

MECHANISMS OF ADDITION OF PRIMARY AROMATIC AMINES AND CYCLOHEXYLAMINE TO TRICARBONYL(CYCLOHEPTATRIENYL)TUNGSTEN CATION

TIMOTHY I. ODIAKA *

Department of Chemistry, University of Ibadan, Ibadan (Nigeria)

and LEON A.P. KANE-MAGUIRE

Department of Chemistry, University of Wollongong, P.O. Box 1144, Wollongong, N.S.W. 2500 (Australia)

(Received October 3rd, 1984)

Summary

X-substituted anilines (X = H, 2-Me, 4-Me or 2-Cl) and cyclohexylamine are shown to add to the tropylium ring of cation $[(\eta\text{-C}_7\text{H}_7)\text{W}(\text{CO})_3]^+$ to give the corresponding ring adducts of tricarbonyl(cyclohepta-1,3,5-triene)tungsten. Kinetic studies have demonstrated that the anilines form the triene ring adducts via the rapid pre-equilibrium formation of a π -complex, which rearranges in a rate-determining fashion to form a cationic triene intermediate $[(1\text{-}\eta\text{-C}_6\text{H}_7\text{-NH}_2\text{R})\text{W}(\text{CO})_3]^+$ (R = C₆H₅, 2-MeC₆H₄, 4-MeC₆H₄ or 2-ClC₆H₄); from this the final product is rapidly formed via amine- or solvent-assisted proton loss. With the aliphatic cyclohexylamine, the cationic triene intermediate is formed directly, followed by competing rate-determining solvent- and amine-assisted proton removal.

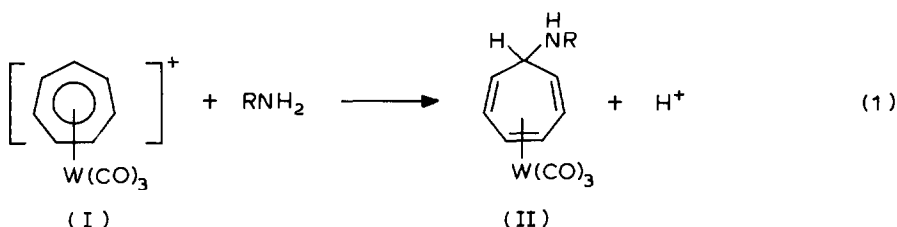
Introduction

Despite the extensive literature on the reactivity of $[(\pi\text{-hydrocarbon})\text{M}(\text{CO})_3]^+$ cations with a wide variety of nucleophiles such as pyridines [1], phosphines [2-4], activated arenes [2,5,6], aromatic heterocycles [7], β -diketones [8], cyanide [9,10] and iodide [11,12] ions, only very few kinetic studies of such systems have been reported to date. Consequently the factors that govern nucleophilicity towards coordinated π -hydrocarbons are poorly understood and the first quantitative study aimed at providing solutions to this problem has only recently appeared [1]. Aniline and substituted anilines have been shown to add to the dienyl rings of the organometallic

* Author to whom correspondence should be addressed.

cations $[(1-5-\eta\text{-dienyl})\text{Fe}(\text{CO})_3]^+$ (dienyl = C_6H_7 , 2-MeOC $_6\text{H}_6$ or C_7H_9) to give the corresponding substituted (1,3-diene) complexes [13]. Detailed synthetic and kinetic studies of these latter reactions have clearly established the importance of basicity and steric factors in controlling amine nucleophilicity towards coordinated π -hydrocarbons [13,14], in agreement with previous findings with pyridines [1].

In this paper we wish to report the results of spectroscopic and mechanistic studies of the addition of anilines and cyclohexylamine to the cation $[(\eta\text{-C}_7\text{H}_7)\text{W}(\text{CO})_3]^+$ (I) in acetone (eq. 1, R = C_6H_5 , 2-MeC $_6\text{H}_4$, 4-MeC $_6\text{H}_4$, 2-ClC $_6\text{H}_4$ or C_6H_{11}).



Before our work, there had been no reports on the formation of anilinium adducts of tricarbonyl(cyclohepta-1,3,5-triene)tungsten of type II. The products II have been isolated for the cases R = C_6H_5 and 4-MeC $_6\text{H}_4$.

Experimental

Materials. The orange crystalline complex, $[(\eta\text{-C}_7\text{H}_7)\text{W}(\text{CO})_3][\text{BF}_4]$ (I) was synthesised and purified by published procedures [11,15]. The amines (B.D.H. or Aldrich) were purchased in the purest grades available. The liquids were distilled under dinitrogen and dried over molecular sieves (grade 3A) prior to use. 4-Methylaniline was recrystallised from acetone before use. AnalaR acetone (B.D.H.) was used as solvent without further purification.

Product isolation and characterisation

Tricarbonyl(1-6- η -7-N-toluidino-cyclohepta-1,3,5-triene)tungsten (IIa)

Solutions of complex I (0.05 g, 0.112 mmol) in AnalaR acetone (5 cm 3) and 4-methylaniline (0.0122 g, 0.114 mmol) in the same solvent (5 cm 3) were mixed under dinitrogen in a 50 cm 3 volumetric flask and allowed to react for 2 d at 45°C in the dark. Rotary evaporation of the mixture under dinitrogen at room temperature left a thick brown solid. This was shaken with 20 ml of 50% diethyl ether/water (vol./vol.) and the organic layer passed through a short alumina-H column under dinitrogen. Rotary evaporation of the red eluant yielded an oily product which was taken up in toluene (5 cm 3), thoroughly shaken, and the solvent removed at reduced pressure under dinitrogen to give an oil. Recrystallisation from acetone/water afforded red needles (20 mg, 40%) which were characterised as the substituted triene product (IIa). This product was found to be air-sensitive in the solid state, turning brownish in colour.

