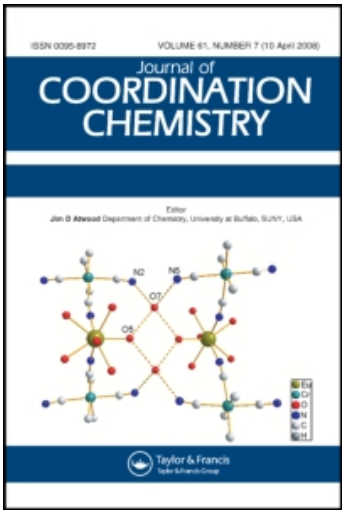

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KINETICS OF NUCLEOPHILIC ATTACK ON COORDINATED ORGANIC MOIETIES. PART 31 ADDITION OF IMIDAZOLES TO [Fe(CO)$_3$(1-5-η-DIENYL)] CATIONS

David J. Evans[a]; Leon A. P. Kane-maguire[b]; Roger Kanitz[b]
[a] AFRC Institute of Plant Science Nitrogen Fixation Laboratory, University of Sussex, Brighton, UK [b] Department of Chemistry, University of Wollongong, Wollongong, N.S.W., Australia

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KINETICS OF NUCLEOPHILIC ATTACK ON COORDINATED ORGANIC MOIETIES. PART 31[a] ADDITION OF IMIDAZOLES TO $[Fe(CO)_3(1\text{-}5\text{-}\eta\text{-DIENYL})]^+$ CATIONS

DAVID J. EVANS

AFRC Institute of Plant Science Nitrogen Fixation Laboratory, University of Sussex, Brighton BN1 9RQ, UK.

LEON A. P. KANE-MAGUIRE* and ROGER KANITZ,

Department of Chemistry, University of Wollongong, Northfields Ave., Wollongong, N.S.W. 2522, Australia

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Synthetic and spectroscopic studies show that imidazole, 2-methylimidazole, and 4-methylimidazole (BH) react with the dienyl cations $[Fe(CO)_3(1\text{-}5\text{-}\eta\text{-dienyl})]^+$ (**Ia-Ic**; dienyl = C_6H_7, $2\text{-}MeOC_6H_6$, or C_7H_9) in CH_3CN or acetone solvent *via* the two-step sequence shown below.

$$(\mathbf{I}) + BH \xrightarrow{k_1} [Fe(CO)_3(BH.diene)]^+ \;(\mathbf{III}) \xrightarrow[k_2]{+BH} [Fe(CO)_3(B.diene)] + BH_2^+ \;(\mathbf{IV})$$

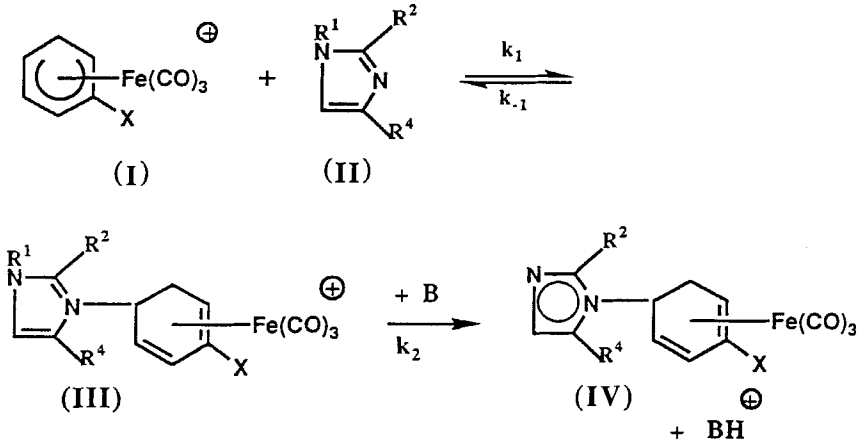
With *N*-methylimidazole, which contains no ring N-H group, reaction stops at the monocationic adduct (**III**). In all cases the rate law, $k_{obs} = k_1$ [amine] is obeyed. This may be rationalised in terms of rate-determining addition (k_1) at the dienyl ring to yield (**III**), followed where applicable by rapid deprotonation (k_2) to yield the final neutral adduct (**IV**). For attack by imidazole, the rate trend is $C_6H_7 > 2\text{-}MeOC_6H_6 > C_7H_9$ (relative rates: 47:4:1), revealing a previous k_1 value for cation (**Ib**) to be erroneous. This rate trend, together with the *exo*-configuration established for adducts (**III**), support direct addition (k_1) of imidazole from above the dienyl ring. The reactivity order 2-methylimidazole > 4-methylimidazole > N-methylimidazole > imidazole is observed towards both cations (**Ia**) and (**Ib**), revealing a strong dependence of rate on nucleophile basicity. Steric effects are less significant than in the related addition of pyridines to these dienyl cations.

