Correlation between the Nature of the Coordinated Organic Ligand and the Entropies and Volumes of Activation for Pyridine Additions to [Fe(CO)$_3$ (1-5-η-dienyl)] BF$_4$ (dienyl = C_6H_7 or C_7H_9)

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Abstract

Detailed kinetic Studies of the reversible additions of 2 – benzylpyridine and 3 – iodopyridine to the [Fe(CO)$_3$ (1-5- η -dienyl) BF$_4$ complexes (1; dienyl = C_6 H_7 or C_7 H_9) have been made as a function of temperature and pressure in acetonitrile using stopped flow techniques. The reported activation parameters ($\Delta H\neq$, $\Delta S\neq$ and $\Delta V\neq$] for both the forward addition and reverse dissociation reactions are consistent with the operation of the previously suggested Odiaka's ordered transition state" Mechanism.

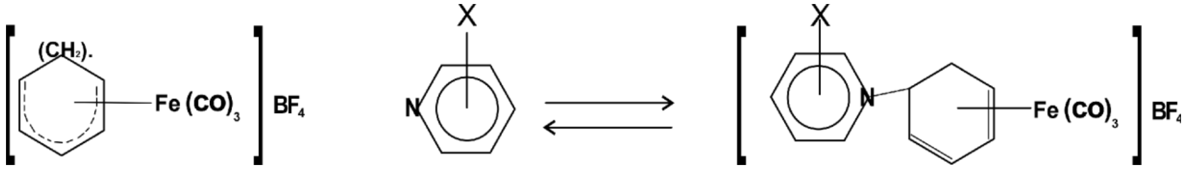
The results allow some quantitative information on the relationship between the nature of the coordinated Organic ligand in (1) and the degree of ordering in the transition state of the reactions between amines and organometallics of type (1).

Keywords: Activation, Pyridine, ligand, transition state, entropies

Introduction

The intimate mechanism of amine additions to Organometallics of the type [Fe (CO)$_3$ (1-5- η -dienyl)] BF$_4$ (1; dienyl= C_6H_7, 2-MeO C_6H_6 or C_7H_9) has been of special interest to us in recent years and has necessitated detailed temperature dependence studies of such systems[1- 4]. We have also studied the influence of pressure and temperature on the reactions of 4-cyanopyridine[5], 4-ethylpyridine[6] and 4-formylpyridine[7] with complexes (1) in CH_3CN. These reactions afforded products of the type tricarbonyl (1-4-n-5-exo-N-pyridiniocyclohexa – (or cyclohepta-) 1,3-diene) iron tetrafluoroborate in good yield, and allowed mechanistic assignments based on the nature and magnitude of the $\Delta H\neq$, $\Delta S\neq$ and $\Delta V\neq$ values. In such studies, associative processes are usually characterized by low $\Delta H\neq$ values and negative $\Delta S\neq$ and $\Delta V\neq$, values. whereas dissociative processes are accompanied by high $\Delta H\neq$ values and positive $\Delta S\neq$ and $\Delta V\neq$ values. However, we have shown [2,3,4] that the dissociative processes of amine additions to Organometallics of type (1) can be associated with large negative $\Delta S\neq$, values and have suggested[3,4] an interchange/"ordered transition state" mechanism to account for this interesting observation. It is also pertinent to note that both the forward addition step (k_1) and reverse dissociation step (k_{-1}) for these latter reactions are not influenced by pressure changes up to 150mpa[5,6] indicating that the volume collapse associated with the formation of the 1,3-diene products {C (diene) – N (amine) bond formation} is cancelled out by the volume increase associated with Fe-C (diene) bond breakage (reverse dissociation step) resulting in a zero-activation volume. The utility of pressure dependence studies in the mechanistic interpretations of other organometallic system has also been demonstrated[8-14] in our laboratories.

In the present work, we wish to report the result of a detailed temperature and pressure dependence study of the addition of 2-benzylpyridine and 3-iodopyridine to the complexes (1; dienyl = C_6H_7 and C_7H_9) in MeCN. {equation (1), X = CH_2Ph-2 or I-3}. The results allow a correlation to be made between the nature of the coordinated organic ligand in complexes (1) and the degree to which the transition state is ordered in the proposed[3-7] interchange/"ordered transition state" mechanism.



