Kinetics of Nucleophilic Attack on Co-ordinated Organic Moieties. Part 15.† Addition of *p*-Toluidine to Tricarbonyl(1—5-η-dienyl)iron Cations

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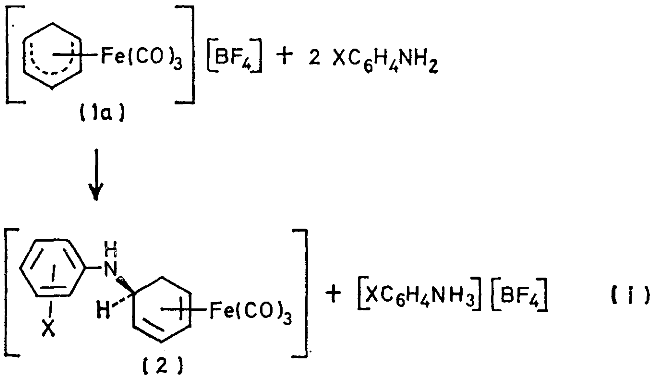
The reactions of the cations $[Fe(\eta^5\text{-dienyl})(CO)_3]^+$ (1 ; dienyl = C_6H_7, C_6H_6OMe-2, or C_7H_9) with *p*-toluidine in CH_3CN have been shown to give the neutral adducts $[Fe(\eta^4\text{-diene}{\cdot}NHC_6H_4CH_3)(CO)_3]$ (2) according to the equation (1) + $2CH_3C_6H_4NH_2 \longrightarrow$ (2) + $[CH_3C_6H_4NH_3]^+$. The products have been characterised by analyses, ^1H n.m.r., i.r., and field-desorption mass spectroscopy. The reactions could be reversed by the addition of acid. A stopped-flow kinetic study of the above reactions in CH_3CN yields the general rate law, Rate = $k[Fe][CH_3C_6H_4NH_2]$. These results are rationalised in terms of a two-step mechanism involving initial reversible addition (k_1, k_{-1}) of *p*-toluidine to the dienyl rings to form the cationic intermediates $[Fe(\eta^4\text{-diene}{\cdot}NH_2C_6H_4CH_3)]^+$ (3), followed by rapid proton loss, k_2 (either solvent- or amine-assisted). For such a mechanism the $k_{obs.}$ values refer to k_1, which is consistent with the observed order of reactivity of the cations at 0 °C ($C_6H_7 > C_6H_6OMe\text{-}2 > C_7H_9$, 17 : 2.6 : 1), and the low $\Delta H^{\ddagger}$ and negative $\Delta S^{\ddagger}$ values.

THE reaction of $[Fe(\eta^5\text{-}C_6H_7)(CO)_3][BF_4]$ (1a) with aniline has been reported[1,2] to give the neutral product (η^4-5-*exo*-*N*-anilinocyclohexa-1,3-diene)tricarbonyliron in high yield. We have recently shown[3] that analogous reactions (i) occur for a wide variety of substituted anilines (X = *o*-, *m*-, *p*-CH_3; *o*-, *m*-, *p*-Cl; *m*-, *p*-OMe; or *m*-NO_2) with complex (1a). Similar processes were found[3] with the related cations $[Fe(\eta^5\text{-}C_6H_6OMe\text{-}2)(CO)_3][BF_4]$ (1b) and $[Fe(\eta^5\text{-}C_7H_9)(CO)_3][BF_4]$ (1c).



Apart from their synthetic utility, these reactions pose several interesting mechanistic problems. Addition to the dienyl rings may be reasonably envisaged to occur either directly or *via* the intermediacy (or 'dead-end' prior formation) of carboxamido-species.[4,5] Furthermore, this could occur either in a concerted or a stepwise fashion, where in the latter proton removal from the initial cationic intermediate (3) could proceed *via* either solvent- or amine-assisted paths. We report here synthetic and kinetic results for the reactions of *p*-toluidine with cations (1a)—(1c). These reactions effectively proceed to completion when [Fe] $\geqslant 1.5 \times 10^{-3}$ mol dm^{-3} and $[p\text{-}CH_3C_6H_4NH_2] \geqslant 0.01$ mol dm^{-3}. Interestingly, the related processes with most of the other aniline nucleophiles (X = H; *o*-, *m*-CH_3; *o*-, *m*-, *p*-Cl; or *m*-NO_2) do not go to completion except at very much higher amine concentrations. Their more complex kinetic behaviour will be reported elsewhere.

