °C) Durrum D110 stopped-flow instrument coupled to an on-line data-acquisition and analysis system.[37] Kinetic experiments at pressures up to 150 MPa were performed on a laboratory-made high-pressure stopped-flow instrument.[38] Kinetic traces showed excellent first-order behaviour under all experimental conditions and the first-order rate constants, k_{obs}, were calculated from plots of ln $(A_\infty - A_t)$ *versus* t in the usual way. Such plots were linear for at least two to three half-lives of the reaction. Each k_{obs} value cited is the average from five or six separate runs. Second-order rate constants, k_1, and activation parameters were calculated using a linear least-squares analysis. The values of k_1 for the rapid addition of 4Et-py to complexes **1a** and **1b** (15–35 °C) were calculated directly from the observed rate constants [see equation (2)].

Results and Discussion

The products formed during the addition of 4Et-py to the dienyl complexes, as in reaction (1), have been isolated in this work and shown to be tricarbonyl[η-5-*exo*-pyridiniocyclohexa- (or cyclohepta-)1,3-diene]iron complexes **2** by IR and ^1H NMR spectral studies (see Fig. 1) and in the case of **2b** by microanalysis. Their IR spectra exhibited two strong carbonyl bands at *ca.* 2055 and 1980 cm^{-1} and a strong $\nu(BF_4^-)$ band at *ca.* 1060 cm^{-1} as previously established[2,5] for cationic 1,3-diene iron complexes formed from the reaction between complexes **1** and pyridines. Products **2a** and **2c** are yellow oils which slowly darken on long exposure to air, thus necessitating storage under a dinitrogen atmosphere; **2b** is a stable cream solid. All three products were isolated in high yields (75–85%) and showed overlapping in their ^1H NMR spectra characteristic of cationic 1,3-diene iron complexes. Thus the outer (H^1 and H^4) diene protons resonate at *ca.* δ 3 while the inner (H^2 and H^3) diene protons appear at *ca.* δ 6. The $H^{5'}$ proton appears at *ca.* δ 5 while the H^6 (*exo*) and $H^{6'}$ (*endo*) methylene protons resonate at *ca.* δ 1.8 and 2.2, respectively. The aromatic protons of the added 4Et-py appear as two doublets at *ca.* δ 7.8 and 8.7, the downfield shift of the latter indicating its assignment to the two protons close to the pyridine nitrogen. The triplet centred at δ 1.25 for all three products **2a**–**2c** is attributed to the CH_3 group of the 4Et-py substituent, while the quartet centred at δ 2.84 is attributed to the CH_2 group of the same moiety. The singlet at δ 3.78 found only for product **2b** is assigned to the methoxy group at the 2 position of the cyclohexa-1,3-diene fragment. The cleanness of these ^1H NMR spectra confirmed the purity of the isolated products.

The observed pseudo-first-order rate constant for reaction (1) shows a linear dependence on the concentration of nucleophile as clearly demonstrated by the data summarized in Table 1. Plots of k_{obs} *versus* [4Et-py] are linear with zero intercepts (see Fig. 2) indicating the validity of the general rate equation (2),

$$k_{obs} = k_1[\text{4Et-py}] \qquad (2)$$

Table 1 Values of k_{obs} as a function of [4Et-py] and temperature for the reactions (1)[a]