[Found: C, 40.1; H, 4.3; N, 4.3. $\text{C}_{17}\text{H}_{15}\text{NWO}_3$ calcd.: C, 43.9; H, 3.3; N, 3.1%]. IR $\nu(\text{NH})$ (Nujol mull): ca. 3400 cm $^{-1}$; $\nu(\text{CO})$ (acetone): 1980, 1900, 1875 cm $^{-1}$.

Tricarbonyl(1-6- η -7-N-anilino-cyclohepta-1,3,5-triene)tungsten (IIb)

An analogous preparation as for IIa above using complex I (0.05 g, 0.112 mmol)

and aniline (20.4 μl , 0.224 mmol) in acetone (10 cm^3) gave 50% yield of the triene product IIb as a reddish-yellow oil after similar work-up. This oil could not be crystallised and a satisfactory microanalysis could not be obtained due to its sensitivity to air. IR $\nu(\text{CO})$ (acetone): 1980, 1900, 1875 cm^{-1} . IR $\nu(\text{NH})$ (Nujol mull): ca. 3400 cm^{-1} .

The products from the reactions of 2-methylaniline, 2-chloroaniline and cyclohexylamine with cation I in acetone were characterised by IR spectroscopy. In each case the reaction mixtures containing excess amine exhibited three $\nu(\text{CO})$ bands at ca. 1980, 1900 and 1875 cm^{-1} characteristic of neutral tricarbonyl (substituted-triene) metal complexes. No other $\nu(\text{CO})$ bands were observed.

Spectroscopic studies

Infrared spectra were recorded on a Perkin-Elmer 257 spectrophotometer using matched 0.5 mm NaCl solution cells. UV-visible spectra were recorded on a Pye Unicam SP 8000 Spectrophotometer using matched 10 mm silica cells. The instability of products IIa and IIb prevented mass-spectral measurements.

Kinetic studies

The slow overall reactions (eq. 1; $\text{R} = \text{C}_6\text{H}_5$, 4-MeC₆H₄, 2-MeC₆H₄ or 2-ClC₆H₄) were studied at 20°C in AnalaR acetone using the IR sampling technique. Separate solutions of the aniline nucleophile (0.05–1.0 mol dm^{-3}) were freshly prepared under dinitrogen and equilibrated in a thermostatted water bath at 20°C ($\pm 0.1^\circ\text{C}$) for 30 min, before addition to a weighed complex salt (3×10^{-3} mol dm^{-3}) in a 10 ml volumetric flask. Each reaction flask was quickly closed with a suba-seal under dinitrogen, wrapped with aluminium foil and placed in the thermostat bath. The strong carbonyl band due to starting complex at 2065 cm^{-1} was followed. Typical IR spectral changes for this reaction using [aniline] = 5.08×10^{-2} mol dm^{-3} are given in Fig. 1. Pseudo-first-order rate constants were calculated from the slopes of plots of $\log A_t$ versus time. Such plots were linear for at least two half-lives and runs were carried out in duplicate, giving k_{obs} values with an average reproducibility of $\pm 4\%$. Plots of k_{obs} versus [amine] were found to be curved and tending to "flatten out" at higher nucleophile concentrations (Fig. 2). However, inverse plots of $1/k_{\text{obs}}$

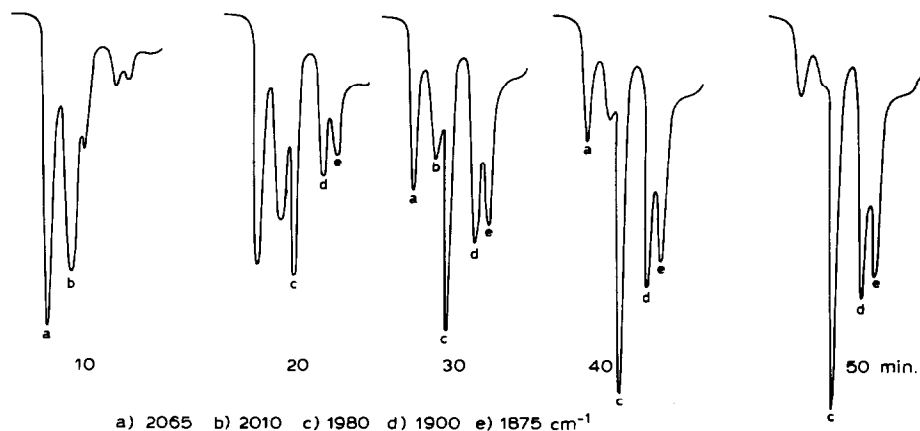


Fig. 1. Typical IR changes for the overall reaction of $[(\eta\text{-C}_7\text{H}_7)\text{W}(\text{CO})_3]^+$ with aniline in acetone at 20.0°C. $[\text{W}] 3.0 \times 10^{-3}$, $[\text{H}_2\text{NC}_6\text{H}_5] 5.08 \times 10^{-2}$ mol dm^{-3} .