EXPERIMENTAL

Materials.—Complexes (1a)—(1c) were prepared and purified using published procedures.[6,7] *p*-Toluidine (BDH) was recrystallised once from acetone before use. Acetonitrile (BDH) solvent was distilled in bulk and stored over molecular sieves (3A) under a nitrogen atmosphere.

Tricarbonyl(1—4-η-5-N-p-*toluidinocyclohexa*-1,3-*diene*)-*iron*, (2a).—Solutions of $[Fe(\eta^5\text{-}C_6H_7)(CO)_3][BF_4]$ (0.10 g, 0.33 mmol) in CH_3CN (10 cm^3) and *p*-toluidine (0.070 1 g, 0.65 mmol) in CH_3CN (10 cm^3) were mixed under nitrogen in a flask (50 cm^3), and allowed to stand at room temperature for 10 min. Rotary evaporation of the mixture under nitrogen at 35 °C yielded a yellow oil. This was shaken with diethyl ether–water (50 : 50 v/v, 40 cm^3) and the aqueous layer set aside. The diethyl ether extract was passed through a short alumina-H column under nitrogen. Rotary evaporation of the yellow filtrate again yielded an oily product. However, upon dissolution in toluene (10 cm^3) and further chromatography on an alumina-H column and evaporation, fine yellow crystals of the product (2a) were obtained and dried *in vacuo* (0.053 g, 50%) (Found: C, 59.6; H, 4.8; N, 4.4. $C_{15}H_{13}FeNO_3$ requires C, 59.1; H, 4.7; N, 4.3%). Infrared spectra: ν(CO) (acetone) at 2 045 and 1 970 cm^{-1}; ν(NH) (Nujol) at 3 400 cm^{-1}. Hydrogen-1 n.m.r. (CD_3COCD_3): 6.87 (2 H, d, aromatic), 6.45 (2 H, d, aromatic), 5.60 (2 H, overlapping resonances, H^2 and H^3), *ca.* 4.45 (1 H, br, NH), 3.93 (1 H, m, H$^{5'}$), 3.20 (2 H, overlapping resonances, H^1 and H^4), 2.35 (1 H, m, H$^{6'}$), 2.13 (3 H, s, CH_3), and 1.40 p.p.m. (1 H, m, H^6). A field-desorption (f.d.) mass spectrum of $[Fe(C_6H_7{\cdot}NHC_6H_4CH_3\text{-}p)(CO)_3]$ (M = 325) showed the following peaks, with their relative intensities in parentheses: 323(5), 325(100), 326(19), and 327(3).

The aqueous phase from the above procedure was passed through a short alumina-H column, and the eluent evaporated to dryness to yield the anilinium salt, $[p\text{-}CH_3C_6H_5NH_3][BF_4]$, as an off-white solid. This was collected, washed several times with diethyl ether, and sucked dry (0.035 g) (Found: C, 41.3; H, 5.1; N, 6.9. $C_7H_{10}BF_4N$ requires C, 43.1; H, 5.2; N, 7.2%). Its i.r. spectrum (Nujol mull) showed a strong band at 1 050 cm^{-1}, as expected for the

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† Part 14 is ref. 3.

$[BF_4]^-$ anion. Hydrogen-1 n.m.r. (CD_3COCD_3): 7.42 (4 H, s, aromatic), 4.63 (3 H, br, NH_3), and 2.37 p.p.m. (3 H, s, CH_3).

