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Synthetic and Mechanistic Studies of the Addition of 2,6-Dimethylaniline to Tricarbonyl (1–5-η-Dienyl) Iron(II) complexes (Dienyl = C_6H_7 or C_7H_9)

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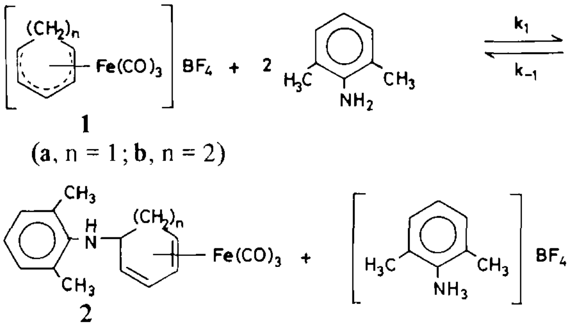
Abstract

Detailed synthetic and mechanistic studies of the addition of 2,6-dimethylaniline to the organometallic complexes $[Fe(CO)_3(1\text{–}5\text{-}\eta\text{-dienyl})]BF_4$ (**1**, dienyl = C_6H_7 or C_7H_9) indicates the general rate law $k_{obs} = k_a\ [2,6\text{-}(Me)_2C_6H_3NH_2] + k_b$ which is consistent with an equilibrium process. The greater reactivity of the C_6H_7 complex and the low ΔH_a^{+} and large negative ΔS_a^{+} values are in accordance with direct addition of the amine to the dienyl rings of **1**. On the other hand the relatively much higher ΔH_b^{+} values are consistent with bond cleavage in dissociation as is the positive ΔS_b^{+} value of +220 J K^{-1} mol^{-1} determined for the C_6H_7 reaction. The negative ΔS_b^{+} value of −43 J K^{-1} mol^{-1} found for the C_7H_9 reaction suggests the presence of an ordered transition state through which the starting dienyl complex is re-formed via some internal S_N2 process.

Introduction

The addition of organic substrates to coordinated π-hydrocarbons of the type $[M(CO)_3(\pi\text{-hydrocarbon})]BF_4$ (e.g. $[Fe(CO)_3(1\text{–}5\text{-}\eta\text{-}C_6H_7)]BF_4$) has in recent years led to the discovery of novel organometallics such as, for example, 1,3-diene-substituted products [1–6], 1,3,5-triene-substituted [7] or other [8] products. Thus the addition of aniline and substituted anilines to the complexes $[(1\text{–}5\text{-}\eta\text{-dienyl})Fe(CO)_3]BF_4$ (**1**, dienyl = C_6H_7, $2\text{-}MeOC_6H_6$ or C_7H_9) affords the neutral substituted-1,3-diene products, $[Fe\{1\text{–}4\text{-}\eta\text{-}(NHC_6H_4X)diene\}(CO)_3]$ (X = H, 2-Me, 3-Me, 4-Me, 2-Cl, 3-Cl, 4-Cl, 4-MeO or 3-NO_2) [9–11] in good yields. However, apart from the reactions of 4-methylaniline [9], 2-methylaniline [10] and 4-chloroaniline [11] with **1** (dienyl = C_6H_7, $2\text{-}MeOC_6H_6$ or C_7H_9) and of aniline [10] with **1** (dienyl = C_6H_7 or $2\text{-}MeOC_6H_6$), very little quantitative information is currently available on the thermodynamics of the reactions of anilines with coordinated π-hydrocarbons.

As an extension to these studies, this paper reports the results of detailed synthetic and mechanistic studies of the reaction of 2,6-dimethylaniline with the complexes (**1**, dienyl = C_6H_7 or C_7H_9) in acetonitrile solvent (eqn. (1)) in order to improve our understanding of the mechanism and thermodynamics of amine additions to coordinated π-hydrocarbons.



(1)

Experimental

The complexes **1a** and **1b** were synthesized and purified by published procedures [12, 13]. 2,6-Dimethylaniline (Aldrich) was purchased in the purest grade available, freshly distilled under a dinitrogen atmosphere and dried over molecular sieves (size 3 Å) prior to use. Acetonitrile (BDH) solvent was distilled in bulk and stored over molecular sieves under a dinitrogen atmosphere.

