

**Preliminary communication**

**KINETICS OF NUCLEOPHILIC ATTACK ON COORDINATED ORGANIC MOIETIES.**

**XIV\*. THE SIGNIFICANCE OF AMINE BASICITY IN DETERMINING THE NUCLEOPHILICITIES OF PYRIDINES AND ANILINES TOWARDS [(1-5- $\eta$ -Dienyl)Fe(CO)<sub>3</sub>]<sup>+</sup> CATIONS**

LEON A.P. KANE-MAGUIRE, TIMOTHY I. ODIAKA, STEVE TURGOOSE, and PETER A. WILLIAMS

*Chemistry Department, University College Cardiff, P.O. Box 78, Cardiff, CF1 1XL, Wales (Great Britain)*

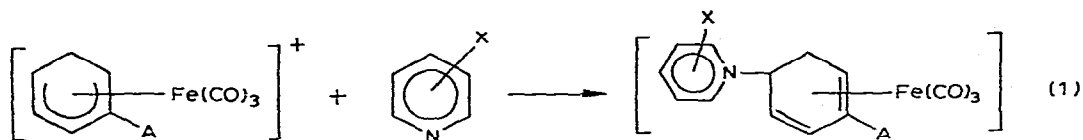
(Received January 10th, 1980)

**Summary**

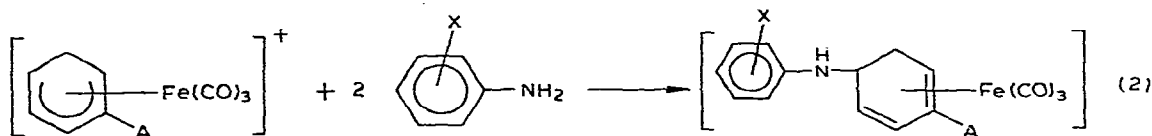
The second-order rate constants,  $k_1$ , for addition of pyridines and anilines to the cations [(1-5- $\eta$ -C<sub>6</sub>H<sub>7</sub>)Fe(CO)<sub>3</sub>]<sup>+</sup> (I), [(1-5- $\eta$ -2-MeOC<sub>6</sub>H<sub>6</sub>)Fe(CO)<sub>3</sub>]<sup>+</sup> (II), and [(1-5- $\eta$ -C<sub>7</sub>H<sub>9</sub>)Fe(CO)<sub>3</sub>]<sup>+</sup> (III) in CH<sub>3</sub>CN decrease along the series I > II > III. The Brönsted relationship,  $\log k_1 = \alpha pK_a + \text{constant}$ , is obeyed for the addition of substituted pyridines to I and of substituted anilines to II. The slopes,  $\alpha$ , of about 1.0 in each case indicate a strong dependence of  $k_1$  on amine basicity. These results, together with previous data on related phosphine additions, suggest a "hard" character for the dienyl ligands in these organometallic cations.

Although the reactions of nucleophiles with [( $\pi$ -hydrocarbon)M(CO)<sub>3</sub>]<sup>+</sup> complexes are of considerable synthetic interest, the factors governing the reactivity of such coordinated  $\pi$ -hydrocarbons are as yet poorly understood. Some progress has been made recently in establishing the relative reactivity of a variety of such cations ( $\pi$ -hydrocarbon = olefin, enyl, diene, dienyl, triene, trienyl) towards common nucleophiles, mainly tertiary phosphines [1–3]. However, apart from some kinetic studies with  $\beta$ -diketones [4], aromatic heterocycles [5], activated arenes [3, 6], and phosphorus nucleophiles [1–3, 7], little quantitative information is currently available concerning nucleophilic reactivities.