Tricarbonyl(1—4-η-5-N-p-*toluidinocyclohepta*-1,3-*diene*)-*iron*, (2c).—An analogous reaction of $[Fe(\eta^5\text{-}C_7H_9)(CO)_3][BF_4]$ (0.10 g, 0.31 mmol) with *p*-toluidine (0.067 1 g, 0.63 mmol) in CH_3CN (20 cm^3), followed by similar work-up to that above, gave the pale yellow solid (2c) (0.053 g, 50%) (Found: C, 60.3; H, 5.0; N, 4.2. $C_{16}H_{15}FeNO_3$ requires C, 60.2; H, 5.1; N, 4.1%). Infrared spectra: ν(CO) (acetone) at 2 045, 1 970 cm^{-1}; ν(NH) (Nujol) at 3 400 cm^{-1}. Hydrogen-1 n.m.r. (CD_3COCD_3): 6.93, (2 H, d, aromatic), 6.50, (2 H, d, aromatic), 5.46 (2 H, overlapping resonances, H^2 and H^3), 4.60 (1 H, br, NH), 3.70 (1 H, m, $H^{5'}$), 3.10 (2 H, overlapping resonances, H^1 and H^4), 2.67 (2 H, br, m, $H^{6',7'}$), 2.13 (3 H, s, CH_3), and 1.69 p.p.m. (2 H, m, $H^{6,7}$).

A f.d. mass spectrum of the $[Fe(C_7H_9{\cdot}NHC_6H_4CH_3\text{-}p)(CO)_3]$ product ($M = 339$) showed the following mass peaks with their relative intensities in parentheses: 337(5), 338(1), 339(100), 340(15), and 341(2). Also isolated from the work-up was *ca.* 30 mg of the anilinium salt $[p\text{-}CH_3C_6H_4NH_3][BF_4]$.

Spectroscopic Studies.—Infrared spectra were recorded on a Perkin-Elmer 257 spectrophotometer using matched 0.5-cm sodium chloride solution cells or as Nujol mulls between sodium chloride plates. Hydrogen-1 n.m.r. (90 MHz) spectra were obtained on a Perkin-Elmer R32 spectrophotometer. F.d. mass spectra were recorded using a combined FD/FI/EI source on a CH5D mass spectrophotometer linked to a Varian 620i data system. Acetone was used as solvent, and only low emitter currents were required.

Equilibrium-constant Studies.—Equilibrium constants for the overall processes (ii) (dienyl = $\eta^5\text{-}C_6H_7$, $\eta^5\text{-}C_6H_6OMe\text{-}2$, or $\eta^5\text{-}C_7H_9$) were determined by dissolving the appropriate dienyl salts in acetonitrile solutions (20 °C) of various *p*-toluidine concentrations, and recording the i.r. spectrum in the region 1 900—2 200 cm^{-1}. The equilibrium concentrations of the $[Fe(\eta^5\text{-dienyl})(CO)_3]^+$ ions were calculated from

$$[Fe(\eta^5\text{-dienyl})(CO)_3]^+ + 2RNH_2 \rightleftharpoons [Fe(\eta^4\text{-diene}{\cdot}NHR)(CO)_3] + RNH_3^+ \quad \text{(ii)}$$

their absorption at 2 120 cm^{-1}, using their known [8] absorption coefficients. From the known starting concentrations, the equilibrium concentrations of the products could then be estimated, allowing calculation of the equilibrium constants ($K_{eq.}$ as defined in (iii).

$$K_{eq.} = \frac{[Fe(\eta^4\text{-diene}{\cdot}NHR)(CO)_3][RNH_3^+]}{[Fe(\eta^5\text{-dienyl})(CO)_3^+][RNH_2]^2} \quad \text{(iii)}$$