Product Isolation and Characterisation

Tricarbonyl[1–4-η-5-(N-2,6-Dimethylanilino)-cyclohexa-1,3-diene]iron (2a)

Solutions of $[(1\text{–}5\text{-}\eta\text{-}C_6H_7)Fe(CO)_3]BF_4$ (0.05 g, 0.164 mmol) in CH_3CN (10 cm^3) and 2,6-dimethylaniline (0.0397 g, 0.328 mmol) in CH_3CN (10 cm^3) were mixed under nitrogen in a 50 cm^3 flask and allowed to stand at room temperature for 10 min. Rotary evaporation of the mixture under dinitrogen at 30 °C afforded a yellow solid. This was shaken with 40 cm^3 of diethylether/water (50/50; *v*/*v*) and the ether layer was passed through an inch-depth Alumina-H column. The yellow filtrate was

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evaporated off at reduced pressure and at 30 °C to give a pale-yellow oil. This was taken up in toluene and treated with a little $MgSO_4$ to remove any traces of water before passing through an inch-depth Alumina-H column. Rotary evaporation of the resulting yellow filtrate under a dinitrogen atmosphere produced a yellow oil which could not be crystallized. The yield of product **2a**, 0.033 g, was 59%. IR ν(CO) (CH_3CN): 2045 and 1970 cm^{-1}. ν(NH) in nujol mull: 3400 cm^{-1} ^1H NMR in d_6-acetone: τ 6.80 (2H, m, $H^{1,4}$), 4.30 (2H, m, $H^{2,3}$), 6.10 (1H, m, $H^{5'}$), 8.50 (1H, m, H^6), 7.60 (1H, m, $H^{6'}$), 3.10 (1H, t, aromatic), 3.50 (2H, d, aromatic), 5.40 (1H, br, N*H*) and 7.90 (6H, s, CH_3). The oil was found to be sensitive to air in the pure state and gave poor microanalyses.

The aqueous phase from the above procedure was passed through a short Alumina-H column, and the eluent evaporated to dryness to give the anilinium salt, $[2,6\text{-}(Me)_2C_6H_3NH_3]BF_4$, as an off-white solid after treatment with Na-dried diethylether.

Tricarbonyl [1–4-η-5-(N-2,6-Dimethylanilino)cyclohepta-1,3-diene] iron (2b)

An analogous reaction of $[(1\text{–}5\text{-}\eta\text{-}C_7H_9)Fe(CO)_3]BF_4$ (0.05 g, 0.156 mmol) with 2,6-dimethylaniline (0.0379 g, 0.313 mmol) in CH_3CN (20 cm^3), followed by similar work-up to that of **2a** above, gave a yellow oil. The yield of product **2b**, 0.04 g, was 73%. IR ν(CO) (CH_3CN): 2045 and 1970 cm^{-1}, ν(NH) (nujol mull): 3400 cm^{-1}. This oily product was found to be sensitive to air, gradually turning brown and showed the absence of nitrogen in its microanalysis indicating the loss of the anilinium group during the decomposition process.

Kinetics Studies

All of the reactions (1) in CH_3CN were studied under pseudo-first-order conditions using a large excess of 2,6-dimethylaniline ($[Fe] = 1.5 \times 10^{-3}$ mol dm^{-3}, $[2,6\text{-}(Me)_2C_6H_3NH_2] = 0.01\text{–}1.0$ mol dm^{-3}). The reactions were monitored at 390 nm using a thermostated (±0.1 °C) stopped-flow spectrophotometer. At this wavelength, a large decrease in absorbance was observed. The reaction traces were captured and analysed using a rapid data capture system purchased from Lombardi Scientific Limited, employing computer programs developed jointly with Lombardi (U.K.) Limited and described elsewhere [14]. Pseudo-first-order rate constants, k_{obs}, were calculated from the slopes of plots of $\log(A_t - A_\infty)$ *versus* time. These plots were linear for at least 75% completion of reaction. Each k_{obs} value is the average from at least six separate runs, with an average reproductivity of ±4%. The second-order rate constants, k_a, were calculated by a least-squares fit to the k_{obs} *versus* $[2,6\text{-}(Me)_2C_6H_3NH_2]$ plots, the errors quoted being the appropriate standard deviations. Activation enthalpies were determined from the slopes of Arrhenius plots of $\log k_a$ or $\log k_b$ *versus* T^{-1}, calculated by a least-squares method. The errors quoted are the standard deviations from the least-squares analysis. Entropies of activation were calculated using the second-order and first-order rate constants, k_a and k_b respectively.