We wish to report here preliminary kinetic results concerning the addition of various pyridines and anilines to [(1-5- $\eta$ -C<sub>6</sub>H<sub>7</sub>)Fe(CO)<sub>3</sub>]<sup>+</sup> (I) and [(1-5- $\eta$ -2-MeOC<sub>6</sub>H<sub>6</sub>)Fe(CO)<sub>3</sub>]<sup>+</sup> (II) cations (eq. 1 and 2). Synthetic studies of the additions of the parent nucleophiles pyridine and aniline to cation I have been prev-



(A = H; X = H, 3-Me, 4-Me, 3,5-Me<sub>2</sub>, 3-CN)



(A = OMe; X = H, 2-Me, 3-Me, 4-Me, 4-MeO, 3-Cl, 4-Cl)

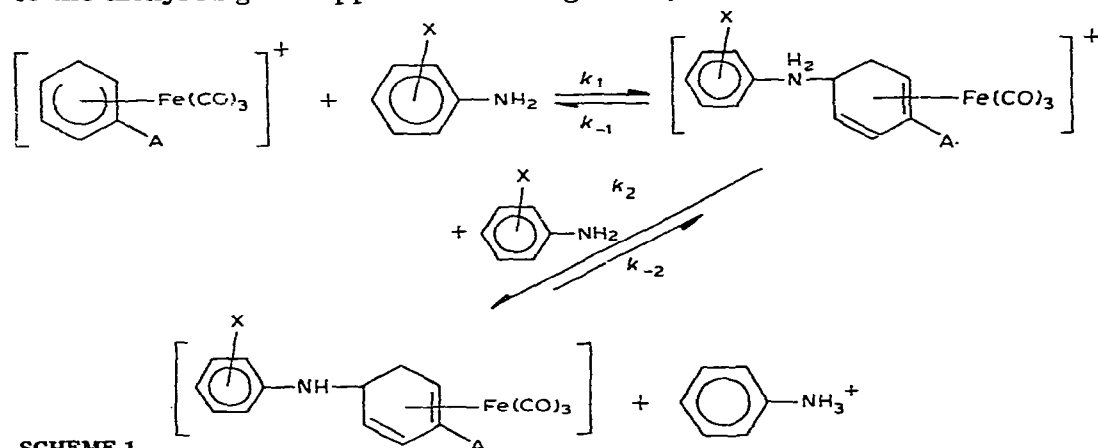
iously reported by others [8, 9]. These studies not only extend the range of nucleophile types investigated, but also throw considerable light on the factors important in determining nucleophilicity towards  $[(\pi\text{-hydrocarbon})\text{M}(\text{CO})_3]^+$  substrates.

Reactions 1 proceed to completion in  $\text{CH}_3\text{CN}$  solvent under the kinetic conditions employed ( $[\text{Fe}] = 3 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[\text{XC}_5\text{H}_4\text{N}] \geq 2 \times 10^{-2} \text{ mol dm}^{-3}$ ), except for X = 3-CN. The rate expression 3 is usually observed, where  $k$  corresponds to the second-order rate constant,  $k_1$ , for direct addition to the dienyl ring. The only exception is the X = 3-CN case, where eq. 3a is obeyed. Here  $k_1$  refers to the reverse dissociation of the pyridinium adduct.

$$k_{\text{obs}} = k [\text{amine}] \quad (3)$$

$$k_{\text{obs}} = k_1 [\text{amine}] + k_{-1} \quad (3a)$$

The corresponding reactions 2 with anilines are stepwise processes as shown in Scheme 1. For the more basic anilines (X = 4-Me, 4-MeO) the reactions proceed to completion in  $\text{CH}_3\text{CN}$  under the kinetic conditions ( $[\text{Fe}] = 3.0 \times 10^{-3} \text{ mol dm}^{-3}$ ;  $[\text{XC}_6\text{H}_4\text{NH}_2] \geq 2 \times 10^{-2} \text{ mol dm}^{-3}$ ). Rate expression (3) is again obeyed. This is most readily rationalised in terms of rapid amine-assisted proton removal ( $k_2 \gg k_1, k_{-1}, k_{-2}$ ), in which case  $k$  again refers to  $k_1$  for initial addition to the dienyl ring. In support of this assignment, the  $k$  values for reactions of