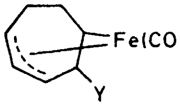
Kinetic Studies.—Separate solutions of complex salt (3.0×10^{-3} mol dm^{-3}) and *p*-toluidine (0.02—0.30 mol dm^{-3}) were freshly prepared and thermostatted at the desired temperature (±0.1°) prior to mixing. All of the reactions were rapid and involved a large decrease in absorbance at 390 nm. They were conveniently followed at this wavelength using a thermostatted (±0.1°) stopped-flow spectrophotometer. Reaction traces were stored on a Tektronix 564B storage oscilloscope fitted with a log converter, giving direct absorbance read-out. Pseudo-first-order rate constants were calculated from the slopes of plots of log ($A_t - A_\infty$) *vs. t*. Linear first-order kinetics were generally obtained for at least two half-lives. Each $k_{obs.}$ is the average of at least three separate runs, with an average reproducibility of ±3%. Second-order rate constants, k_1, were estimated by least-squares analyses of the plots of $k_{obs.}$ *vs.* [*p*-toluidine], the errors quoted being the appropriate standard deviations.

Activation enthalpies were calculated from a least-squares fit to the Arrhenius equation. The errors quoted are the standard deviations derived from the least-squares analyses. Entropies of activation were estimated using the calculated second-order rate constants, k_1.

RESULTS AND DISCUSSION

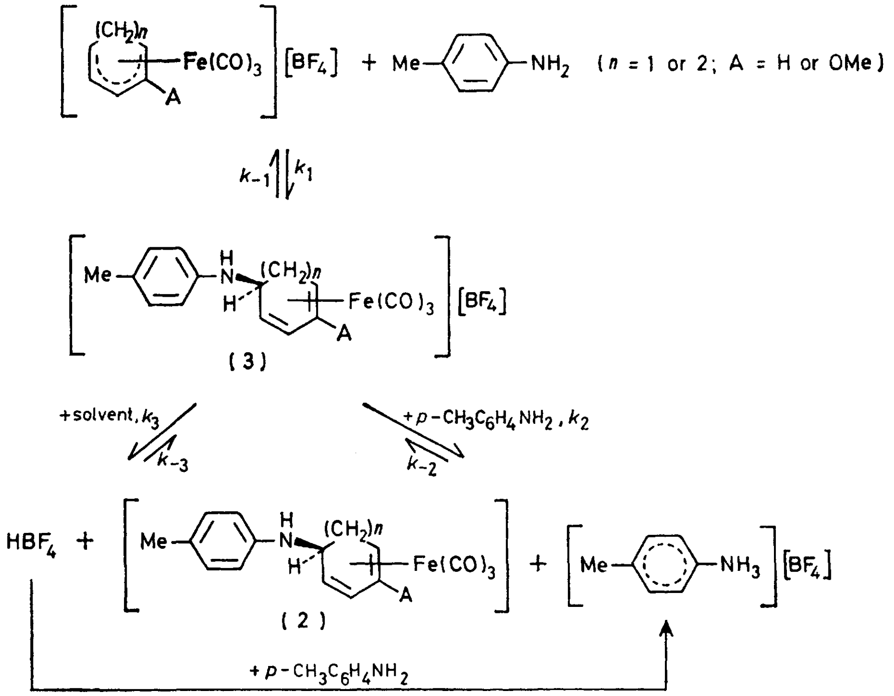
Spectroscopic Studies.—The products (2a) and (2c) isolated from the reactions of cations (1a) and (1c) with *p*-toluidine in CH_3CN are yellow crystalline solids, stable in air for several months. Spectroscopic studies clearly show that they are tricarbonyl(1—4-η-5-*N*-toluidino-1,3-diene)iron derivatives. Although their microanalyses and f.d. mass spectra are also consistent with the alternative carboxamido-formation, $[Fe(\eta^5\text{-dienyl})(CO)_2(CONHC_6H_4CH_3)]$, this possibility is excluded by ^1H n.m.r. spectroscopy. The ^1H n.m.r. spectrum of (2a) in $[^2H_6]$acetone (see Experimental section) is very similar to that previously reported [1] for the analogous anilino-product. Overlapping resonances characteristic of the inner (H^2 and H^3) and outer (H^1 and H^4) diene protons are well separated, at 5.60 and 3.20 p.p.m. respectively. The $H^{6,6'}$ methylene protons appear at 1.40 and 2.35 p.p.m. while the $H^{5'}$ proton adjacent to the *N*-toluidino-substituent is shifted downfield to 3.93 p.p.m. The broad resonance at *ca.* 4.45 p.p.m. is assigned to the NH proton since it disappears on addition of D_2O. The other assignments were confirmed by spin-decoupling experiments. The pair of doublets at 6.85 and 6.50 p.p.m. in free *p*-toluidine (assigned to the aromatic protons) have a distinctively wider separation in the adduct (2a), appearing at 6.87 and 6.45 p.p.m. respectively.