versus $1/[\text{RNH}_2]$ gave excellent straight lines with non-zero intercepts (e.g. Fig. 3), indicating an expression of the form (eq. 2) for k_{obs} where a and b are constants.

$$k_{\text{obs}} = \frac{a[\text{RNH}_2]}{(1+b)[\text{RNH}_2]} \quad (2)$$

In addition to the slow IR changes during the aniline reactions (eq. 1) above, a fast initial process was also observed and was monitored at 390 nm in acetone (0°C) with $[\text{aniline}] = 1.0\text{--}7.0 \times 10^{-2} \text{ mol dm}^{-3}$ and $[\text{W}] = 5 \times 10^{-4} \text{ mol dm}^{-3}$ using a thermostatted ($\pm 0.1^\circ\text{C}$) spectrophotometer of the type described elsewhere [16]. At this wavelength, an increase in absorbance was observed due to the formation of an intermediate. Pseudo-first-order rate constants, k_{obs} , were calculated from the slopes of plots of $\log(A_\infty - A_t)$ versus time. These plots were linear for at least 75% completion of reaction and each k_{obs} value was the average of at least three runs

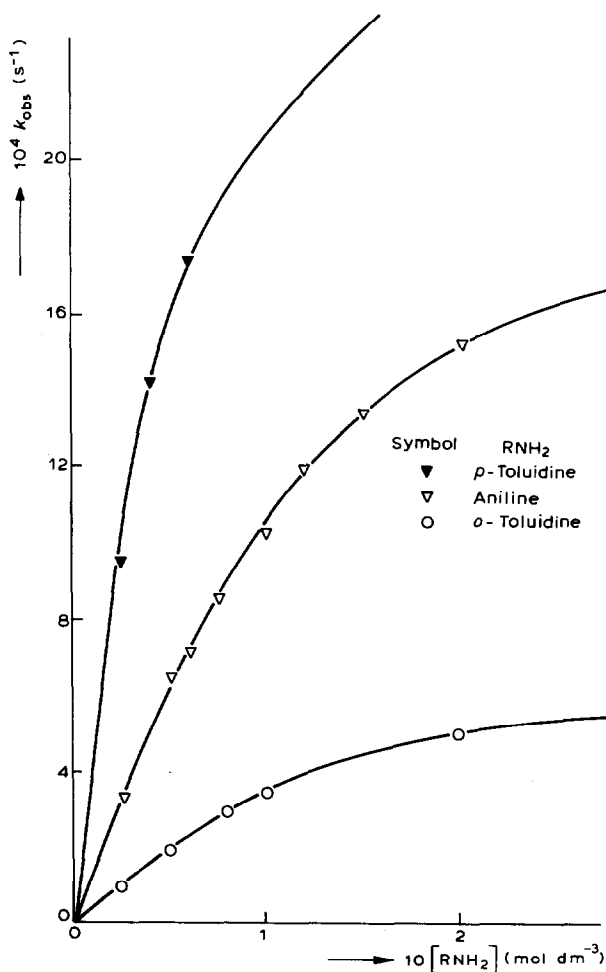


Fig. 2. Dependence of k_{obs} on $[\text{RNH}_2]$ for the overall reaction of $[(\eta\text{-C}_7\text{H}_7)\text{W}(\text{CO})_3]^+$ with anilines in acetone at 20.0°C .

with an average reproducibility of $\pm 3\%$. A plot of k_{obs} versus [aniline] is linear with a non-zero intercept (Fig. 4) indicating the two-term rate law (eq. 3).

$$k_{\text{obs}} = k_c[\text{RNH}_2] + k_d \quad (3)$$

Due to the rapidity of this initial step it could only be monitored at 0°C under pseudo-first-order conditions.

The overall reaction with cyclohexylamine (eq. 1, $\text{R} = \text{C}_6\text{H}_{11}$) was very rapid and was monitored at 0°C in acetone at a wavelength of 550 nm. The complex concentration was maintained at $1.5 \times 10^{-3} \text{ mol dm}^{-3}$ while $[\text{C}_6\text{H}_{11}\text{NH}_2] = 0.50\text{--}2.0 \times 10^{-2} \text{ mol dm}^{-3}$. At this wavelength, a large increase in absorbance was observed, reflecting the formation of the neutral tricarbonyl (substituted-triene) product (II, $\text{R} = \text{C}_6\text{H}_{11}$). Pseudo-first-order rate constants were estimated from the slopes of plots of $\log(A_\infty - A_t)$ versus time. These plots were linear for at least two half-lives and each k_{obs} value was the average of at least three separate runs with an average reproducibility of $\pm 4\%$. A plot of k_{obs} versus $[\text{RNH}_2]$ was found to exhibit a strong upward curvature (Fig. 5). However a plot of $k_{\text{obs}}/[\text{RNH}_2]$ versus $[\text{RNH}_2]$