[a]Part 30: S. Chapman and L.A.P. Kane-Magurie, *J. Chem. Soc., Dalton Trans.*, 2021 (1995).

*Author for correspondence

INTRODUCTION

As part of a programme investigating the interaction of organometallic compounds with biologically significant molecules, we have reported[1] synthetic and kinetic studies of the addition of imidazole (**II**; $R^1 = R^2 = R^4 = H$) to the dienyl rings of $[Fe(CO)_3(1\text{-}5\text{-}\eta\text{-}XC_6H_6]^+$ cations (**I**; X = H or OMe) (Scheme 1). These reactions were observed to proceed in two stages. In the first step, cationic adducts (III) were produced in which the imidazole is attached to the diene ring *via* its tertiary nitrogen atom. Subsequent deprotonation of the pyrrolic ring nitrogen by excess imidazole yielded the neutral species (**IV**).



Scheme 1

An unusual feature was the very much slower (factor of 85) reaction of imidazole with $[Fe(CO)_3(1\text{-}5\text{-}\eta\text{-}2\text{-}MeOC_6H_6)]^+$ (**Ib**) compared with $[Fe(CO)_3(1\text{-}5\text{-}\eta\text{-}C_6H_7)]^+$ (**Ia**). With other neutral nucleophiles cation (**Ib**) is generally only 5–10 times less reactive than (**Ia**). It was suggested[1] that the exceptionally slow reaction with (**Ib**) may be associated with hydrogen bonding between the imidazole-NH and the oxygen of the 2-MeO substituent.

In order to test this hypothesis and to delineate the importance of steric and electronic factors in these processes, detailed synthetic, kinetic and spectroscopic studies have now been carried out on the related reactions of *N*-methylimidazole (**II**; $R^1 = Me$, $R^2 = R^4 = H$), 2-methylimidazole (**II**; $R^1 = R^4 = H$, $R^2 = Me$) and 4-methylimidazole

(**II**; $R^1 = R^2 = H$, $R^4 = Me$) on cations (**Ia**) and (**Ib**). These studies clearly eliminate the involvement of such a specific H-bonding interaction. All the reactions are seen to involve direct *exo*-addition to the dienyl rings and to be strongly dependent on the basicity of the amine nucleophile.

Synthetic and kinetic/spectroscopic data are also reported for the analogous addition of imidazole to the cycloheptadienyl cation $[Fe(CO)_3(1\text{-}5\text{-}\eta\text{-}C_7H_9)]^+$ (**Ic**).

EXPERIMENTAL

Materials

The cations (**Ia**), (**Ib**) and (**Ic**) were prepared as their $[BF_4^-]$ salts and purified using published methods.[2,3] Imidazole and the various substituted imidazoles were purchased in pure form from BDH and Aldrich, and used without further purification. Acetonitrile (BDH/Aldrich) solvent was distilled in bulk and stored over molecular sieves (3A) under a dinitrogen atmosphere prior to use.