SCHEME 1

TABLE 1

KINETIC RESULTS FOR ADDITION OF AMINES TO [(1-5- $\eta$ -dienyl)Fe(CO)<sub>3</sub>]<sup>+</sup> CATIONS IN CH<sub>3</sub>CN<sup>a</sup>

Cation	Amine	$k_1$ (mol <sup>-1</sup> dm <sup>3</sup> s <sup>-1</sup> )
I	pyridine	2130
	4-methylaniline	6470
	2-methylaniline	1270
II	pyridine	425
	4-methylaniline	1010
	2-methylaniline	128
III	pyridine	140
	4-methylaniline	386
	2-methylaniline	71

<sup>a</sup>Temperatures. 0.0°C for pyridine and 4-methylaniline, 10.0°C for 2-methylaniline.

these anilines with cation I are considerably larger than those found for the related reactions of [(1-5- $\eta$ -2-MeOC<sub>6</sub>H<sub>6</sub>)Fe(CO)<sub>3</sub>]<sup>+</sup> (II) and [(1-5- $\eta$ -C<sub>7</sub>H<sub>9</sub>)Fe(CO)<sub>3</sub>] (III) (Table 1). Addition to the dienyl rings in these latter cations is predicted to be slower on electronic and steric grounds, respectively. In contrast, for the less basic anilines (X = H, 2-Me, 3-Me, 3-Cl, 4-Cl) the reactions 2 are equilibrium processes even at the highest nucleophilic concentrations employed. For these anilines the two-term rate law 4 is observed. Derivation of a general rate expression for Scheme 1 would be very complex. However, by making the

$$k_{\text{obs}} = k'[\text{amine}] + k'' \quad (4)$$

reasonable assumption that the establishing of equilibrium  $K_2$  occurs much more rapidly than  $K_1$ ,  $k'$  and  $k''$  can be equated to  $k_1$  and  $k_{-1}[\text{H}^+]/[\text{H}^+] + K_2K_a$ , respectively. That the experimentally derived  $k'$  values do in fact correspond to  $k_1$  is again supported by the decrease in  $k'$  along the series I > II > III (Table 1).

The  $k_1$  values summarised in Table 2 for reactions 1 and 2 reveal a very strong dependence on the basicity of the amine nucleophile. This is demonstrated quantitatively by the LFER's obtained on plotting  $\log k_1$  vs.  $\text{p}K_a$  of the amine

TABLE 2

KINETIC RESULTS FOR ADDITION OF SUBSTITUTED (X) PYRIDINES AND ANILINES TO [(1-5- $\eta$ -dienyl)Fe(CO)<sub>3</sub>]<sup>+</sup> CATIONS IN CH<sub>3</sub>CN

Cation	X	$\text{p}K_b$	$k_1(0^\circ\text{C})(\text{mol}^{-1} \text{dm}^3 \text{s}^{-1})$
<i>pyridines (C<sub>5</sub>H<sub>5</sub>N)</i>			
I	3,5-Me <sub>2</sub>	7.83	10400
	4-Me	7.97	8340
	3-Me	8.32	6980
	H	8.77	2130
	3-CN	11.10	8
<i>anilines (X-C<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>)</i>			
II	4-MeO	8.64	1730
	4-Me	8.92	1010
	3-Me	9.27	375
	H	9.40	372
	4-Cl	9.85	82
	3-Cl	10.54	34

