

SYNTHETIC AND MECHANISTIC STUDIES OF THE ADDITION OF 4-CHLOROANILINE TO TRICARBONYL (1-5- η -DIENYL)IRON(II) CATIONS (DIENYL = C₆H₇, 2-MeOC₆H₆ OR C₇H₉)

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(Received September 15th, 1986)

Summary

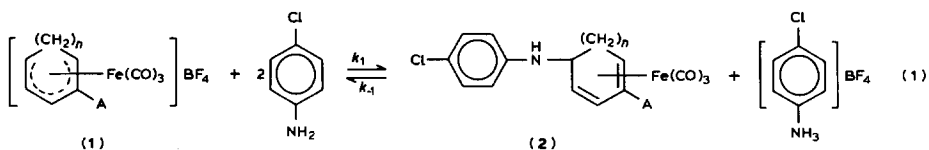
A kinetic study of the reactions between the organometallic complexes [(Fe(CO)₃(1-5- η -dienyl)]BF₄ (**1**, dienyl = C₆H₇, 2-MeOC₆H₆ or C₇H₉) and 4-chloroaniline in CH₃CN reveal the general two-term expression $k_{\text{obs}} = k_a[4\text{-ClC}_6\text{H}_4\text{NH}_2] + k_b$, which is consistent with an equilibrium process. The observed rate sequence C₆H₇ > 2-MeOC₆H₆ > C₇H₉ and the low ΔH_a^\ddagger and large negative ΔS_a^\ddagger values are in accordance with direct addition to the dienyl rings of **1**. On the other hand, the much higher ΔH_b^\ddagger values are consistent with bond cleavage in dissociation. The values of ΔS_b^\ddagger are negative, indicating the presence of an ordered transition state through which the starting dienyl complexes are reformed via some internal S_N² process.

Introduction

The formation of 1,3-diene organometallics [1-7] or 1,3,5-triene [8] or other products [9] from the reactions of organic substrates with coordinated π -hydrocarbons has been fully established. Thus attack on the organometallic compounds [(Fe(CO)₃(1-5- η -dienyl)]BF₄ (**1**, dienyl = C₆H₇, 2-MeOC₆H₆ or C₇H₉) by anilines [10,11] affords the neutral products (Fe(η^4 -diene · NHC₆H₄X)(CO)₃) (**2**, X = H, 2-Me, 3-Me, 4-Me, 2-Cl, 3-Cl, 4-OMe or 4-NO₂) in high yields. However, apart from data for the reactions of 4-methyl-aniline [10] and 2-methylaniline [11] with the dienyl complexes **1** and of aniline [11] with (**1**, dienyl = C₆H₇ or 2-MeOC₆H₆) there is very little quantitative information available on the thermodynamics of the reactions of anilines with coordinated π -hydrocarbons.

In order to improve the understanding of the mechanism and thermodynamics of

these novel reactions we have carried out a detailed synthetic and kinetic study of the reactions of 4-chloroaniline with complexes **1a–c** in CH_3CN (eq. 1).



- (1a, $n = 1$, $A = \text{H}$;
 1b, $n = 1$, $A = \text{MeO}$;
 1c, $n = 2$, $A = \text{H}$)

Experimental

Materials

The organometallics **1a–c** were synthesized and purified by published procedures [12,13]. 4-Chloroaniline (B.D.H.) was purchased in the purest grade available and recrystallised from acetone before use. Acetonitrile solvent (B.D.H.) was distilled then stored over molecular sieves (size 3\AA) under nitrogen.