Results and Discussion

Nature of the Reactions

The products **2a** and **2b** are yellow oils which are sensitive to air in their pure states. These products exhibited two strong carbonyl bands at *ca.* 2045 and 1970 cm^{-1} in their infrared spectra as well as ν(NH) peaks at 3400 cm^{-1} (nujol mull), characteristic of tricarbonyl (1–4-η-5-*N*-anilino-1,3-diene) iron complexes [9–11]. 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 (**1a**, **1b**), no interference is expected from the instability of the products (**2**) and their subsequent decomposition. The ^1H NMR spectrum of a fresh sample of **2a** in d_6-acetone showed overlapping resonances characteristic of the outer ($H^{1,4}$) and inner ($H^{2,3}$) 1,3-diene protons at τ 6.80 and 4.30 respectively while the $H^{5'}$ proton appears at 6.10 τ. The $H^{6,6'}$ methylene protons resonate at 8.5 and 7.6 τ respectively while the singlet at 7.90 τ is attributed to the methyl groups of the 2,6-dimethylaniline substituent. The broad resonance at *ca.* 5.4 τ is assigned to the N*H* proton since it disappears on addition of D_2O. The triplet at 3.1 τ and doublet at 3.5 τ are assigned to the aromatic protons. Reactions (1) were shown to be reversible processes by the addition of a few drops of trifluoroacetic acid to equilibrium mixtures of the reactions; the starting organometallics (**1a** and **1b**) formed quantitatively as evidenced by the appearance of strong ν(CO) bands at 2120 and 1965 cm^{-1} and the disappearance of bands due to the products (**2a** and **2b**) at 2045 and 1970 cm^{-1}. Also the presence of the former bands in the reaction solutions of eqn. (1) even at infinite time is indicative of an equilibrium process. The anilinium salt, $[2,6\text{-}(Me)_2C_6H_3NH_3]BF_4$, shown in eqn. (1) was obtained as an off-white solid from the aqueous phase of the reaction with the C_6H_7 complex but was not characterised in this work. Its 4-methylanilino derivative has previously been isolated and fully characterised on the basis of its IR, ^1H NMR and microanalytical measurements [9].

Kinetics and Mechanism

Kinetic results for the addition of 2,6-dimethylaniline to the complexes **1a** and **1b** in CH_3CN are

TABLE I. Kinetic Results for Reactions of $[Fe(CO)_3(1\text{–}5\text{-}\eta\text{-dienyl})]BF_4$ with 2,6-Dimethylaniline in MeCN ($[Fe] = 1.5 \times 10^{-3}$ mol dm^{-3})

Dienyl	Temperature (°)	$10^1 \times [2,6\text{-}(Me)_2C_6H_3NH_2]$ (mol dm^{-3})	k_{obs} (s^{-1})	k_a[a] (dm^3 mol^{-1} s^{-1})	k_b[a] (s^{-1})
C_6H_7	0.0	0.1	5.10		
	0.0	0.2	9.01		
	0.0	0.4	15.4		
	0.0	0.6	23.2		
	0.0	0.8	30.5		
	0.0	1.0	37.2	358(4)	1.57(0.53)
	5.4	0.2	12.7		
	5.4	0.4	23.0		
	5.4	0.6	30.2		
	5.4	0.8	39.0		
	5.4	1.0	49.4	448(2)	4.00(0.13)
	10.5	0.2	23.2		
	10.5	0.4	33.7		
	10.5	0.6	45.1		
	10.5	0.8	55.0		
	10.5	1.0	65.2	527(5)	12.9(0.40)
	15.4	0.2	41.2		
	15.4	0.4	53.1		
	15.4	0.6	66.0		
	15.4	0.8	75.1		
	15.4	1.0	88.3	619(5)	30.0(0.33)
C_7H_9	0.0	1.0	2.69		
	0.0	2.0	3.87		
	0.0	4.0	6.50		
	0.0	8.0	11.5		
	0.0	10.0	14.1	12.7(0.05)	1.39(0.03)
	8.9	0.5	4.30		
	8.9	1.0	5.25		
	8.9	2.0	7.40		
	8.9	4.0	11.7		
	8.9	5.0	13.8	21.3(0.10)	3.18(0.03)
	15.1	0.5	7.02		
	15.1	1.0	8.50		
	15.1	2.0	11.5		
	15.1	4.0	17.4		
	15.1	5.0	20.4	29.7(0.40)	5.54(0.10)
	20.1	0.5	9.40		
	20.1	1.0	11.3		
	20.1	2.0	15.1		
	20.1	4.0	23.2		
	20.1	5.0	26.7	38.8(0.30)	7.43(0.10)