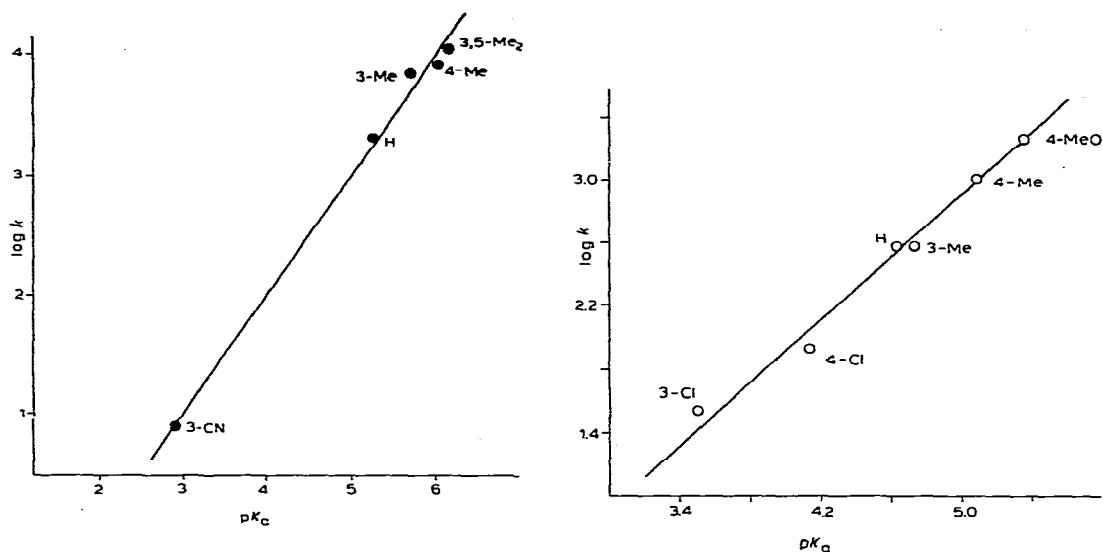


Fig. 1. (a) Plot of  $\log k_1$  vs.  $pK_a$  of amine conjugate acid for addition of pyridines to  $[(1-5-\eta-C_6H_7)Fe(CO)_3]BF_4$ ; (b) Plot of  $\log k_1$  vs.  $pK_a$  of amine conjugate acid for addition of amines to  $[(1-5-\eta-2MeO-C_6H_6)Fe(CO)_3]BF_4$ .

conjugate acid (in water\*) (Fig. 1a, b). Reactions 1 and 2 thus obey the Brønsted relationship 5, with slopes,  $\alpha$ , of about 1.0 in each case.

$$\log k_1 = \alpha pK_a + \text{constant} \quad (5)$$

These high slopes contrast with the very low  $\alpha$  values of about 0.05 previously found [11] for attack by pyridines and other amines on the very "soft" platinum(II) centre in complexes such as *trans*- $[Pt(py)_2Cl_2]$ . For amine attack on moderately "soft" substrates such as alkyl halides  $\alpha$  values of about 0.2 have been reported [12]. Interestingly, they are also somewhat larger than the  $\alpha$  values of about 0.5 found by Ritchie et al. [13], for amine additions to free carbonium ions. Following the reasoning of Pearson [14], this suggests that the dienyl rings in cations such as I–III are "hard" moieties.

Assignment of a "hard" character to the dienyl groups of cations I–III is consistent with their frequent representation as stabilized carbonium ions, and with the relatively high positive charges calculated [15] to reside on the ring carbons.

We have recently observed [16] a similar strong dependence of  $k_1$  on nucleophile basicity for the related additions of phosphines and phosphites to cations I and II in acetone. Plots of  $\log k_1$  vs. the half-neutralisation potentials,  $\Delta(\text{h.n.p.})$  which have been used [17] as a quantitative measure of basicity for phosphorus nucleophiles, give slopes of  $-8.72$  and  $-8.49 \text{ volt}^{-1}$ , respectively. A revealing

\*Comprehensive  $pK_a$  values for amines are not yet available in  $CH_3CN$ . However, a similar but less extended LFER is obtained on plotting  $\log k_1$  vs. the basicities of  $XC_6H_4NH_2$  ( $X = H, 4-Me, 4-MeO, 3-Cl$ ) determined in  $CH_3NO_2$  [10].

comparison for present purposes is with *trans*-[Pt(py)<sub>2</sub>Cl<sub>2</sub>] and methyl iodide substrates. Employing data from ref. 14, slopes of -2.3 and -4.6 volt<sup>-1</sup>, respectively, are estimated for attack by phosphorus nucleophiles on these "soft" substrates. The much higher slopes for cations I and II are again consistent with their proposed "hard" nature.