Complex	T/°C	10^2[4Et-py]/ mol dm^{-3}	$k_{obs}{}^b$/s^{-1}	$k_1{}^c$/dm^3 mol^{-1} s^{-1}	$\Delta H^‡$/ kJ mol^{-1}	$\Delta S^‡$/ J K^{-1} mol^{-1}
1a	10.0	1.0	127 ± 1	1.26×10^4	17.2 ± 0.3	−105 ± 1
		1.5	190 ± 2			
		2.0	253 ± 3			
	15.6	1.0	148 ± 1	1.48×10^4		
	20.3	1.0	170 ± 3	1.70×10^4		
	25.0	1.0	190 ± 5	1.90×10^4		
	30.2	1.0	220 ± 2	2.20×10^4		
1b	10.3	1.0	21.5 ± 0.7	2.15×10^3	15.5 ± 0.4	−126 ± 1
		2.0	42.8 ± 0.8			
		3.0	64.4 ± 0.2			
		4.0	86.0 ± 0.4			
		6.0	129 ± 1			
	15.1	1.0	24.0 ± 0.3	2.40×10^3		
	20.3	1.0	27.6 ± 0.6	2.75×10^3		
	25.2	1.0	31.3 ± 0.5	3.13×10^3		
	30.4	1.0	34.7 ± 0.4	3.47×10^3		
	35.2	1.0	39.8 ± 0.2	3.98×10^3		
1c	10.3	1.0	5.02 ± 0.13	5.00×10^2	25.7 ± 1.7	−102 ± 6
		2.0	10.2 ± 0.4			
		4.0	19.9 ± 0.6			
		6.0	29.8 ± 0.8			
		10	50.1 ± 0.8			
	15.3	1.0	6.20 ± 0.13	5.83×10^2		
		2.0	13.0 ± 0.3			
		4.0	24.0 ± 0.4			
		6.0	36.1 ± 0.5			
		10	59.0 ± 0.4			
	20.4	1.0	8.01 ± 0.03	7.21×10^2		
		2.0	14.5 ± 0.4			
		4.0	29.1 ± 0.5			
		6.0	44.0 ± 0.5			
		10	72.5 ± 0.7			
	25.0	1.0	9.03 ± 0.10	8.44×10^2		
		2.0	16.3 ± 0.4			
		4.0	36.1 ± 0.5			
		6.0	53.0 ± 1.4			
		10	84.2 ± 1.4			
	30.3	1.0	11.0 ± 0.5	1.11×10^3		
		2.0	21.1 ± 0.3			
		4.0	43.2 ± 0.2			
		6.0	66.1 ± 1.2			
		10	110 ± 3			

[a] [Fe] = 1.5×10^{-3} mol dm^{-3}, solvent = MeCN. [b] Mean value from five or six kinetic runs. [c] Calculated from $k_1 = k_{obs}$/[4Et-py].

Table 2 Effect of pressure on the addition of 4Et-py to complexes **1b** and **1c** in MeCN[a]

Complex	T/°C	10^2[4Et-py]/ mol dm^{-3}	p/MPa	$k_{obs}{}^b$/s^{-1}	$\Delta V^‡$/cm^3 mol^{-1}
1b	15.1	1.0	0.1	24.0 ± 0.3	−7.8 ± 0.2
			10	25.3 ± 0.5	
			50	29.4 ± 0.3	
			100	34.2 ± 0.4	
			150	40.1 ± 0.9	
1c	25.0	2.0	0.1	16.3 ± 0.4	−6.4 ± 0.2
			10	17.6 ± 0.5	
			50	19.2 ± 0.3	
			100	22.0 ± 0.8	
			150	25.2 ± 0.7	

[a] [Fe] = 1.5×10^{-3} mol dm^{-3}. [b] Mean value from five to six kinetic runs.

where k_1 is the second-order rate constant for the direct addition of 4Et-py to the dienyl fragments of complexes **1** to form the 1,3-diene products **2**. The values of k_1 as a function of temperature are included in Table 1 together with the corresponding activation parameters. The effect of pressure on k_{obs} for the reactions of 4Et-py with **1b** and **1c** was studied using 0.01 and 0.02 mol dm^{-3} amine, respectively; the results (Table 2) demonstrate a rate enhancement with increasing pressure.

Strong support for direct addition of 4Et-py comes from the relative rates found for each of the dienyl complexes **1a**–**1c**. Thus the k_1 values follow the sequence C_6H_7 > 2-MeOC$_6$H$_6$ > C_7H_9 (*e.g.* 25:4:1 at 10 and 15.4 °C) (Table 3). The slower reactivity of [Fe(CO)$_3$(η^5-2-MeOC$_6$H$_6$)]BF$_4$ **1b** compared with the parent complex [Fe(CO)$_3$(η^5-C$_6$H$_7$)]BF$_4$ **1a** is attributed to the mesomeric influence of the methoxide group which has been shown from intermediate neglect of differential overlap (INDO) molecular-orbital calculations[39] 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(CO)$_3$(η^5-C$_7$H$_9$)]BF$_4$ **1c** is readily attributed to the steric hindrance caused by the additional methylene group if approach of 4Et-py from above the dienyl fragments of complexes **1a**–**1c** is assumed.