Product isolation and characterisation

Tricarbonyl[1–4- η -5-(N-4-chloroanilino)cyclohexa-1,3-diene]iron (2a). Solutions of $[\text{Fe}(\eta^5\text{-C}_6\text{H}_7)(\text{CO})_3][\text{BF}_4]$ (0.1 g, 0.33 mmol) in CH_3CN (10 cm^3) and 4-chloroaniline (0.0836g, 0.66 mmol) in CH_3CN (10 cm^3) were mixed under nitrogen in a flask (50 cm^3), and the mixture was kept at room temperature for 10 min, then evaporated under reduced pressure to leave a yellow solid. This was shaken with diethyl ether/water (20/20, vol/vol) and the aqueous layer set aside. The diethyl ether extract was passed through a short alumina-H column under nitrogen and the solvent removed in a rotary evaporator under reduced pressure to leave an intractible oily product. This was dissolved in toluene (15 cm^3) and the solution passed through an alumina-H column. Rotary evaporation of the yellow solution emerging from the columns afforded a yellow oil, (**2a**) which could not be crystallised; $\nu(\text{CO})$ (acetone) 2045 and 1970 cm^{-1} ; $\nu(\text{NH})$ (Nujol mull), 3400 cm^{-1} ; it was found to be sensitive to air, gradually turning brown; samples after some time showed no nitrogen in the microanalysis, indicating that the anilino group had been lost in the decomposition.

Tricarbonyl[1–4- η -5-(N-4-chloroanilino)2-methoxycyclohexa-1,3-diene]iron (2b). An analogous reaction of $[\text{Fe}(\eta^5\text{-2-MeOC}_6\text{H}_6)(\text{CO})_3][\text{BF}_4]$ (0.1 g, 0.298 mmol) with 4-chloroaniline (0.076 g, 0.596 mmol) in CH_3CN (20 cm^3) followed by similar work-up to that described for **2a** above, gave a yellow oil which was taken up in acetone (15 cm^3), and the solution chromatographed on alumina-H column. The yellow eluate was evaporated under nitrogen to give a pale yellow oil (40% yield) which was stable in air. (Found: C, 51.0; H, 5.41; N, 4.06. $\text{C}_{16}\text{H}_{14}\text{FeClNO}_4$ calc: C, 51.2; H, 3.76; N, 3.73%) $\nu(\text{CO})$ (acetone) 2045 and 1970 cm^{-1} ; $\nu(\text{NH})$ (Nujol mull) 3400 cm^{-1} . $^1\text{H NMR}$ (CD_3COCD_3); τ 6.75 (1H, m, H^1), 4.60 (1H, m, H^3), 7.20 (1H, m, H^4), 6.30 (1H, m, $\text{H}^{5'}$), 8.65 (1H, m, H^6), 7.60 (1H, m, $\text{H}^{6'}$) 3.10 (2H, d, aromatic) 3.50 (2H, d, aromatic), 5.40 (1H, br, NH) and 6.40 (3H, s, OCH_3). Rotary evaporation of the aqueous phase at reduced pressure followed by treatment with diethyl ether afforded $[\text{4-ClC}_6\text{H}_4\text{NH}_3][\text{BF}_4]$ as an off-white solid. Its IR spectrum in Nujol mull showed a band at ca. 1060 cm^{-1} attributed to the BF_4^- anion.

Tricarbonyl[1-4- η -5-(N-4-chloroanilino)cyclohepta-1,3-diene]iron (2c). An analogous reaction of $[\text{Fe}(\eta^5\text{-C}_7\text{H}_9)(\text{CO})_3][\text{BF}_4]$ (0.1 g, 0.31 mmol) with 4-chloroaniline (0.08 g, 0.63 mmol) in CH_3CN (20 cm^3), followed by similar work-up to that of **2a** above, gave the yellow solid (**2c**) in 54% yield (Found: C, 53.9; H, 4.20; N, 3.58. $\text{C}_{16}\text{H}_{14}\text{FeClNO}_3$ calc: C, 53.4; H, 3.92; N, 3.89%); $\nu(\text{CO})$ (acetone), 2045 and 1970 cm^{-1} ; $\nu(\text{NH})$ (Nujol), 3400 cm^{-1} .

