Effect of Temperature and Pressure on the Addition of 4-Tertiarybutylpyridine to Tricarbonyl (1-5-n-Dienyl) Iron (II) Complexes (Dienyl = C_6H_7, 2-MeoC_6H_6 or C_7H_9)

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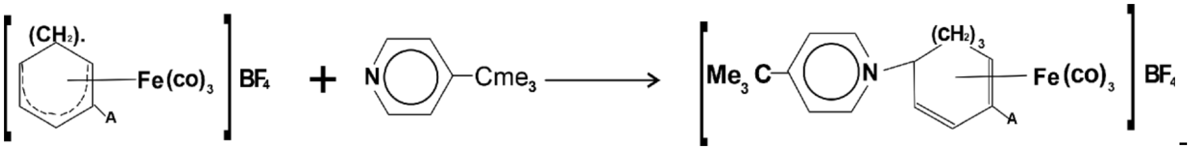
Abstract
A detailed kinetic study of the addition of 4-tertiarybutylpyridine to the coordinated dienyl ligand in tricarbonyl (1-5-ɳ-dienyl) iron (II) complexes (1; dienyl = C_6H_7, 2-MeoC_6H_6 and C_7H_9) has been made as a function of temperature and pressure in acetonitrile using stopped-flow techniques. The reactions proceed to completion under pseudo-first-order conditions, i.e. $k_{obs} = k_1$ [4-Me_3CPy]. The observed rate sequence C_6H_7 > 2-Meo C_6H_6 > C_7H_9 (e.g. 18:3:1 at 20ºC and 0.1 MPa) and the low $\Delta H^{\neq}$ and large negative $\Delta S^{\neq}$ and $\Delta V^{\neq}$ values support direct addition (k_1) to the dienyl fragments of complexes (1). The results contrast sharply with the reversible additions of 4-Cyanopyridine, 4-formyldypridine, 2-benzylpyridine and 3-iodopyridine to complexes (1) where k_{obs} was not influenced by pressure changes up to 150 MPa, indicating a zero, volume of activation and the consequent operation of the Odiaka's "ordered transition state" mechanism.

Keywords: Temperature, complexes, stopped-flow, pyridine, volume

Introduction

Our keen interest in the intimate mechanism of amine additions to organometallics of the type $[Fe(CO)_3$ (1-5-ɳ-dieny)] BF_4 (1; dienyl = C_6H_7, 2-MeoC_6H_6 or C_7H_9) recently led us to investigate the influence of temperature and pressure on the reactions of 4-Cyanopyridine[1], 4-ethylpyridine[2] and 4-formylpyridine[3], with complexes (1) in MeCN. The reactions afforded products of the type tricarbonyl (1-4-ɳ-5-exo-N-pyridiniocyclohexa- (or Cyclohepta-) 1, 3-diene) iron complexes in good yields as previously established[4-7] for a wide range of pyridine additions to complexes (1), and allowed mechanistic assignments based on the nature and magnitude of the $\Delta H^{\neq}$, $\Delta S^{\neq}$ and $\Delta V^{\neq}$ values. The addition reactions are generally associated with low $\Delta H^{\neq}$ values, large negative $\Delta S^{\neq}$ values and negative $\Delta V^{\neq}$ values. Whereas the reverse dissociation step is usually accompanied by significant higher $\Delta V^{\neq}$ values and positive $\Delta S^{\neq}$ and $\Delta V^{\neq}$ values. These results are consistent with direct nucleophilic attack at the coordinated organic ligand in complexes (1) during bond formation and vice-versa during bond dissociation. Cases are also known[8-11] where the dissociative processes of amine additions to complexes (1) are associated with large negative $\Delta S^{\neq}$ values and we have explained this interesting observation in terms of the Odiaka's "ordered transition state" mechanism [8, 9]. Interestingly, 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 150 MPa[1,3] 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. Progress has also been made in establishing the influence of amine basicity[4] as well as the electronic and steric nature[6] of the coordinated ligand in complexes (1) on the intimate nature of the mechanism of amine additions to organometallics of type (1). The mechanistic utility of pressure dependence studies in other organometallic systems has been demonstrated in the laboratories of R.Van Eldik[12-18]