The ^1H n.m.r. spectrum of the cycloheptadiene derivative (2c) is broadly similar to that of (2a), except for the presence of extra $H^{7,7'}$ methylene protons. Assignment of the $H^{2,3}$ and $H^{1,4}$ diene protons was confirmed by spin-decoupling. Product (2c) therefore also has a 1,3-diene structure, its spectrum being clearly inconsistent with the alternative σ-allyl-bonded formulation (4; Y = $NHC_6H_4CH_3\text{-}p$). Although the product (2b) from addition of *p*-toluidine to cation (1b) has not been isolated, *in situ* i.r. studies (see below) again support a tricarbonyl-(substituted 1,3-diene)iron product. By analogy with earlier studies [6,9,10] with other nucleophiles, addition at the 5-position of the dienyl ring is assumed.



(4)

The stoicheiometry of reaction (i) (X = *p*-Me) was also established by ^1H n.m.r. spectroscopy. A mixture of cation (1a) or (1c) (0.25 mol dm^{-3}) and a ten-fold excess of *p*-toluidine (2.5 mol dm^{-3}) in $[^2H_6]$acetone showed no resonances due to the original dienyl salts. The only peaks present are those assignable to (2a) or (2c), the anilinium salt [p-$CH_3C_6H_4NH_3$][BF_4] (7.27 p.p.m.), and excess of free p-toluidine. Thus, the reactions proceed to completion under these conditions with the effective consumption of 2 mol of p-toluidine per mol of iron. It should be pointed out, however, that the isolation (see Experimental section) and spectroscopic detection of [p-$CH_3C_6H_4NH_3$][BF_4] as a product does not establish that a second p-toluidine molecule is involved in proton removal from the proposed cationic intermediate (3) (see Scheme). The alternative solvent-assisted proton-removal path in the Scheme must also ultimately lead to the production of the anilinium salt in the presence of excess of p-toluidine.



SCHEME

Acetone solutions of (2a) and (2c) show two strong carbonyl bands in their i.r. spectra at 2 045 and 1 970 cm^{-1}, characteristic of neutral tricarbonyl(diene)iron complexes. Both products also exhibit peaks at 3 400 cm^{-1} (Nujol) as expected for the presence of a NH group. Analogous carbonyl bands at 2 045 and 1 975 cm^{-1} were observed after treating each of the cations (1a)—(1c) ([Fe] = 1.5×10^{-3} mol dm^{-3}) with excess of p-toluidine ([p-$CH_3C_6H_4NH_2$] $\geqslant 1.0 \times 10^{-2}$ mol dm^{-3}) in CH_3CN, confirming the occurrence of the same reaction in the kinetic solvent. These latter experiments also established that, under the kinetic conditions employed (Table 2), each of the reactions proceeds to completion.

However, experiments employing smaller excesses of p-toluidine ([Fe] = 5.0×10^{-3}, [p-$CH_3C_6H_4NH_2$] = 1.0×10^{-2}—1.5×10^{-2} mol dm^{-3}) showed that reactions (i) with cations (1a)—(1c) are equilibrium processes. Static equilibrium constants, K_{eq}, calculated for these reactions (see Experimental section) are summarised in Table 1. No carbonyl bands other than those assignable to the dienyl cations (1) and products (2) are observed under these latter conditions, although a slight broadening of the band of products (2) at 1 975 cm^{-1} is evident at [p-$CH_3C_6H_4NH_2$] = 1.0×10^{-2} mol dm^{-3} [Figure (*a*)].