1a (n =1)
1b (n=2)

2a) **(1)**
2b)

Materials and Methods

Materials: The complexes 1a and 1b were synthesized and purified as described before.[15,16] 2-benzylpyridine ($2\text{-}CH_2PhC_5H_4N$) and 3-iodopyridine ($3\text{-}Ic_5H_4N$) were purchased (Aldrich) in the purest grade available and used without further purification. Acetonitrile was distilled in bulk and stored over molecular sieves (Size 3A) under dinitrogen.

Instrumentation: Reaction 1 is characterized by significant UV-VIS spectral changes, in particular an absorbance decrease at 400mm (2-benzylpyridine reaction) or 410nm (3-iodopyridine reaction) which were monitored with a shimadzu UV 250 Spectrophotometer. Infrared studies of the products (2) were performed on a Perkin Elmer 397 Spectrophotometer. The reactions in CH_3CN were studied under pseudo-first-order conditions involving a large excess of the pyridine nucleophile ([Fe] = 1.5×10^{-3} mol dm-3, [amine] = 0.01 – 0.10mol dm^{-3}). The addition reactions are fast and were monitored by use of the thermostatted ($\pm 0.1^{0}$c) Durrum D110 stopped flow instrument coupled to an on-line data acquisition and analysis system.[17] Kinetic experiments at pressure up to 150 MPa were performed on a home-made high pressure stopped-flow instrument.[18] Kinetic traces showed excellent first-order rate constants, and k_{obs}' were calculated from the slopes of plots of log (A_t - $A\infty$) versus time which were linear for at least two half- lives. Each k_{obs}' value is the average from at least six separate determinations. The second- order rate constants, $^{k}{}_{1}$, where derived by a least- squares fit to plots of k_{obs} versus [amine], and the errors quoted are the standard deviations. Activation enthalpies and entropies were calculated by a least – squares fit to the Eyring – Polanyi plots of lnK/T versus T^{-1}. Activation volumes were obtained from the slopes of lnK versus Pressure (Mpa), calculated by a least-squares method. The errors quoted are the standard errors of estimation from these analysis.

Result and Discussion

Nature of the Reactions: The nature of the reactions between the Organometallic complexes (1: dienyl = C_6H_7 and C_7H_9) and a wide variety of pyridines has been established by the isolation and characterization of the pyridinium adducts and by in situ i.r and ^{1}H n.m.r spectral studies[1,2,5,6,7,19]. The i.r. spectra exhibited two strong carbonyl bands at ca. 2055 and 1980cm^{-1}. The same two carbonyl bands were observed during the i.r. studies of reactions (1) using a large excess of the amine nucleophile, indicating the formation of the same (1-4- η -5-exo-N-pyridiniocyclohexa- (or cyclohepta-1,3-diene) tricarbonyliron complexes. In addition to the two strong carbonyl bands at 2055 and 1980cm^{-1}, these products (2) also exhibited the characteristic broad band at ca. 1060cm^{-1} attributed to the BF_4^- anion. For each of the reactions of complex 1a or 1b with equimolar amounts of 2-benzylpyridine or 3-iodopyridine, in situ IR studies showed the presence of carbonyl bands at 2120 and 2065cm^{-1} as well as those due to the products (2), indicating that reactions (1) are reversible.

Kinetics and Mechanism: Kinetic results for the reactions of complexes 1a and 1b with 2-

benzylpyridine are collected in Table 1 while results for the 3-iodopyridine reactions are summarized in Table 2. Plots of k_{obs} versus [amine] are linear with non- zero intercepts, which is characteristic of an equilibrium process, and can be rationalized by the rate law (2), where

$$k_{obs}= k_1 [amine] + k_{-1} \qquad …….. \quad (2)$$

k_1 is the forward and k_{-1} the reverse rate constant for reaction (1). The values of k_1 and k_{-1} at various temperatures are listed in Tables 1 and 2 and the corresponding activation parameters are summarized in Table 3.