As an extension of these studies, we now report the results of a dtailed temperature and pressure dependence study of the addition of 4-tertiarybutylpyridine to complexes (1; dienyl = C_6H_7, $2\text{-MeoC}_6\text{H}_6$ or C_7H_9) in MeCN (eqn. 1). A comparison of this work to those reported[1-3] for similar addition processes allows some correlation to be made between the basicity of the amine nucleophile and the intimate nature of amine additions to organometallics of type (1).



---(1)

1

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

Materials and Methods

Materials: The complexes (1a) – (1c) were synthesized and purified as described before[19, 20] Chemical and Spectroscopic analysis confirmed their purity. 4-tertiarybutylpyridine (4-Me$_3$cPy) was freshly distilled over KOH pellets and under vacuum prior to use. Acetonitrile (MeCN) was distilled in bulk and stored over molecular sieves (3A) under a dinitrogen atmosphere.

Instrumentation: Reaction I is characterized by significant UV-VIS spectral changes, in particular an absorbance decrease at 400nm, which was monitored with a Shimadzu UV 250 Spectrophotometer. Infrared studies of the products (2) were performed on a Perkin-Elmer 397 Spectrophotometer. The kinetics of reaction I was studied under pseudo-first-order conditions involving the use of a large excess of 4-Me$_3$cPy. The addition reactions are fast and were monitored by use of a thermostat (± 0.1°C) Durrum D110 stopped-flow instrument coupled to an on-line data acquisition and analysis system.[21] Kinetic experiments at pressures up to 150 MPa were performed on a home-made high pressure stopped-flow instrument.[22] Kinetic traces showed excellent first-order behaviour under all experimental conditions, and the first-order rate constants. k_{obs}, were calculated from plots of $\iota n\ (A_\infty - A_t)$ versus t in the usual way. Such plots were linear for at least 2 to 3 half-lives of the reaction. Reported rate constants are the mean values of 5 or 6 separate determinations. All rate and activation parameters were calculated by linear least-squares analysis. The second-order rate constants, k_1, for the rapid addition of 4-Me$_3$ cPy to {1; dienyl = C_6H_7 and $2\text{-MeOC}_6\text{H}_6$ (15-35°C)} were calculated directly from the observed rate constant (see equation 2).

Results and Discussion

Nature of the Reaction: The reaction products formed from the addition of a wide variety of pyridines to the dienyl complexes (1; dienyl = C_6H_7 and $2\text{-MeoC}_6\text{H}_6$ or C_7H_9) have been isolated for X = H, 2-Me, 4-Me, 2-Et, 4-Et, 4-CN, 4-CH_3 CO and 2,4,6-Me$_3$[1-6] and shown to be pyridinium adducts of the type (2). In addition, in situ IR and ‘Hnmr Spectral studies of several other pyridine adducts of the type (2) have clearly established the nature of such products as tricarbonyl (1-4-n-5-ex0-N-pyridiniocyclohexa- (or Cyclohepta-)) 1, 3-diene iron complexes[4]. The IR spectra exhibited two strong carbonyl bands at ca. 2055 and 1980 cm^{-1}. The same two VCO bands were observed during the IR studies of reaction (1) when a large excess of 4-Me$_3$ cPy was used, indicating the formation of the same tricarbonyl (1-4-n-5-exo-N-pyridiniocyclohexa- (or Cyclohepta-)) 1, 3-diene iron complexes. In addition to the two strong V_{CO} banks at 2055 and 1980 cm^{-1}, products (2) also exhibited the characteristic broad band at ca. 1060 cm^{-1} attributed to the BF_4^- anion. Thus reaction (1) proceeds to completion under the kinetic conditions employed.