Kinetic studies

The reactions in CH_3CN were studied under pseudo-first-order conditions involving a large excess of 4-chloroaniline ($[\text{Fe}] = 1.5 \times 10^{-3}$ mol dm^{-3} , $[\text{4-Cl-C}_6\text{H}_4\text{NH}_2] = 0.01\text{--}0.20$ mol dm^{-3}). The reactions were monitored at 390 nm by use of a thermostatted ($\pm 0.1^\circ\text{C}$) stopped-flow spectrophotometer; at this wavelength there was a large decrease in absorbance. The reaction traces were recorded and analysed by use of a rapid data capture system purchased from Lombardi Scientific Ltd., employing computer programs developed jointly with Lombardi (U.K.) Ltd. and described elsewhere [14]. Pseudo-first-order rate constants, k_{obs} , were calculated from the slopes of plots of $\log(A_t - A_\infty)$ vs. time which were linear for at least two half-lives. Each k_{obs} value is the average of at least six separate runs, with an average reproducibility of $\pm 3\%$. The second-order rate constants, k_a , were derived by a least-squares fit to the k_{obs} vs. $[\text{4-Cl-C}_6\text{H}_4\text{NH}_2]$ plots, and the errors quoted are the standard deviations. Activation enthalpies were obtained from the slopes of Arrhenius plots of $\log k_a$ or $\log k_b$ vs. T^{-1} , calculated by a least-squares method; again the errors quoted are the standard deviations. Entropies of activation were calculated from 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** were isolated as yellow oils from the reactions of the organometallics **1a** and **1b** with 4-chloroaniline in CH_3CN . Product **2a** is sensitive to air in the pure state but product **2b** is more stable. The product **2c** obtained from the reaction of **1c** with 4-chloroaniline is a stable yellow solid. All the products (**2a**–**c**) exhibited two strong carbonyl bands at ca. 2045 and 1970 cm^{-1} in their infrared spectra as well as $\nu(\text{NH})$ peaks at 3400 cm^{-1} (Nujol mull), characteristic of tricarbonyl (1-4- η -5-*N*-anilino-1,3-diene)iron derivatives [10,11]. The ^1H NMR spectrum of **2b** in acetone- d_6 is very similar to that previously reported [15] for the analogous tricarbonyl [1-4- η -5-(*N*-4-methylanilino)2-methoxy-cyclohexa-1,3-diene]iron. Thus overlapping resonances characteristic of the outer (H^1 and H^4) protons are clearly separated at τ 6.75 and 7.20, respectively, while the lone H^3 proton appears at τ 4.60. The $\text{H}^{6,6'}$ methylene protons appear at τ 8.65 and 7.60, while the $\text{H}^{5'}$ proton adjacent to the *N*-4-chloroanilino substituent is shifted downfield to τ 6.30. The broad resonance at ca. τ 5.40 is attributed to the *NH* proton since it disappears on addition of D_2O . The pair of doublets at τ 3.10 and 3.50 is assigned to the aromatic protons, and the singlet at τ 6.40 to the methoxy group of the 1,3-diene substituent. The reversibility of reactions 1 was demonstrated by the addition of a few drops of trifluoroacetic acid to equilibrium mixtures as obtained from the reactions; the original organometallics were regenerated quantitatively, as