The effect of pressure on k_{obs} for reaction (1) was studied at low and high amine concentrations in order to obtain the pressure dependence of mainly the reverse dissociation step (k_{-1}) or the forward addition step (k_1), respectively. The results are collected in Table 4 and clearly reveals within the limits of experimental error that k_{obs} (i.e. k_1 or k_{-1}) does not show any significant pressure dependence and $\Delta V\neq$ is approximately zero. This result indicates that the volume collapse associated with the formation of the 1,3-diene products (2) {C (diene)- N (amine) bond formation} is cancelled out by the volume increase associated with Fe-C(diene) bond breakage (reverse dissociation step), resulting in a zero activation volume.

Table 3 clearly show that the C_6H_7 complex is at least 30 times more reactive than the C_7H_9 analogue towards 2-benzlpyridine and 3 – iodopyrindine. The less reactivity of the C_7H_9 complex may be associated with its greater enthalpies of activation for reaction (1), attributed to the steric hindrance caused by the additional methylene group if one assumes approach of the amine nucleophile from above the dienyl fragment of the complex. The large negative $\Delta S_1 \neq$ values (Table 3) are consistent with an associative bond formation process as the amine nucleophiles add to the C(5) atom of the dienyl fragments to form the 1,3-diene products (2). On the other hand, the relatively much higher $\Delta H_{-1}\neq$ values compared to the $\Delta H_{-1}\neq$ values, are consistent with bond cleavage during dissociation of the amine from the products (2).

The observation that both the forward (k_1) and reverse (k_{-1}) steps exhibit no significant pressure dependence (Table 4) may be partly attributed to a later, more product- like transition state in which the volume collapse resulting from C(diene) – N(amine) bond formation is cancelled by a volume increase associated with Fe-C (diene) bond breakage, and vice versa for the reverser process. It is interesting to note that k_{-1} exhibits significantly negative $\Delta S\neq$ values (Table 5) which have led to the suggestion of an "ordered transition state [3,4], or in terms of the associated volume changes, an "interchange of bonds". [5-7] it should also be noted that the transition state is more ordered for the more electrophilic complex (Table 5) in agreement with the greater accumulation of positive charge on the amine N in the transition state of the C_6H_7 reaction. [19]. Thus $\Delta S\neq_{-1}$ values for the reaction of 2-benzylpyridine with the C_6H_7 (1a) and C_7H_9 (1b) complexes are -88 and -48 JK^{-1} mol^{-1} respectively, and -128 (C_6H_7) and -43 (C_7H_9) JK^{-1} mol^{-1} for the 3-iodopyridine reaction (Table 5). These results clearly demonstrate that the nature of the coordinated dienyl ligand in Organometallics such as (1) plays a crucial role in the degree of ordering of the transition state during such addition reactions. We have also shown[1,-4] that the basicity of the amine nucleophile has a strong influence in determining the location of the transition state in the systems. The mechanism of amine additions to Organometallics of type (1) can thus vary from a pure interchange of bonds (zero activation volume) as demonstrated in this work and elsewhere[5,7] to a highly associative bond process[6] (negative volume of activation).

It is therefore evident that pressure dependence studies of reactions such as (i) have revealed important information on the intimate nature of the underlying reaction mechanism.[20]

This work has clearly established the operation of the recently proposed[3,4], Odiaka's "ordered Transition State" mechanism in amine additions to organometallics of type (1) and shown that the nature of the coordinated organic ligand and basicity[1-4] of the amine nucleophile are the crucial parameters that determine the location of the transition state during such addition reactions.

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Table 1: Kinetic results for reactions of [Fe (CO)$_3$ (1-5- η -dienyl)] BF$_4$ (1.5 X 10^{-3} mold m^{-3}) with 2-benzylpyridine in MeCN.