Kinetics and Mechanism: Kinetic results for the reactions of complexes (1a) – (1c) with 4-Me$_3$ cPy are collected in Table 1. Plots of k_{obs} versus [4-Me$_3$cPy] are linear with zero intercepts for all three complexes, thus showing close adherence to the second-order rate law (2), where k_1 is the second-order rate constant for the direct addition of 4-Me$_3$cPy 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 and the corresponding activation parameters are summarized in Table 2. The effect of pressure on k_{obs} for the reactions of 4-Me_3cPy with 1b and 1c was studied using 0.01 mol dm^{-3} and 0.02 mol dm^{-3} amine concentrations, respectively, for which the results (Table 3) demonstrate a rate enhancement with increasing pressure. The rapidity of the reaction of 4-Me_3cPy with 1a did not permit measurable k_{obs} values at high pressures.

$k_{obs} = k_1$ [4-Me_3cPy]…. ….. ….. (2)

Strong support for direct addition of 4-Me_3 cPy to complexes (1) comes from the rates found for reaction (1). Thus the k_1 values are seen from Table 2 to decrease in the order C_6H_7 > 2-Me0C_6H_6 > C_7H_9 (18:3:1 at 20ºC and 1 atm.). The greater reactivity of the parent complex [Fe(C0)$_3$(1-5-ɳC_6H_7)] BF_4 (1a) compared with Fe $(CO)_3$ (1-5-ɳ-2-MeoC_6H_6) BF_4 (1b) is due to the mesomeric influence of the methoxide group which has been demonstrated[23] 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$(CO)_3$ (1-5-ɳ-C_7H_9)] BF_4 (1c) is readily attributed to the steric hindrance caused by the additional methylene group in the latter if one assumes approach of 4-Me_3cPy from above the dienyl rings. The low $\Delta H^{\neq}$values and large negative $\Delta S^{\neq}$ values found for reaction (1) are also consistent with an associative mechanism (Table 2). The observed rate sequence in the order C_6H_7 > 2-MeoC_6H_6 > C_7H_9 is seen to arise from a play-off between enthalpy and entropy effects. Thus while the greater reactivity of the C_6H_7 complex compared with the C_7H_9 analogue is associated with a less negative $\Delta S^{\neq}$ value of -87 JK^{-1} mol^{-1}. The intermediate rate of the 2-$M_eOC_6H_6$ complex is associated in the largest $\Delta V^{\neq}$ value of 27.8KJ $^{-1}mol^{-1}$ and a very similar $\Delta V^{\neq}$ value as fpr the C_6H_7 complex of -87$JK^{-1}mol^{-1}$ (Table 2).

Added support for the associative mechanism demonstrated above for reaction (1) comes from the $\Delta V^{\neq}$ values of -7.2 cm^3 mol^{-1} and -5.8 cm^3mol^{-1} found for the 2-MeoC_6H_6 (1b) and C_7H_9 (1c) reactions respectively (Table 3). Similar results are expected for the C_6H_7 reaction whose rapidity did not permit measurable k_{obs} values. The results contrast sharply with our reports on the reversible addition of 4-cyanopridine[1], and 4-formylpyridine[3], to complexes (1) where application of pressure showed no effect on the forward (k_1) and reverse (k_{-1}) steps and was explained in terms of an interchange of bonds/"ordered transition state" concept. However, in the present study, it must be the bond formation {i.e C(diene)- N(4-Me_3cPy)} as the 4-Me_3cPy molecule adds to the C(5) atom of the dienyl fragment, that results in a volume collapse as reflected by the negative $\Delta V^{\neq}$ values found for reaction (1).