TABLE 1

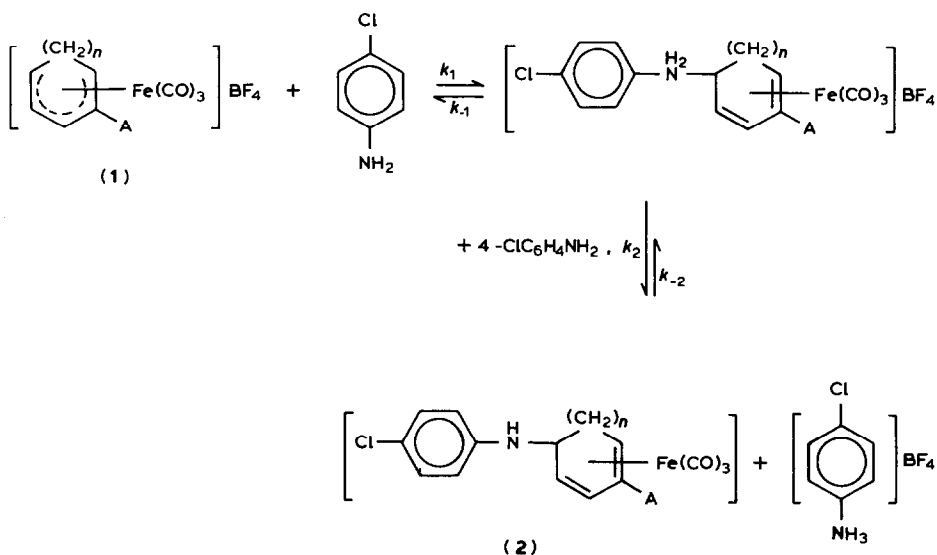
KINETIC RESULTS FOR REACTIONS OF $[\text{Fe}(\text{CO})_3(1-5-\eta\text{-dienyl})]\text{BF}_4$ WITH 4-CHLOROANILINE IN MeCN: $[\text{Fe}] = 1.5 \times 10^{-3} \text{ mol dm}^{-3}$

Dienyl	T (°C)	$10^2[\text{4-ClC}_6\text{H}_4\text{NH}_2]$ (mol dm ⁻³)	k_{obs} (S ⁻¹)	k_a^a (dm ³ mol ⁻¹ s ⁻¹)	k_b^a (S ⁻¹)
C ₆ H ₇	0.0	1.0	24.2		
	0.0	2.0	30.4		
	0.0	4.0	44.4		
	0.0	5.0	49.6		
	0.0	8.0	70.2	657(8)	17.5(0.39)
	5.4	1.0	30.5		
	5.4	2.0	40.9		
	5.4	4.0	56.5		
	5.4	5.0	64.8		
	5.4	8.0	90.5	845(12)	22.8(0.55)
	10.4	1.0	41.4		
	10.4	2.0	54.2		
	10.4	4.0	70.1		
	10.4	5.0	82.5		
	10.4	8.0	112.0	993(23)	32.4(1.07)
	15.3	1.0	54.2		
	15.3	2.0	66.7		
	15.3	4.0	90.0		
	15.3	5.0	104.0	1229(20)	41.9(0.68)
	2-MeOC ₆ H ₆	0.0	2.5	8.26	
0.0		5.0	10.1		
0.0		10.0	14.6		
0.0		15.0	19.2		
0.0		20.0	23.4	87.7(1)	5.90(0.12)
5.5		1.0	11.6		
5.5		2.0	13.1		
5.5		4.0	15.4		
5.5		6.0	17.9		
5.5		8.0	20.5	125(2)	10.4(0.08)
10.4		1.0	15.4		
10.4		2.0	17.2		
10.4		4.0	20.0		
10.4		6.0	23.4		
10.4		8.0	26.5	158(2)	13.9(0.10)
15.4		1.0	21.1		
15.4		2.0	23.4		
15.4		4.0	28.1		
15.4		6.0	32.8		
15.4		8.0	37.6	236(1)	18.7(0.03)
C ₇ H ₉	0.0	2.5	2.29		
	0.0	5.0	3.63		
	0.0	10.0	5.90		
	0.0	15.0	8.40		
	0.0	20.0	10.8	48.4(4)	1.13(0.47)
	8.3	2.5	3.61		
	8.3	5.0	5.50		
	8.3	10.0	9.20		
	8.3	15.0	12.5		
	8.3	20.0	16.3	71.9(1)	1.87(0.10)
	15.2	2.5	5.34		