Dienyl	**Temp./^{0}C**	**10^2.[2-CH$_2$PhC$_5$H$_4$N] (mold m^{-3})**	**k_{obs} $^a/_s{}^{-1}$**	**$k_{-1}{}^b$/dm^3 mol^{-1}□$_{-1}$**	**$k_{-1}{}^b$/□$_{-1}$**
C$_6$H$_7$	10.3	1.0	13.2±0.2	281±5	10.3±0.3
		2.0	16.1±0.3		
		4.0	21.0±0.3		
		6.0	27.1±0.4		
		10.0	38.5±0.6		
	15.2	1.0	19.2±0.4	330±5	16.3±0.3
		2.0	23.1±0.4		
		4.0	29.8±0.5		
		6.0	36.2±0.6		
		10.0	49.1±0.6		
	20.3	1.0	26.1±0.5	418±5	22.3±0.2
		2.0	31.0±0.5		
		4.0	39.1±0.6		
		6.0	47.2±0.7		
		10.0	64.1±0.9		
	25.1	1.0	33.3±0.5	520±9	28.2±0.5
		2.0	39.1±0.6		
		4.0	48.2±0.7		
		6.0	60.0±0.8		
		10.0	80.1±1.4		
	30.2	1.0	39.5±0.6	629±10	32.5±0.5
		2.0	44.8±0.7		
		4.0	56.8±0.8		
		6.0	70.4±1.4		
		10.0	95.6±2.1		
C$_7$H$_0$	10.1	1.0	0.205±0.003	7.59±0.38	0.142±0.021
		2.0	0.312±0.005		
		4.0	0.420±0.008		
		6.0	0.628±0.008		
		10.0	0.890±0.019		
	15.2	1.0	0.293±0.005	11.0±0.3	0.184±0.016
		2.0	0.398±0.006		
		4.0	0.650±0.009		
		6.0	0.820±0.019		
		10.0	1.29±0.02		
Dienyl	Temp./^{0}C	10^2.[2-CH$_2$PhC$_5$H$_4$N] (mold m^{-3})	k_{obs} $^a/_s{}^{-1}$	$k_{-1}{}^b$/dm^3 mol^{-1}□$_{-1}$	$k_{-1}{}^b$/□$_{-1}$
C$_7$H$_9$	20.3	1.0	0.501±0.006	14.0±0.2	0.351±0.012
		2.0	0.620±0.007		
		4.0	0.901±0.019		
		6.0	1.21 ±0.02		
		10.0	1.75 ±0.02		
	25.1	1.0	0.686±0.007	16.9 ±0.4	0.523±0.023
		2.0	0.851±0.018		
		4.0	1.19 ±0.02		
		6.0	1.58 ±0.03		
		10.0	2.19 ±0.03		
C$_7$H$_9$	30.1	1.0	0.962±0.021	22.5±0.7	0.760±0.041
		2.0	1.23 ± 0.02		
		4.0	1.62 ±0.03		
		6.0	2.18 ±0.03		
		10.0	2.98 ±0.04		

[a] Mean value of 5 to 6 kinetic runs

[b] Estimated by a least-squares fit to equation 2

Table 2: Kinetic Results for Reactions of [Fe(CO)$_3$(1-5- η -dienyl)] BF$_4$ (1.5 x 10^{-3} mol dm^{-3}) with 3 – iodopyridine in MeCN

Dienyl	Temp./^{0}C	10^2.[3-IC$_5$H$_4$N]/mold m^{-3}	k_{obs} ^{a}/$_s$$^{-1}$	k_{-1}^{b}/dm^3 mol^{-1}□$_{-1}$	k_{-1}^{b}/□$_{-1}$
C_6H_7	5.1	1.0	21.1± 0.6	604±3	15.1 ±0.2
		2.0	27.1±0.3		
		4.0	29.2±0.8		
		6.0	51.3±1.2		
		10.0	75.4±1.8		
	10.2	1.0	25.7±0.4	872±2	16.9±0.1
		2.0	34.2±0.4		
		4.0	51.6±0.5		
		6.0	69.3±1.6		
		10.0	104±3		
	15.1	1.0	32.1±0.5	1,270±10	19.5±0.5
		2.0	44.3±0.7		
		4.0	71.2±0.8		
		6.0	95.4±1.1		
		10.0	146±3		
	20.2	1.0	42.4±0.7	1,710±30	25.1 ±1.0
		2.0	59.4±1.5		
		4.0	92.1±2.5		
		6.0	128 ±3		
	25.3	1.0	59.0±1.0	2,380±10	35.4±0.5
		2.0	83.1±2.0		
		4.0	131 ±3		
		6.0	178 ±4		
C_7H_9	15.2 – 35.2	1.0 – 10.0	0.9 – 23.7	41.4 – 211	0.5 – 2.7

[a] Mean value of 5 to 6 kinetic runs

[b] Estimated by a least-squares fit to equation 2

Table 3: Rate and Activation Parameters for Reactions of [Fe(CO)$_3$ (1-5- η -dienyl)] BF$_4$ with 2-benzylpyridine and 3-lodopyridine in MeCN[a]