A comparison of the results obtained in this work to those reported[1-3] for pyridine additions to complexes (1) clearly reveals that the less basic pyridines (i.e. $pK_a < 5$) tend to go through a late, product-like transition state allowing simultaneous bond formation and bond-breaking. In terms of the associated volume changes, this means that bond formation will be partially cancelled out by bond breakage. Such reactions are consequently accompanied by a net zero volume of activation [1, 3] (inertness, to pressure change for the k_1 and k_{-1} steps) and exhibit the Odiaka's "ordered transition state: mechanism proposed earlier[8,9]. On the other hand, the more basic pyridines ($pK_a > 5$) go through an early transition state in which bond formation plays a crucial role (negative volume of activation)[2]. For the reactions that are reversible (pKa < 5) but which do not demonstrate the "ordered transition state" mechanism (i.e. negative entropy of activation for the dissociative step and inertness to pressure changes for the forward and reverse reactions), the k_1 step shows rate enhancement while the k_{-1} step shows rate retardation, respectively, with increasing pressure.[3] In conclusion, the mechanism of amine additions to organometallics of type (1) can vary from an "ordered transition state" type (zero activation volume) to a highly associative bond process (negative activation volume).

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Table 1: Kinetic Results for Reactions of [Fe(CO)$_3$ (1-5-ɳ-dienyl)] BF$_4$ (1.5 x 10^{-3} mol dm^{-3}) with 4-tertiarybutylpyridine in MeCN

Dienyl	Temp./°C	10^2[4-Me$_3$^{c}C$_5$H$_4$N]/ mol dm^{-3}	k^a obs	k_1^b/dm^{3}mol^{-1} s^{-1}
C_6H_7	10.3	1.0	91.0±2.0	9,100±200
		2.0	182±5	9,100±250
	15.3	1.0	115±3	11,500±300
	20.3	1.0	132±3	13,200± 300
	25.1	1.0	165±4	16,500±400
	30.2	1.0	185±5	18,500±400
2-MeoC_6H_6	10.4	1.0	13.4±0.3	1,310±20
		2.0	26.4±0.6	
		4.0	52.2±1.3	
		6.0	76.3±1.8	
		10.0	132±3	
	15.3	1.0	16.7±0.2	1, 670±20
	20.3	1.0	21.6±0.3	2, 160±30
	25.1	1.0	26.3±0.3	2, 630±30
	30.1	1.0	31.5±0.4	3, 150±40
	35.2	1.0	36.4±0.4	3, 640±40
C_7H_9	10.4 – 25.1	1.0 – 10.0	5.90 – 82.2	580 – 826

[a] Mean value of 5-6 kinetic runs

[b] Derived from equation 2

Table 2: Rate and Activation Parameters for Reactions of $[Fe(CO)_3(1\text{-}5\text{-}n\text{-}dienyl)]\ BF_4$ with 4-tertiarybutylpyridine in MeCN[a]

Dienyl	$k_1(20^oC)$ / $dm^3mol^{-1}s^{-1}$	k_1 relative (20^oC)	$\Delta H_1^{\neq}$/ $kJmol^{-1}$	$\Delta S_1^{\neq}$/ $JK^{-1}mol^{-1}$
C_6H_7	13,200±300	18	23.2±1.5	-87±5
2-$MeOC_6H_6$	2,160±30	3	27.8±1.3	-87±4
C_7H_9	726±9	1	14.2±0.7	-142±2

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

Table 3: Effect of pressure on the addition of 4-tertiary-butylpyridine to $[Fe(CO)_3\ (1\text{-}5\text{-}\eta\text{-}dienyl)]BF_4$ in MeCN

Dienyl	Temp./°C	10^2[amine]/mol dm^{-3}	Pressure/MP a	K_{obs}/S^{-1}	$\Delta V_1^{\neq}/cm^3\ mol^{-1}$
C_6H_7			A	a	A
2-$MeoC_6H_6$	20.1	1.0 1.0 1.0 1.0	10 50 100 150	19.8±0.5 23.2±0.5 26.6±0.6 30.2±0.7	-7.2±0.5
C_7H_9[b]	20.1	2.0 2.0 2.0 2.0	10 50 100 150	12.8±0.3 14.5±0.3 15.6±0.4 18.1±0.4	-5.8±0.6

[a] Reaction is too fast for the high pressure S/F system.

[b] Results from reference 13

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