The low $\Delta H^‡$ values and large negative $\Delta S^‡$ values found for reactions (1) are also consistent with an associative process. The observed rate sequence in the order C_6H_7 > 2-MeOC$_6$H$_6$ > C_7H_9 is seen to arise from a balance between enthalpy and entropy effects. Thus the rapidity of the C_6H_7 reaction compared with that of C_7H_9 arises almost entirely from a much smaller $\Delta H^‡$, while the intermediate rate for the 2-MeOC$_6$H$_6$

Table 3 Steric and electronic effects on the rates of addition of 4Et-py and 2Et-py to complexes **1a**–**1c** in MeCN at 15.4 °C

Complex	k_1 (4Et-py)/ dm^3 mol^{-1} s^{-1}	k_1 (rel)	k_1 (2Et-py)*/ dm^3 mol^{-1} s^{-1}	k_1 (rel)	k_1 (4Et-py)/ k_1 (2Et-py)
1a	1.48×10^4	25	4.8×10^2	28	31
1b	2.4×10^3	4	1.8×10^2	10	13
1c	5.8×10^2	1	17.5	1	33

* Data from ref. 5.

complex is associated with the smallest $\Delta H^\ddagger$ and the most negative $\Delta S^\ddagger$ value.

The steric and electronic effects on the rate of addition of pyridines to complexes **1a**–**1c** can be seen from Table 3. The relative rate of addition of 4Et-py to complexes **1a**–**1c** at 15.4 °C is 25:4:1, *i.e.* the C_6H_7 complex is 25 times more reactive than that of C_7H_9, but only 6 times more reactive than the 2-$MeOC_6H_6$ complex. The relative rate of addition of 2Et-py to the complexes at the same temperature is 28:10:1. Again, the C_6H_7 complex is 28 times more reactive than the C_7H_9 complex and 3 times more reactive than the 2-$MeOC_6H_6$ analogue. Also, at 15.4 °C, 4Et-py is at least 30 times more reactive than 2Et-py[5] towards complexes **1a** and **1c** but only 13 times more reactive towards **1b** (Table 3). These results reveal the steric and electronic effects of both the dienyl fragments in complexes **1a**–**1c** and the amine nucleophile on the rate of addition of pyridines to dienylium organometallics. Thus steric blocking at the 2 position of the pyridine N or the steric nature of the co-ordinated organic group in organometallics of type **1** has a greater influence on the rate than does the electronic effects.

Added support for the associative mechanism demonstrated above for reactions (1) comes from the $\Delta V^\ddagger$ values of -7.8 and -6.4 cm^3 mol^{-1} found for the 2-$MeOC_6H_6$ (**1b**) and C_7H_9 (**1c**) reactions, respectively (Table 2). The rate of the C_6H_7 reaction did not permit measurable k_{obs} values at high pressures. Interestingly, the more negative $\Delta V^\ddagger$ value found for the more reactive 2-$MeOC_6H_6$ complex compared to that of C_7H_9 is in agreement with its more negative $\Delta S^\ddagger$ value of -126 J K^{-1} mol^{-1} (Table 1), consistent with a balance between enthalpy, entropy and volume effects during the associative process established here for reactions (1). The results contrast sharply with our recent report[34] on the reversible addition of 4-cyanopyridine to complexes **1** (dienyl = C_6H_7 or C_7H_9), where application of pressure showed no effect on the forward (k_1) and reverse (k_{-1}) steps and was rationalized in terms of an interchange of bonds/'ordered transition state' concept.[9] However, in the present study it must be the bond formation [*i.e.* C(diene)–N(4Et-py)] as the 4Et-py molecule adds to the C(5) atom of the dienyl fragment which results in a volume collapse as reflected by the negative $\Delta V^\ddagger$ values found for reaction (1). A comparison of the corresponding rate constants reveals that addition of 4Et-py is at least an order of magnitude faster than addition of 4CN-py at 25 °C, which could point to an earlier transition state involving greater bond formation and less breakage (ring slippage) for the more basic 4Et-py ligand. This means that bond breakage in the present systems mainly occurs following the transition state, such that the addition process will have a more associative bond-formation character than the interchange process suggested for the binding of 4CN-py to the co-ordinated ligand. The absolute magnitude of $\Delta V^\ddagger$ found in this study is smaller than that found for typical bond-formation processes with co-ordinated ligands,[40] which may be related to a less-efficient overlap of the molecular spheres since bond formation occurs at a site remote from the metal centre. These results provide the first quantitative information on the applicability of pressure as a kinetic parameter in the mechanistic interpretation of amine additions to dienylium organometallics of type **1**.

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