However, under equimolar conditions ([Fe] = [p-$CH_3C_6H_4NH_2$] = 1.5×10^{-3} or 5.0×10^{-3} mol dm^{-3}), a new band at 1 985 cm^{-1} is also present in each case. Its shift of 10 cm^{-1} to higher frequency compared with that of (2) suggests that it may be due to the intermediate cationic species (3) (with the positive charge largely localised on the nitrogen atom), and that its expected second carbonyl band is masked by the original dienyl cation band at 2 065 cm^{-1}. Thus, the ν(CO) bands for (3) are, not surprisingly, similar to those previously found [9] for the cationic phosphonium adducts formed between (1a) and tertiary phosphines, namely at *ca.* 2 055 and 1 985 cm^{-1}. Further strong support for the assignment to (3) of the ν(CO) band at 1 985 cm^{-1} comes from experiments in which trifluoroacetic acid was added to these equilibrium mixtures [Figure (*b*)]. Addition of one drop of acid resulted in the disappearance of bands at 2 045 and 1 975 cm^{-1} due to the product (2) with the retention of a strong band at 2 085 cm^{-1} and an increase

TABLE 1

Equilibrium constants for the reactions of [Fe(η^5-dienyl)-$(CO)_3$]$^+$ cations with p-toluidine in CH_3CN at 20 °C

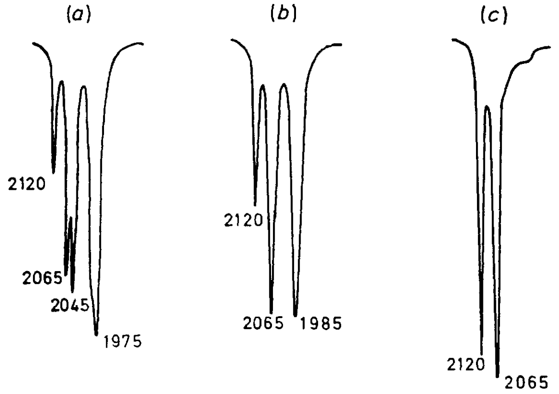
Dienyl	$K_{eq.}/dm^3\ mol^{-1}$
C_6H_7	2.8
C_6H_6OMe-2	0.27
C_7H_9	1.9

in the original dienyl peaks at 2 120 and 2 065 cm^{-1}. Further addition of trifluoroacetic acid regenerated the spectrum of the original dienyl salts quantitatively. Reactions (i) are thus completely reversed by addition of acid.

Kinetics and Mechanism.—Kinetic results for the addition of *p*-toluidine to each of the dienyl cations (1) in CH_3CN are summarised in Table 2. In all cases the rate law (iv) is seen to be obeyed. The absence of a second-order dependence on [amine] is striking, and

$$k_{obs.} = k[p\text{-}CH_3C_6H_4NH_2] \qquad \text{(iv)}$$

eliminates a concerted process involving base-catalysed nucleophilic attack by amine, as has been proposed for example for carboxamido-formation[5] with *trans*-$[M(CO)_4L_2]^+$ (M = Mn or Re; L = PR_3) and for the reactions of amines with pentacarbonyl(methoxycarbene)chromium to give the corresponding aminocarbene complexes.[11]



Infrared spectra (cm^{-1}) of mixtures of $[Fe(\eta^5\text{-}C_6H_7)(CO)_3][BF_4]$ in CH_3CN at 20 °C. (*a*) [Fe] = 5.03×10^{-3} mol dm^{-3}, $[p\text{-}CH_3C_6H_4NH_2] = 1.01 \times 10^{-2}$ mol dm^{-3}; (*b*) as in (*a*), plus one drop of CF_3CO_2H; (*c*) as in (*a*), plus four drops of CF_3CO_2H