[a] Estimated by a least-squares fit to eqn. (2). Values in parentheses are standard errors of estimate.

collected in Table I. Plots of k_{obs} versus $[2,6\text{-}(Me)_2C_6H_3NH_2]$ are linear with non-zero intercepts indicating close adherence to the rate law (2) which is consistent with an equilibrium process. The separate k_a and k_b values obtained respectively from the slopes and intercepts of these plots (Table I) were calculated by a least-squares fit to eqn. (2).

$$\text{Rate} = k_a[\text{complex}][2,6\text{-}(Me)_2C_6H_3NH_2] + k_b[\text{complex}]$$

$$\text{i.e. } k_{obs} = k_a[2,6\text{-}(Me)_2C_6H_3NH_2] + k_b \qquad (2)$$

Rate law (2) may be rationalised in terms of the amine-assisted pathway shown in Scheme 1.

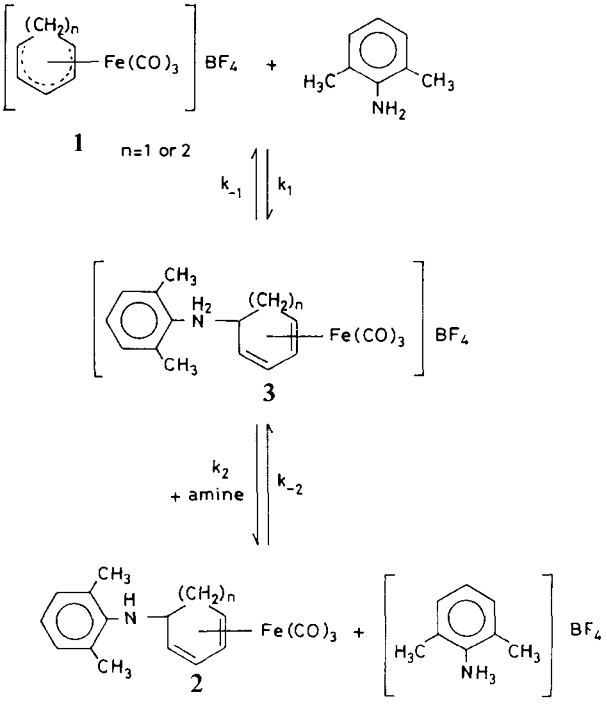
If one assumes that the establishment of the equilibrium, K_2 is much more rapid than K_1 (see for example refs. 9–11) then this clearly affords the relationship (3) and (4) (obtained from ref. 10)

$$k_a = k_1 \qquad (3)$$

$$k_b = k_{-1}[H^+]/[H^+] + K_2K_a \qquad (4)$$

TABLE II. Rate and Activation Parameters for Reactions of [Fe(CO)$_3$(1–5-η-dienyl)]BF$_4$ with 2,6-Dimethylaniline in MeCN

Dienyl	k_a relative (0 °C)	$\Delta H_a^{\ddagger}$ (kJ mol^{-1})	$\Delta S_a^{\ddagger}$ (J K^{-1} mol^{-1})	$\Delta H_b^{\ddagger}$ (kJ mol^{-1})	$\Delta S_b^{\ddagger}$ (J K^{-1} mol^{-1})
C_6H_7	28	20.8 ± 0.8	−119 ± 3	126 ± 5.4	+220 ± 19
C_7H_9	1	34.6 ± 0.8	−96 ± 3	54 ± 1.0	−43 ± 3



Scheme 1.