Amine	Dienyl	k_1(15^{0}C) / dm^{3}mol^{-1}s^{-1}	k_1 relative (15^{o}C)	ΔH_1^ ≠/kJmol^{-1}	ΔS_1^ ≠/kJ^{-1}mol^{-1}	ΔH_(−1)^ ≠/kJmol^{-1}	ΔS_(−1)^ ≠/ Jk^{-1}mol^{-1}
$NC_5H_4CH_2Ph$-2	C_6H_7	330±5	30	27.3±1.1	-102±4	38.7±4.6	-88±16
	C_7H_9	11.0±0.3	1	34.9±2.0	-104±7	60.5±4.4	-48±15
NC_5H_4I-3	C_6H_7	1270±10	31	44.4±0.9	-31±3	26.3±4.1	-128±14
	C_7H_9	41.4±0.4	1	58.3±1.0	-11±3	60.0±6.0	-43±20

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

Table 4: Effect of Pressure on the Addition of XC_5H_4N to $[Fe(CO)_3$ (1-5- η -dienyl)] BF_4 in MeCN

Dienyl	XC_5H_4N	Temp. /°C	10^2.[XC_5H_4N] / mold m^{-3}	Pressure/MPa	$k_{obs}{}^a$/S^{-1}	ΔV_1^ ≠/cm^{3}mol^{-1}	ΔV_(−1)^ ≠/ cm^{3}mol^{-1}
C_6H_7	2-$CH_2PhC_5H_4N$	15.1	1.0	10	20.4 ±0.5	-	0.27±0.14
			1.0	50	20.2 ±0.5		
			1.0	100	20.0±0.5		
			1.0	150	20.1±0.5		
		15.1	10.0	10	50.4±1.3	0.10±0.07	-
			10.0	50	50.6±1.3		
			10.0	100	50.3±1.2		
			10.0	150	50.2±1.2		
	3-IC_5H_4N	10.3	1.0	10	24.7±0.7		0.43±0.04
			1.0	50	24.6±0.7		
			1.0	100	24.3±0.7	-	
			1.0	150	24.1±0.7		
		10.3	6.0	10	64.3±1.5	0.20±0.02	
			6.0	50	64.2±1.4		
			6.0	100	63.8±1.4		
			6.0	150	63.6±1.4		
C_7H_9	2-$CH_2PhC_5H_4N$	20.1	1.0	10	0.507±0.007	-	
			1.0	50	0.506±0.007		0.14±0.01
			1.0	100	0.504±0.007		
			1.0	150	0.503±0.006		
		20.1	10.0	10	1.76±0.04	0.51±0.03	
			10.0	50	1.75±0.04		
			10.0	100	1.73±0.04		
			10.0	150	1.71±0.03		
	3-$IC_5H_4N^a$	15.2	1.0 – 10.0	10 – 150	0.89 – 5.84	0.07±0.03	0.06±0.03

Table 5: Correlation between the nature of the coordinated organic ligand in $[Fe(CO)_3$(1-5 η --dienyl)] BF_4 and the entropies and volumes of activation for the reaction: $[Fe(CO)_3$(1-5-n-dienyl)] BF_4 + NC_5H_4 X $\xrightleftharpoons[k_{-1}]{k_1}$ $[Fe(CO)_3$(1-4-n-diene. $NC_5H_4X)]$ BF_4

Dienyl	NC_5H_4X	k_1 (15°C) / dm^{3}mol^{-1}S^{-1}	ΔS_1^ ≠/JK^{-1} mol^{-1}	ΔV_1^ ≠/cm^{3}mol^{-1}	ΔS_1^ ≠/JK^{-1}mol^{-1}	ΔV_1^ ≠/cm^{3}mol^{-1}
C_6H_7	$NC_5H_4CH_2Ph$-2	330±5	-102.3±4	0.10±0.007	-88±16	0.27±0.14
	NC_5H_4I-3	1270±0.10	-31.9±3	0.20±0.02	-128±14	0.43±0.04
C_7H_9	$NC_5H_4CH_2Ph$-2	11.0±0.3	-104±7	0.51±0.03	-48±15	0.14±0.01
	NC_5H_4I-3	41.4±0.4	-11±3	0.07±0.03	-43±20	0.06±0.03

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