In summary, kinetic results for addition of amine and phosphorus nucleophiles to the dienyl cations I-III show a very marked dependence of rate on nucleophile basicity. This suggests a "hard" nature for the dienyl ligands. Further studies are in progress with a variety of neutral and anionic nucleophiles on other [( $\pi$ -hydrocarbon)M(CO)<sub>3</sub>]<sup>+</sup> complexes to determine if basicity is in general a major factor controlling nucleophilicity.

The SRC is thanked for support.

## References

- 1 D.M. Birney, A.M. Crane, and D.A. Sweigart, *J. Organometal. Chem.*, 152 (1978) 187, and refs. therein.
- 2 L. Cosslett and L.A.P. Kane-Maguire, *J. Organometal. Chem.*, 178 (1979) C17, and refs. therein.
- 3 T.I. Odiaka and L.A.P. Kane-Maguire, *Inorg. Chim. Acta*, 37 (1979) 85.
- 4 C.A. Mansfield and L.A.P. Kane-Maguire, *J. Chem. Soc. Dalton*, (1976) 2187, and refs. therein.
- 5 G.R. John, C.A. Mansfield, and L.A.P. Kane-Maguire, *J. Chem. Soc. Dalton*, (1977) 574, and refs. therein.
- 6 (a) T.G. Bonner, K.A. Holder, P. Powell, and E. Styles, *J. Organometal. Chem.*, 131 (1977) 105.  
(b) G.R. John, Ph.D. Thesis, University College Cardiff, 1977.
- 7 M. Gower, G.R. John, L.A.P. Kane-Maguire, T.I. Odiaka, and A. Salzer, *J. Chem. Soc. Dalton*, (1979) 2003.
- 8 J. Evans, D.V. Howe, B.F.G. Johnson, and J. Lewis, *J. Organometal. Chem.*, 61 (1973) C48.
- 9 (a) Y. Becker, A. Eisenstadt, and Y. Shvo, *Tetrahedron Letts.*, (1972) 3183.  
(b) A.L. Burrows, Ph.D. Thesis, Cambridge University, 1977.
- 10 H.K. Hall, *J. Amer. Chem. Soc.*, 60 (1956) 63.
- 11 L. Cattalini, *Reaction Mechanisms in Inorganic Chemistry*, MTP International Review of Science, Inorganic Chemistry, Series 1, Vol. 9, Ch. 7, Butterworths, London, 1972, and refs. therein.
- 12 R.F. Hudson and G. Loveday, *J. Chem. Soc.*, (1962) 1068, and refs. therein.
- 13 (a) C.D. Ritchie and P.O.I. Virtanen, *J. Amer. Chem. Soc.*, 95 (1973) 1882;  
(b) C.D. Ritchie, *ibid.*, 97 (1975) 1170.
- 14 R.G. Pearson, H. Sobel, and J. Songsted, *J. Amer. Chem. Soc.*, 90 (1968) 319.
- 15 D.W. Clack, M. Monshi, and L.A.P. Kane-Maguire, *J. Organometal. Chem.*, 107 (1976) C40.
- 16 G.R. John and L.A.P. Kane-Maguire, *J. Chem. Soc. Dalton*, (1979) 873.
- 17 D.E. Morris and F. Basolo, *J. Amer. Chem. Soc.*, 90 (1968) 2531, and refs. therein.