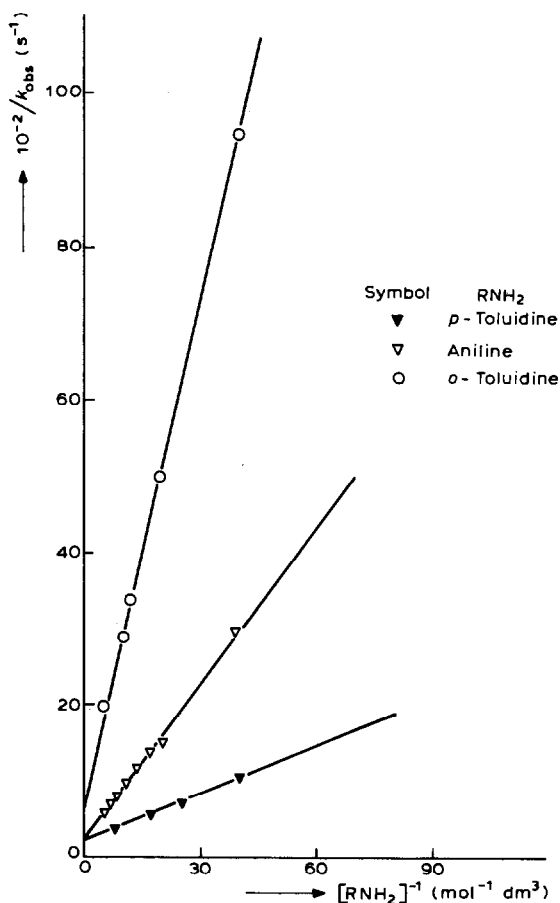


Fig. 3. Plot of $1/k_{\text{obs}}$ versus $1/[\text{RNH}_2]$ for the overall reaction of $[(\eta\text{-C}_7\text{H}_7)\text{W}(\text{CO})_3]^+$ with anilines in acetone at 20.0°C .

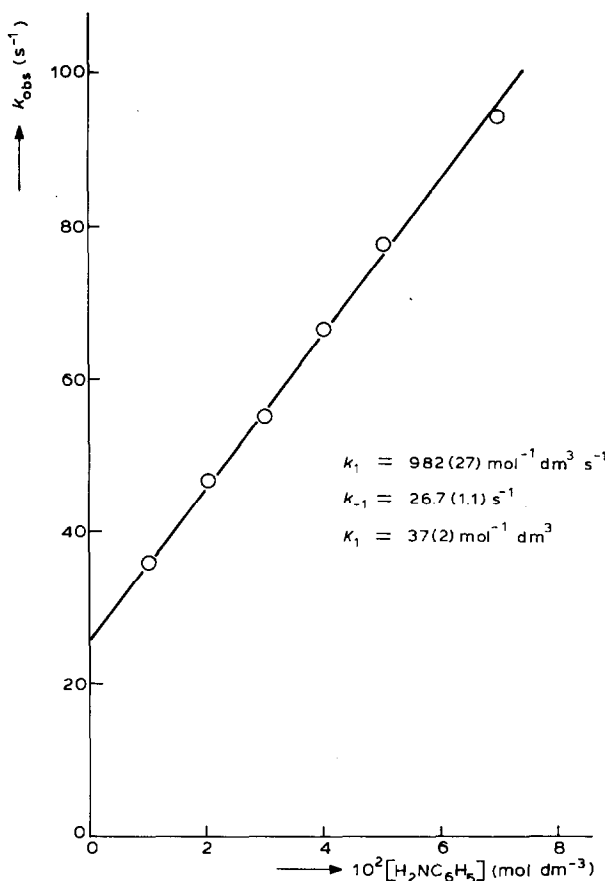


Fig. 4. Dependence of k_{obs} on $[\text{RNH}_2]$ for the rapid initial reaction of $[(\eta\text{-C}_7\text{H}_7)\text{W}(\text{CO})_3]^+$ with aniline in acetone at 0.0°C .

is linear with a non-zero intercept (Fig. 6) indicating a rate law of the form (eq. 4) for k_{obs} where e and f are constants.

$$k_{\text{obs}} = e[\text{RNH}_2] + f[\text{RNH}_2]^2 \quad (4)$$

Results and discussion

Spectroscopic studies

During IR studies of reactions 1 ($\text{R} = \text{C}_6\text{H}_5$, 2-MeC₆H₄, 4-MeC₆H₄ or 2-ClC₆H₄), the two carbonyl bands due to the original tropylium salt at 2065 and 2010 cm^{-1} were eventually replaced by three strong carbonyl bands at ca. 1980, 1900 and 1875 cm^{-1} (e.g. Fig. 1) characteristic of neutral tricarbonyl(substituted-1,3,5-triene)-tungsten products. The products (IIa and IIb) also showed characteristic $\nu(\text{NH})$ bands at ca. 3400 cm^{-1} (Nujol mull). These isolated products are both air-sensitive, gradually turning brown due to decomposition to unknown species. The 4-methyl-anilinotriene product (IIa) crystallises as red needles. Its anilino analogue, (IIb), is a

reddish-yellow oil. Their unstable nature accounts for the difficulty in obtaining good microanalyses. The observed $\nu(\text{CO})$ bands for these new organometallic compounds (II) are, not surprisingly, at lower frequencies than those reported for the related cationic phosphonium adducts (ca. 1996, 1929 and 1896 cm^{-1}) obtained via addition to the tropylium ring of cation $[(\eta\text{-C}_7\text{H}_7)\text{W}(\text{CO})_3]^+$ (I) by tertiary phosphines [2,17]. The shift (ca. 20 cm^{-1}) of $\nu(\text{CO})$ to higher frequency in the latter products compared with the neutral tricarbonyl(substituted-1,3,5-triene)tungsten products (II) must be attributed to the presence of positive charge, which is largely localised on the phosphorus atom of the phosphine substituent. The reactant solutions of 2-methylaniline, 2-chloroaniline and cyclohexylamine with the tropylium cation (I) showed the same $\nu(\text{CO})$ bands at 1980, 1900 and 1875 cm^{-1} indicating the formation of the same triene products (II). No ring- or carbonyl-displaced products were detected spectroscopically during the IR studies of reactions 1.