TABLE 1 (continued)

Dienyl	T (°C)	$10^2[4\text{-ClC}_6\text{H}_4\text{NH}_2]$ (mol dm ⁻³)	k_{obs} (S ⁻¹)	k_a^a (dm ³ mol ⁻¹ s ⁻¹)	k_b^a (S ⁻¹)
	15.2	5.0	7.60		
	15.2	10.0	12.9		
	15.2	15.0	18.2		
	15.2	20.0	23.0	102(1)	2.68(0.12)
	20.1	2.5	7.0		
	20.1	5.0	10.4		
	20.1	10.0	16.1		
	20.1	15.0	22.1		
	20.1	20.0	28.6	122(1)	4.0(0.16)

^a Estimated by a least-squares fit to eq. 2. Values in parentheses are the standard deviations.



SCHEME 1

evidenced by the appearance of strong $\nu(\text{CO})$ bands at 2120 and 1965 cm^{-1} and the disappearance of bands due to the products **2a-c** at 2045 and 1970 cm^{-1} . The presence of the former bands in the reaction solutions of **1** even at infinite time

TABLE 2

RATE AND ACTIVATION PARAMETERS FOR REACTIONS OF $[\text{Fe}(\text{CO})_3(1\text{-}5\text{-}\eta\text{-dienyl})]\text{BF}_4$ WITH 4-CHLOROANILINE IN MeCN

Dienyl	k_a (rel) (0°C)	k_b (rel) (0°C)	ΔH_a^* (kJ mol ⁻¹)	ΔS_a^* (J K ⁻¹ mol ⁻¹)	ΔH_b^* (kJ mol ⁻¹)	ΔS_b^* (J K ⁻¹ mol ⁻¹)
C ₆ H ₇	13.6	15.5	23.7 ± 1.6	-103 ± 6	35.8 ± 1.4	-89 ± 5
2-MeOC ₆ H ₇	1.8	5.2	39.0 ± 5.8	-64 ± 21	46.3 ± 7.1	-58 ± 25
C ₇ H ₉	1.0	1.0	28.7 ± 1.0	-106 ± 3	38.5 ± 1.2	-101 ± 4

further confirms that there is an equilibrium. The anilinium salt $[4\text{-ClC}_6\text{H}_4\text{NH}_3]\text{BF}_4$ shown in eq. 1 was isolated as an off-white solid from the aqueous phase of the reaction of 4-chloroaniline with **1b**. The 4-methylanilino derivative has previously been isolated and fully characterised on the basis of its IR ^1H NMR and microanalytical data [10].

Kinetics and mechanism

Kinetic results for the addition of 4-chloroaniline to each of the dienyl complexes **1a–c** in CH_3CN are listed in Table 1. Plots of k_{obs} vs. $[4\text{-ClC}_6\text{H}_4\text{NH}_2]$ are linear with non-zero intercepts, indicating the general two-term rate law (2) which is consistent with an equilibrium process.

$$\text{Rate} = k_a[\text{complex}][4\text{-ClC}_6\text{H}_4\text{NH}_2] + k_b[\text{complex}]$$

$$\text{i.e. } k_{\text{obs}} = k_a[4\text{-ClC}_6\text{H}_4\text{NH}_2] + k_b \quad (2)$$

The separate k_a and k_b values shown in Table 1 were calculated by a least-squares fit to eq. 2. Rate law (2) may be rationalised in terms of the amine-assisted pathway shown in Scheme 1. It is assumed that the establishment of the equilibrium K_2 is much more rapid than that of K_1 , then the relationships 3 [15] and 4 [15] follow where k_1 represents the second-order rate constant for attack on the dienyl rings