Rate law (iv) may be rationalised in terms of the amine-assisted pathway in the Scheme. Assuming a steady-state concentration for the intermediate (3) (and assuming k_{-2} is negligible, since the reactions proceed to completion under the kinetic conditions), this path leads to the general rate expression (v). Provided $k_2[p\text{-}CH_3C_6H_4NH_2] \gg k_{-1}$ this equation simplifies to the observed form

$$k_{obs.} = \frac{k_1k_2[p\text{-}CH_3C_6H_4NH_2]^2}{k_{-1} + k_2[p\text{-}CH_3C_6H_4NH_2]} \qquad \text{(v)}$$

(iv), in which the calculated second-order rate constants k refer to the initial ring addition step, k_1. Alternatively, a steady-state treatment of the solvent-assisted path in the Scheme (assuming k_{-3} is negligible) leads to expression (vi), which is also compatible with the observed rate law (iv). Since the $[Fe(diene)(CO)_3]$ moiety is known[12] to be an electron-withdrawing group, proton removal

$$k_{obs.} = \frac{k_1k_3[p\text{-}CH_3C_6H_4NH_2]}{k_{-1} + k_3} \qquad \text{(vi)}$$

from intermediate (3) may reasonably be assumed to be rapid (*i.e.* k_2 and $k_3 \gg k_{-1}$). Under this condition equation (vi) simplifies to (vii). Thus, irrespective of the pathway followed (see Scheme), the second-order rate

$$k_{obs.} = k_1[p\text{-}CH_3C_6H_4NH_2] \qquad \text{(vii)}$$

constants calculated for reactions (i) are considered to represent the ring addition processes (k_1). The relative rates found (Table 2) for reaction of *p*-toluidine with cations (1), namely $C_6H_7 > C_6H_6OMe\text{-}2 > C_7H_9$ (17 : 1.6 : 1), are consistent with this view. Similar rate variations have been observed for the reactions of these cations with phosphines[9] and pyridines,[10] processes which are known to involve simple direct addition to the dienyl rings. The slower rate for the C_6H_6OMe-2 cation compared with the parent cyclohexadienyl complex is in accordance with the mesomeric and slight steric[2] influence of the methoxide group, while the cycloheptadienyl cation (1c) is expected to show the slowest rate on steric grounds for reactions involving addition of a nucleophile from above the dienyl rings.

TABLE 2

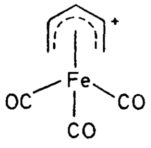
Kinetic results for addition of *p*-toluidine to $[Fe(\eta^5\text{-dienyl})(CO)_3][BF_4]$ complexes in acetonitrile[a]

Dienyl	θ_c/°C	[Amine]/ mol dm^{-3}	$k_{obs.}$/s^{-1}	k_1/dm^3 mol^{-1} s^{-1} [b]
C_6H_7	0.0	0.010	69.1	6 470(260)
		0.015	93.8	
		0.020	133	
		0.025	164	
	5.9	0.010	82.5	8 250
	10.0	0.010	98.3	9 830
C_6H_6OMe-2	0.0	0.010	11.4	1 010(5)
		0.020	20.9	
		0.040	40.6	
		0.050	51.1	
		0.080	81.5	
		0.100	102	
	10.0	0.010	21.8	2 180
	15.4	0.010	29.6	2 960
	20.0	0.010	38.9	3 890
C_7H_9	0.0	0.010	3.48	386(5)
		0.020	6.78	
		0.040	15.7	
		0.080	29.6	
		0.100	39.0	
		0.150	57.2	
	10.0	0.010	5.70	570
	15.2	0.010	7.29	729
	20.0	0.010	9.39	939
	25.2	0.010	11.8	1 180

[a] [Fe] = 1.50×10^{-3} mol dm^{-3}. [b] Estimated standard deviations in parentheses.