Kinetics and mechanisms

Kinetic results for the slow overall and fast reactions of the aniline nucleophiles with cation I in acetone are summarized in Tables 1 and 2 respectively.

Kinetic results for the rapid overall reaction of I with cyclohexylamine in acetone

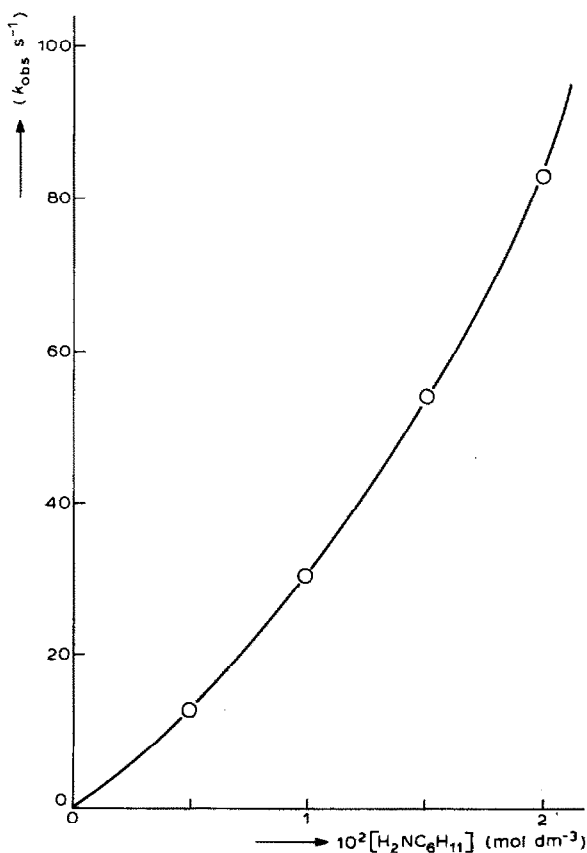
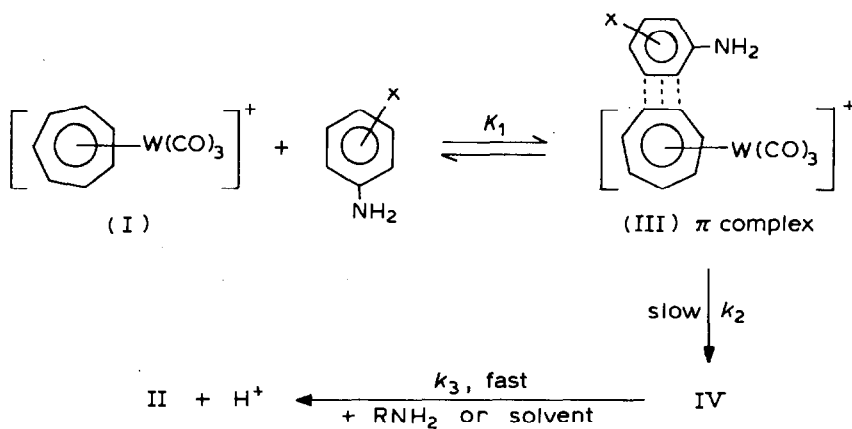


Fig. 5. Dependence of k_{obs} on $[\text{RNH}_2]$ for the reaction of $[(\eta\text{-C}_7\text{H}_7)\text{W}(\text{CO})_3]^+$ with cyclohexylamine in acetone at 0.0°C.



SCHEME 1

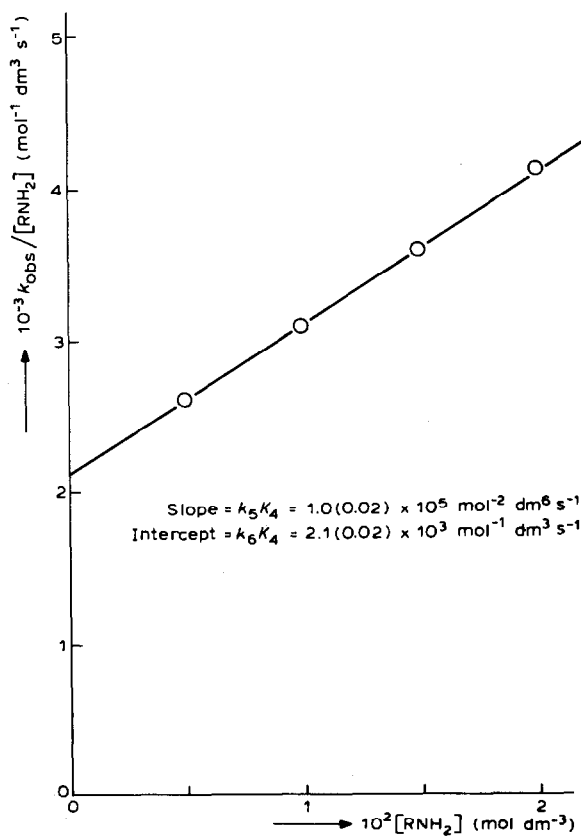


Fig. 6. Plot of $k_{\text{obs}}/[\text{RNH}_2]$ versus $[\text{RNH}_2]$ for the reaction of $[(\eta\text{-C}_7\text{H}_7)\text{W}(\text{CO})_3]^+$ with cyclohexylamine in acetone at 0.0°C .