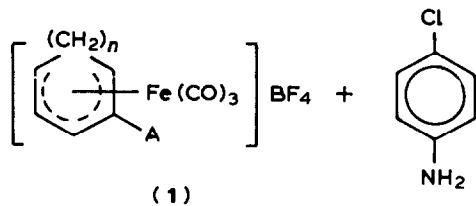
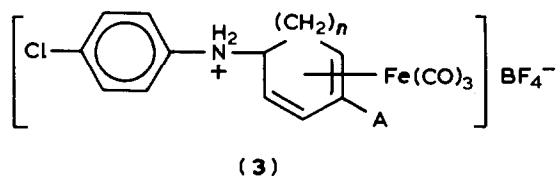
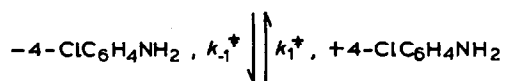
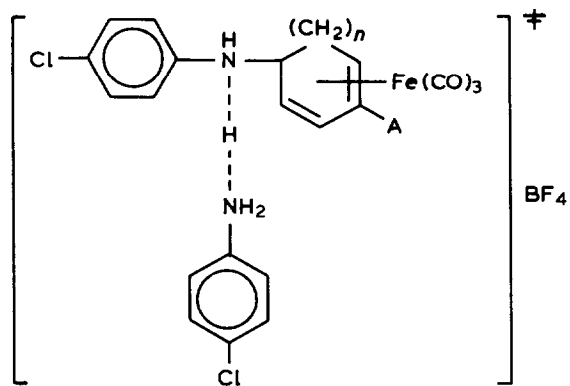
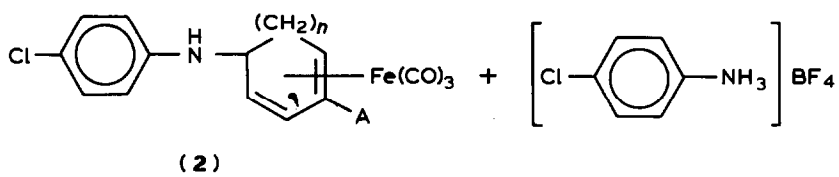
$$k_a = k_1 \quad (3)^*$$

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

of **1a–c** and k_{-1} the first-order rate constant for the dissociation of 4-chloroaniline from the anilinium adduct **2a–c**.

As expected for direct addition to the dienyl fragments of **1a–c**, the k_1 ($=k_a$) values, can be seen from Table 1 to decrease in the order $\text{C}_6\text{H}_7 > 2\text{-MeOC}_6\text{H}_6 > \text{C}_7\text{H}_9$ (e.g., 13.6, 1.8, 1 at 0°C). The higher reactivity of the parent complex $[\text{Fe}(1\text{-}5\text{-}\eta\text{-C}_6\text{H}_7(\text{CO})_3][\text{BF}_4]$ (**1a**) compared with that of $[\text{Fe}(1\text{-}5\text{-}\eta\text{-}2\text{-MeO-C}_6\text{H}_6(\text{CO})_3][\text{BF}_4]$ (**1b**) is due to the mesomeric influence of the methoxide group, which has been shown by INDO molecular orbital calculations [16] to decrease the positive charge on the dienyl C(5) atom, the site of nucleophilic addition. The more pronounced increase in rate on going from the parent complex **1a** to $[\text{Fe}(1\text{-}5\text{-}\eta\text{-C}_7\text{H}_9)(\text{CO})_3][\text{BF}_4]$ (**1c**) can be rationalised in terms of the steric hindrance caused by the additional methylene group in (**1c**) if the 4-chloroaniline is assumed to approach from above the dienyl rings of **1**. The low ΔH_a^* ($=\Delta H_1^*$) values and large negative ΔS_a^* ($=\Delta S_1^*$) values found for reactions 1 (Table 2) are also consistent with direct addition to the dienyl rings. The observed rate trend in the order $\text{C}_6\text{H}_7 > 2\text{-MeOC}_6\text{H}_6 > \text{C}_7\text{H}_9$ is seen from Table 2 to arise from a play-off between enthalpy and entropy effects. Thus while the higher rate of reaction of the C_6H_7 complex compared with that of C_7H_9 arises from a much smaller ΔH_a^* , the intermediate rate for the $2\text{-MeOC}_6\text{H}_6$ complex is associated with the least negative ΔS_a^* of $-64 \text{ J K}^{-1} \text{ mol}^{-1}$ and the highest ΔH_a^* of 39 kJ mol^{-1} . On the other hand, the much larger ΔH_b^* ($=\Delta H_{-1}^*$) values are as expected for bond cleavage in