An *exo* configuration is assumed for the toluidino-substituents in the products (2) since this geometry has been established[2] for the analogous anilino-compound [(1—4-η-5-*N*-anilinocyclohexa-1,3-diene)tricarbonyliron. Additional support for direct *exo* addition of *p*-toluidine to the dienyl rings of cations (1) comes from a comparison with previous studies[13-15] of the reactions of aniline and substituted anilines with (acyclic dienyl)tricarbonyliron cations. Maglio and Palumbo[14] have found that addition of anilines RNH_2 to cation (4) leads not only to the expected $[Fe(diene{\cdot}NHR)(CO)_3]$ products, (5), but also to significant amounts of the binuclear species $[(OC)_3Fe(diene{\cdot}NR{\cdot}diene)Fe(CO)_3]$ (6), arising from nucleophilic attack by the initial product (5) on cation

(4). However, analogous reactions with the more sterically demanding cation (7) gave only simple products of the type (5).[13] Similarly, our failure here to observe any binuclear products related to (6) from reactions (i) may be rationalised in terms of steric hindrance by the methylene group(s) of the dienyl rings in cations (1), preventing approach by the potentially nucleophilic products (2).



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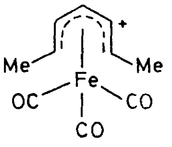

(7)

An explanation for the observed rate law (iv) may also be sought in terms of a pre-equilibrium mechanism, *i.e.* assuming steps k_1 and k_{-1} in the Scheme are very much faster than the subsequent proton-removal processes k_2 and/or k_3. For example, for the amine-assisted proton-removal path this assumption leads to the general expression (viii), which simplifies to (ix) if $K_1[p\text{-}CH_3C_6H_4NH_2] \gg 1$, *i.e.* if there is almost complete conversion into intermediate (3) under the kinetic conditions. However, no spectroscopic evidence has been found for an intermediate under any of the kinetic conditions employed here.

$$k_{obs.} = \frac{k_2K_1[p\text{-}CH_3C_6H_4NH_2]^2}{1 + K_1[p\text{-}CH_3C_6H_4NH_2]} \qquad \text{(viii)}$$

$$k_{obs.} = k_2[p\text{-}CH_3C_6H_4NH_2] \qquad \text{(ix)}$$

Furthermore, the absorbance at the commencement of the stopped-flow traces for the related reactions of cation (1a) with aniline was identical to that of the pure cation. A steady-state assumption is therefore favoured.

The rapid rates of reactions (i) are seen from Table **3** to be associated with low enthalpies of activation, while the negative entropies of activation are as expected for simple addition processes. The uncertainties in the activation parameters for the C_6H_7 complex are probably somewhat larger than those indicated in Table **3** because of the small temperature range over which its rapid reaction could be followed with accuracy. Nevertheless, the relative rates for the different cations are seen to arise from a play-off between enthalpy and entropy effects. Thus, while the slower rate for the C_7H_9 cation compared with that containing C_6H_7 arises from a higher $\Delta H_1^‡$ and a more negative $\Delta S_1^‡$, the intermediate rate for the C_6H_6OMe-2 complex is associated with both the largest $\Delta H_1^‡$ and the least negative $\Delta S_1^‡$ value.

TABLE 3

Rate and activation parameters for addition of *p*-toluidine to $[Fe(\eta^5\text{-dienyl})(CO)_3][BF_4]$ complexes in acetonitrile with estimated standard deviations in parentheses

Dienyl	k_1 (0 °C)/ $dm^3\ mol^{-1}\ s^{-1}$	$\Delta H_1^‡$/ $kJ\ mol^{-1}$	$\Delta S_1^‡$/ $J\ K^{-1}\ mol^{-1}$
C_6H_7	6 470(260)	24.4 (0.6)	−82(2)
C_6H_6OMe-2	1 010(5)	42.5 (1.5)	−31(5)
C_7H_9	386(5)	27.9 (1.3)	−93(5)

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