where k_1 represents the second-order rate constant for direct addition of 2,6-dimethylaniline to the dienyl rings of **1a** and **1b** and k_{-1} refers to the first-order rate constant for the dissociation of the amine from the anilinium adducts (**2a** and **2b**). The k_1 values are seen from Tables I and II to decrease in the order $C_6H_7 > C_7H_9$. For example, at 0 °C the C_6H_7 complex is twenty-eight times more reactive than its C_7H_9 analogue (Table II) indicating direct addition to the dienyl rings of these complexes. Similar rate trends have been established for the addition of a wide range of nucleophiles to complexes **1a** and **1b**, processes known to involve direct addition to the dienyl rings [2–11]. The greater reactivity of the parent complex [Fe(1–5-η-C_6H_7)(CO)$_3$]BF$_4$ (**1a**) compared with [Fe(1–5-η-C_7H_9)(CO)$_3$]BF$_4$ (**1b**) is due to the steric hindrance caused by the additional methylene group in **1b** if one assumes an approach of 2,6-dimethylaniline from above the dienyl rings of **1**. The low $\Delta H_a^{\ddagger}$ ($=\Delta H_1^{\ddagger}$) values and large negative $\Delta S_a^{\ddagger}$ ($=\Delta S_1^{\ddagger}$) values found for reactions (1) (Table II) are as expected for direct addition to the dienyl rings. The greater reactivity of the C_6H_7 complex is seen from Table II 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 arises from a much smaller $\Delta H_a^{\ddagger}$ of 20.8 kJ mol^{-1}, the latter complex has a relatively lower $\Delta S_a^{\ddagger}$ value of −96 J K^{-1} mol^{-1}. Table II also reveals that the $\Delta H_b^{\ddagger}$ values for both complexes are much larger than their corresponding $\Delta H_a^{\ddagger}$ values as expected for a dissociative process. In addition, the $\Delta S_b^{\ddagger}$ value of +220 J K^{-1} mol^{-1} determined for the C_6H_7 reaction is also as expected for bond cleavage in dissociation. The negative $\Delta S_b^{\ddagger}$ value found here for the C_7H_9 complex (−43 J K^{-1} mol^{-1}) is an interesting result as large negative entropies of activation appear to be a common feature in the dissociative processes of amine reactions with organometallics of type **1** [15]. Such large negative entropies of activation have recently been reported [11] for the addition of 4-chloroaniline to the organometallics [Fe(CO)$_3$(1–5-η-dienyl)]BF$_4$ (dienyl = C_6H_7, 2-MeOC_6H_6 or C_7H_9) and for the addition of 2-ethylpyridine to the 2-MeOC_6H_6 and C_7H_9 complexes [16]. These results may be rationalised by the 'ordered transition state mechanism' recently proposed by Odiaka [11]. Such a mechanism involves the formation of an ordered transition state (e.g. Fig. 1) which results from a rather tight bonding and undergoes an internal S_N2 process in the reformation of the starting dienyl complexes (**1**) (dissociative process) or protonation to the anilinium salt and the products (**2**) (associative process).

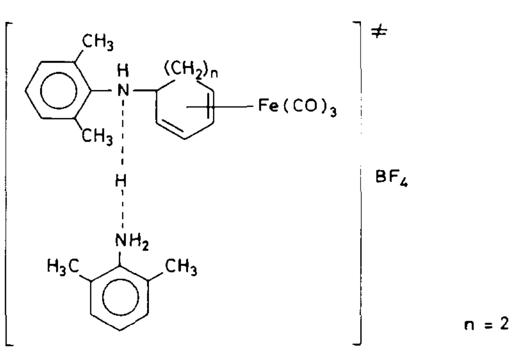


Fig. 1. Ordered transition state.

It is pertinent to note that two moles of amine are used up per mole of complex in the formation of the products (**2**) (eqn. (1)). Such a novel mechanism would no doubt give rise to the observed negative entropies of activation. Thus part of the energy necessary to effect the breaking of the amine–C (diene) bond in complex **3** (Scheme 1) to form the starting dienyl complexes (**1**) is supplied by that produced in forming the NH_2–HN bond (Fig. 1), thus assisting the dissociation of the amine nucleophile. An ordered transition state of the type shown in Fig. 1 must be associated with significant bond formation and a considerable build-up of positive charge on the nitrogen atom of the amine nucleophile. Strong support that this is in fact the case in reactions (1) is provided by the large negative slope of −2.7 determined [17] from the plot of $\log k_1$ *versus* σ (the Hammett coefficient for various X-substituted anilines) for the reaction of anilines with $[Fe(CO)_3(1\text{–}5\text{-}\eta\text{-}2\text{-}MeOC_6H_6)]BF_4$ in CH_3CN.

Although the 'Ordered Transition State Mechanism' proposed here and elsewhere [11] quite reasonably rationalizes the large negative entropies of activation found in the dissociative processes of most amine additions to coordinated π-Hydrocarbons of type **1**, MeCN–C (dienyl) bond making with the resultant formation of an endo-MeCN intermediate cannot be completely excluded as this too could give a negative entropy of activation.

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