at 0°C are presented in Table 3. The rate law (eq. 2) observed for the slow overall reaction of anilines with cation I is consistent with the mechanism shown in Scheme 1. In this mechanism, addition of the aniline nucleophile to cation I occurs via rapid

TABLE 1

KINETIC RESULTS FOR THE OVERALL REACTION OF $[(\eta\text{-C}_7\text{H}_7)\text{W}(\text{CO})_3]^+$ WITH VARIOUS ANILINES IN ACETONE AT 20.0°C ($[\text{W}] = 3.01 \times 10^{-3} \text{ mol dm}^{-3}$)

$10[\text{Amine}] \text{ (mol dm}^{-3}\text{)}$	$10^3 k_{\text{obs}} \text{ (s}^{-1}\text{)}$	$K_1 \text{ (mol}^{-1} \text{ dm}^3\text{)}$	$10^3 k_2 \text{ (s}^{-1}\text{)}$	Relative k_2
<i>4-Methylaniline</i>				
0.250	0.960			
0.401	1.43	10.7(0.96)	4.58(0.38)	30
0.601	1.74			
1.20	2.58			
<i>Aniline</i>				
0.254	0.338			
0.508	0.672			
0.604	0.723			
0.750	0.855	4.33(0.34)	3.45(0.26)	22.7
1.02	1.03			
1.21	1.20			
1.51	1.34			
2.03	1.54			
<i>2-Methylaniline</i>				
0.252	0.106			
0.504	0.199			
0.802	0.294	3.60(0.29)	1.28(0.10)	8.4
1.01	0.346			
2.01	0.502			
<i>2-Chloroaniline</i>				
1.00	0.0187			
2.50	0.0378			
5.00	0.0620	1.39(0.07)	0.152(.007)	1
7.51	0.0806			
10.0	0.0894			

TABLE 2

KINETIC RESULTS FOR THE RAPID INITIAL REACTION OF $[(\eta\text{-C}_7\text{H}_7)\text{W}(\text{CO})_3]^+$ WITH ANILINE IN ACETONE AT 0.0°C ($[\text{W}] = 5 \times 10^{-4} \text{ mol dm}^{-3}$)

$10^2 [\text{H}_2\text{NC}_6\text{H}_5] \text{ (mol dm}^{-3}\text{)}$	$k_{\text{obs}} \text{ (s}^{-1}\text{)}$	$k_1^a \text{ (mol}^{-1} \text{ dm}^3 \text{ s}^{-1}\text{)}$	$k_{-1}^a \text{ (s}^{-1}\text{)}$	$K^b \text{ (mol}^{-1} \text{ dm}^3\text{)}$
1.0	35.7	900		
2.0	46.7	1000		
3.0	55.2	950		
4.0	67.0	1010	26.7(1.1)	37(2)
5.0	78.0	1030		
7.0	93.8	959		

^a Derived from rate expression (eq. 3), where $k_c = k_1$ and $k_d = k_{-1}$. ^b K_{eq} estimated from k_1/k_{-1} (k_1 982(27) $\text{mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$).

pre-equilibrium (K_1) to form a π -complex (III) followed by the slow rate-determining formation of a σ -complex (IV) which rapidly loses a proton (either via amine- or solvent-assisted pathway) to form the triene product II. This scheme predicts rate

$$k_{\text{obs}} = \frac{k_2 K_1 [\text{RNH}_2]}{1 + K_1 [\text{RNH}_2]} \quad (5)$$

expression (5) for k_{obs} , which has the same form as the observed rate law (eq. 2). If $K_1 [\text{RNH}_2] \gg 1$, then expression (5) collapses to the simple eq. 6 explaining why plots of k_{obs} versus $[\text{RNH}_2]$ (Fig. 2) become curved at $[\text{RNH}_2] > 0.05 \text{ dm}^{-3}$, and

$$k_{\text{obs}} = k_2 \quad (6)$$

tend towards limiting values. Inversion of eq. 5 affords the expression (7) which predicts the linear plots of $1/k_{\text{obs}}$ versus $1/[\text{RNH}_2]$ shown in Fig. 3. From the slope, $1/k_2 K_1$, and intercept, $1/k_2$, for the aniline reaction, a K_1 value of 4.33

$$1/k_{\text{obs}} = 1/k_2 + 1/k_2 K_1 [\text{RNH}_2] \quad (7)$$

$(0.34) \text{ mol}^{-1} \text{ dm}^3$ is thus estimated at 20°C . This indicates that a very significant concentration of the π -complex (III) must be present at the start of IR runs. For example, with $[\text{aniline}] = 0.203 \text{ mol dm}^{-3}$ and $[\text{W}]_0 = 3.01 \times 10^{-3} \text{ mol dm}^{-3}$, ca. 47% of the tungsten species is estimated from expression 8 to be present as III. The fact that no new $\nu(\text{CO})$ bands assignable to this intermediate III are observed clearly