* See Ref. 15 for full derivation.



SCHEME 2

dissociation. It is pertinent to note that the ΔS_b^\ddagger ($=\Delta S_{-1}^\ddagger$) values are large and negative, which is very interesting for a dissociative process. Similar results were recently reported [7] for the reversible addition of 2-ethylpyridine to complexes **1b** and **1c**. The negative ΔS_b^\ddagger values reported here for reactions 1 can be readily accounted for in terms of the formation of an ordered transition state such as that shown in Scheme 2 for the dissociative process. It is possible that the 'ordered transition state mechanism' proposed here (Scheme 2) results from a rather tight bonding, and that there is an internal S_N^2 process to reform the starting dienyl complexes **1** or to protonate the anilinium salt and the products **2**; such a novel mechanism would 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 **3** (Scheme 2) to form the starting dienyl complexes **1** is supplied by that produced in forming the $\text{NH}_2 \cdots \text{HN}$ bond (in the transition state), thus assisting the dissociation of the amine nucleophile. The 'ordered transition state mechanism' proposed in Scheme 2 may be a general phenomenon in the addition of amine nucleophiles to coordinated π -hydrocarbons of the type **1**, since most of the ΔS_{-1}^\ddagger values determined [17] to date for such systems are large and negative. In such an ordered transition state there must be significant bond formation and a considerable build-up of positive charge on the nitrogen atom of the amine nucleophile. Strong support for the view that this is the case in reactions 1 is provided by the large negative slope of -2.7 determined [15] from the plot of $\log k_1$ vs. σ (the Hammett coefficient for various X-substituted anilines including 4-chloroaniline) for the reaction of anilines with complex **1b**. The extent of dissociation of 4-chloroaniline from products **2** to form the starting organometallics **1** decreases in the order $\text{C}_6\text{H}_7 > 2\text{-MeOC}_6\text{H}_6 > \text{C}_7\text{H}_9$ (e.g. 15.5, 5.2, 1.0 at 0°C) and this is seen from Table 1 to be both enthalpy and entropy controlled. Thus the more rapid dissociation of 4-chloroaniline from the C_6H_7 compared with that from the C_7H_9 complex arises from the much smaller ΔH_b^\ddagger of 35.8 kJ mol^{-1} , while the intermediate behaviour of the $2\text{-MeOC}_6\text{H}_6$ complex is associated with the least negative ΔS_b^\ddagger of $-58 \text{ J K}^{-1} \text{ mol}^{-1}$ and the highest ΔH_b^\ddagger of 46.3 kJ mol^{-1} . It is possible that the reversibility of reactions 1 demonstrated here with 4-chloroaniline is a general phenomenon in the reaction of anilines with the complexes **1a-c**. In particular the 'ordered transition state mechanism' proposed in Scheme 2 rationalizes the large negative ΔS_{-1}^\ddagger ($=\Delta S_b^\ddagger$) values found in such systems. However MeCN-C(dienyl) bond making with the resultant formation of an *endo*-MeCN intermediate cannot be completely excluded, as this could also lead to a negative entropy of activation.

Acknowledgements

I am grateful to Professor R.D. Gillard of University College, Cardiff (Great Britain) for permitting the use of his laboratories, and to the University of Ibadan authorities for permission to spend a study leave at Cardiff.

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