$$K_{\text{eq}} = \frac{[x]}{[a-x][b]} \quad (8)$$

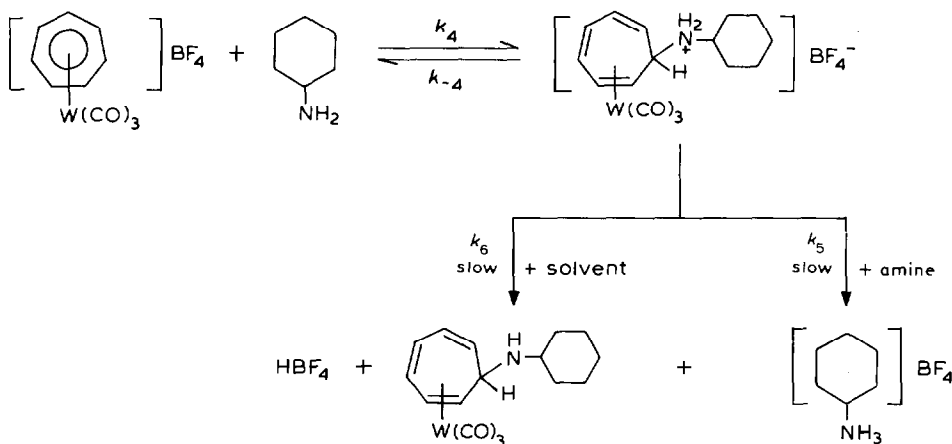
support its formulation as a π -complex of the type shown in Scheme 1. It also precludes the alternative mechanism in which a σ -complex of the type $[(1-6-\eta\text{-C}_7\text{H}_7\text{NH}_2\text{R})\text{W}(\text{CO})_3]^+$ (IV) (with the positive charge largely residing on the nitrogen atom) is formed in the rapid pre-equilibrium (K_1) and this is followed by a slow rate-determining proton removal by the solvent (k_2) to give the final product II. Such cationic intermediates (IV) are known [4] to have much higher frequency $\nu(\text{CO})$ bands than the neutral products derived from them. A π -complex of the type III might be expected to exhibit similar $\nu(\text{CO})$ bands to the original cation I (and thus not be detected during the IR runs) since even substituents on the tropylium ring in complexes of the type $[(\eta\text{-C}_7\text{H}_6\text{X})\text{Cr}(\text{CO})_3]^+$ are known [18] to have negligible effects on carbonyl frequencies. The K_1 values in Table 1 are seen to decrease in the order 4-methylaniline > aniline > 2-methylaniline > 2-chloroaniline

TABLE 3

KINETIC RESULTS FOR THE REACTION OF $[(\eta\text{-C}_7\text{H}_7)\text{W}(\text{CO})_3]^+$ WITH CYCLOHEXYLAMINE IN ACETONE AT 0.0°C ($[\text{W}] = 1.5 \times 10^{-3} \text{ mol dm}^{-3}$)

$10^2 [\text{H}_2\text{NC}_6\text{H}_{11}]$ ($\text{mol}^{-1} \text{ dm}^3$)	k_{obs} (s^{-1})	$10^{-3} k_6 K_4^a$ ($\text{mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$)	$10^{-5} k_5 K_4^a$ ($\text{mol}^{-2} \text{ dm}^6 \text{ s}^{-1}$)	k_5/k_6
0.50	13.2			
1.00	31.2	2.12(0.02)	1.0(0.02)	47(1)
1.50	53.9			
2.00	82.9			

^a Derived from Fig. 6 assuming rate expression (eq. 10).



SCHEME 2

(relative values 7.7/3.1/2.6/1), as expected from the decreasing basicity of the amines. Rearrangement (k_2) of the π -complex to intermediate IV in Scheme 1 is even more sensitive to amine basicity (relative rates 30/23/8/1), which is consistent with nucleophilic addition of the amine nitrogen to the tropylium ring. The rapid initial process monitored by stopped-flow at 0°C for the reaction of aniline with cation I is believed to be the pre-equilibrium (K_1) in Scheme 1. The two term rate law (eq. 3) observed for this rapid process is consistent with an equilibrium process, so that k_c may be equated with k_1 (the second-order rate constant for π -complex formation) and k_d with k_{-1} (the first-order rate constant for the reverse dissociation of the π -complex to reform I). The observation that the rapid absorbance increase at 390 nm becomes markedly larger with increasing aniline concentration is also consistent with an equilibrium process. Combination of the k_1 and k_{-1} values in Table 2 for the rapid initial step with aniline leads to a K_1 value for π -complex formation of $37(2) \text{ mol}^{-1} \text{ dm}^3$ at 0°C . This is much higher than the K_1 value of $4.33(0.34) \text{ mol}^{-1} \text{ dm}^3$ calculated independently from the IR results for the overall reaction at 20°C suggesting that π -complex formation is strongly temperature dependent, being favoured by lower temperatures. Finally, the reaction of amines with cation I to form the triene products II via π -complex intermediates contrasts with their direct addition to the diene rings of cations $[(1-5-\eta\text{-dienyl})\text{Fe}(\text{CO})_3]^+$ (dienyl = C_6H_7 , 2-MeOC $_6\text{H}_6$ or C_7H_9) to form the corresponding 1,3-diene derivatives [13]. The absence of π -complex intermediates in the latter case may be attributed to steric hindrance to approach of the aniline nucleophiles by the methylene group(s) above the diene rings.

The rate expression (eq. 4) observed for the reaction of cyclohexylamine with cation I may be rationalised by the mechanism shown in Scheme 2. In this mechanism, the σ -complex triene intermediate, $[(1-6-\eta\text{-C}_7\text{H}_7\text{-NH}_2\text{C}_6\text{H}_{11})\text{W}(\text{CO})_3]^+$ is formed directly in a rapid pre-equilibrium (K_4), followed by competing solvent- and amine-assisted proton removal to give the final neutral product. Such a Scheme obeys the rate expression (eq. 9) which is of the same form as the observed rate law

$$k_{\text{obs}} = \frac{k_5 K_4 [\text{RNH}_2]^2 + k_6 K_4 [\text{RNH}_2]}{1 + K_4 [\text{RNH}_2]} \quad (9)$$

(eq. 4). Provided $K_4[\text{RNH}_2] \ll 1$, eq. 9 collapses to eq. 10 which is consistent with the linear plot of $k_{\text{obs}}/[\text{RNH}_2]$ versus $[\text{RNH}_2]$ (Fig. 6), together with the non-zero intercept (k_6K_4).

$$k_{\text{obs}} = k_5K_4[\text{RNH}_2]^2 + k_6K_4[\text{RNH}_2] \quad (10)$$

Alternatively, a steady-state treatment of the cationic triene intermediate leads to the general expression (eq. 11) which also has the same form as the observed rate law (eq. 4), and predicts the plot shown in Fig. 6. In this case, however, the slope in Fig. 6 is $k_4k_5/k_{-4} + k_6$ while the intercept is $k_4k_6/k_{-4} + k_6$. Unfortunately, the

$$k_{\text{obs}} = \frac{k_4k_5[\text{RNH}_2]^2 + k_4k_6[\text{RNH}_2]}{k_{-4} + k_6} \quad (11)$$

complexity of eqs. 10 and 11 does not allow the determination of rate constants for any of the individual steps in Scheme 2. However, the slope/intercept ratio from Fig. 6 gives a k_5/k_6 value (using either pre-equilibrium or steady-state assumptions) of 47(1) at 0°C (Table 3). Thus, the amine-assisted proton removal is considerably faster than spontaneous or solvent-assisted proton removal from the cationic triene intermediate. The observed difference in kinetic behaviour of cyclohexylamine and anilines towards cation I no doubt partly arises from the inability of the former aliphatic amine to form π -complex intermediates.

Acknowledgement

We are grateful to Professor R.D. Gillard (University College, Cardiff, Wales) for permitting use of his laboratories.

References

- 1 T.I. Odiaka and L.A.P. Kane-Maguire, *J. Chem. Soc., Dalton Trans.*, (1981) 1162.
- 2 G.R. John, Ph.D. Thesis, University of Wales (1977).
- 3 D.M. Birney, A.M. Crane and D.A. Sweigart, *J. Organomet. Chem.*, 152 (1978) 187.
- 4 T.I. Odiaka, Ph.D. Thesis, University of Wales (1980).
- 5 T.I. Odiaka and L.A.P. Kane-Maguire, *Inorg. Chim. Acta*, 37 (1979) 85.
- 6 T.G. Bonner, K.A. Holder, P. Powell and E. Styles, *J. Organomet. Chem.*, 131 (1977) 105.
- 7 G.R. John, C.A. Mansfield and L.A.P. Kane-Maguire, *J. Chem. Soc.*, (1977) 574 and refs. therein.
- 8 C.A. Mansfield and L.A.P. Kane-Maguire, *J. Chem. Soc., Dalton Trans.*, (1976) 2187 and refs. therein.
- 9 P.L. Pauson, G.H. Smith and J.H. Valentine, *J. Chem. Soc.*, (1967) 1057, 1061.
- 10 A. Burrows, Ph.D. Thesis, University of Cambridge (1978).
- 11 R.B. King and A. Fronzaglia, *Inorg. Chem.*, 5 (1966) 1837.
- 12 M.A. Hashmi, J.D. Munro, P.L. Pauson and J.M. Williamson, *J. Chem. Soc. (A)*, (1967) 240.
- 13 L.A.P. Kane-Maguire, T.I. Odiaka, S. Turgoose and P.A. Williams, *J. Chem. Soc., Dalton Trans.*, (1981) 2489.
- 14 L.A.P. Kane-Maguire, T.I. Odiaka and P.A. Williams, *J. Chem. Soc., Dalton Trans.*, (1981) 200 and ref. 3 therein.
- 15 A. Salzer and H. Werner, *Z. Anorg. Allg. Chem.*, 418 (1975) 88.
- 16 L.A.P. Kane-Maguire and G. Thomas, *J. Chem. Soc., Dalton Trans.*, (1975) 1890.
- 17 D.A. Sweigart, M. Gower and L.A.P. Kane-Maguire, *J. Organomet. Chem.*, 108 (1976) C15.
- 18 P.L. Pauson and K.H. Todd, *J. Chem. Soc. (C)*, (1970) 2638.