Preparation of Imidazolium Adducts

(i) Cationic Adducts

*Tricarbonyl (1-4-η-5-imidazoliocyclohexa-1,3-diene)iron hexafluorophosphate (***IIIa**)

This known complex was prepared and purified by the published procedure.[1] Electrospray MS (m/z): 287 ($[M]^+$), 219 ($[M\text{-}Im]^+$). I.r.: ν(CO) (acetone): 2055, 1984 cm^{-1}. Its ^1H n.m.r. spectrum in both CD_3COCD_3 and CD_3CN indicated partial deprotonation of the cationic adduct to give an *ca* 50/50 mixture of (**IIIa**) and the neutral adduct (**IVa**). ^1H n.m.r. of the cationic adduct (CD_3COCD_3): δ 7.35- 8.6 (m, Im), 5.83 (t, 1H, diene H^2, $J_{2,3} = J_{2,1} \sim 5$ Hz), 5.70 (t, 1H, diene H^3, $J_{3,2} = J_{3,4} = 5.0$ Hz), 5.01 (dt, 1H, diene $H^{5'}$, $J_{5',6'} = 10.8$, $J_{5'4} = J_{5',6} \sim 3$ Hz), 3.19 (overlapping dt's, 1H, diene H^1, $J_{1,2} = 5.9$ Hz, $J_{1,6'} = J_{1,6} = 2.0$ Hz), 3.06 (dd, 1H, diene H^4, $J_{4,3} = 5.8$, $J_{4,5'} = 3.6$ Hz), 2.65 (m, 1H, $H^{6'}$, $J_{6',6} = 15.6$, $J_{6',5'} = 11.2$, $J_{6',1} = 3.9$ Hz), 1.69 (br d, 1H, H^6, $J_{6',6} = 16.0$ Hz). ^1H n.m.r. (CD_3CN)/2 drops TFA): δ 7.35–8.6 (m, Im), 5.83 (diene H^2, masked by free **Ia** peak), 5.70 (t, 1H, diene H^3, $J_{3,2} = J_{3,4} = 5.0$ Hz), 5.01 (dt, 1H, diene $H^{5'}$, $J_{5',6'} = 10.8$, $J_{5',4} = J_{5',6} = 3.2$ Hz),

3.19 (overlapping dt's, 1H, diene H^1, $J_{1,2}$ = 6.2, $J_{1,6'}$ = $J_{1,6}$ = 2.4 Hz), 3.06 (overlapping dd, 1H, diene H^4, $J_{4,5'} \sim 3.5$, $J_{4,3} \sim 5.5$ Hz), 2.65 (septet, 1H, diene $H^{6'}$, $J_{6',6}$ = 15.8, $J_{6',5'}$ = 11.0, $J_{6',1}$ = 4.0 Hz), 1.69 (br d, 1 H, diene H^6, $J_{6,6'}$ = 16.0 Hz).

*Tricarbonyl(1-4-η-5-2-methylimidazoliocyclohexa-1,3-diene)iron tetrafluoroborate (***IIIb**)

This complex was prepared by a slight modification of the above procedure in that 2-methylimidazole (0.027 g, 0.329 mmol) in 10 cm^3 of acetone was added to $[Fe(CO)_3(C_6H_7)]BF_4$ (**Ia**) (0.100 g, 0.327 mmol) under dinitrogen and the yellow solution stirred for 5 min. At this stage the i.r. spectrum indicated that the reaction had proceeded to completion. The solution was rotary evaporated to dryness to give a yellow oil. This was dissolved in the minimum amount of acetone and diethylether added until a precipitate began to form. After cooling in a freezer for 1 hour, the mixture was filtered to give the product as a pale yellow solid (0.083 g, 65% yield). I.r.: ν(CO) (acetone): 2056, 1985 cm^{-1}. (Anal. Found: C, 39.4; H, 3.3; N, 6.8%. Calc. for $C_{13}H_{13}O_3N_2BF_4Fe$: C, 40.2; H, 3.3; N, 7.2%). Electrospray MS (m/z): 301 ($[M]^+$), 219 ($[M\text{-MeIm}]^+$). It's ^1H n.m.r. spectrum in d^6-acetone indicated partial deprotonation of the cationic adduct (**IIIb**) to give an *ca* 50/50 mixture of (**IIIb**) and the neutral adduct (**IVb**). ^1H n.m.r. of the cationic adduct (CD_3COCD_3): δ 7.64 (m, 2H, H^4 and H^5 of Im), 5.99 (t, 1H, diene H^2, $J_{2,3}$ = $J_{2,1}$ = 5.4 Hz), 5.90 (t, 1H, diene H^3, $J_{3,2}$ = $J_{3,4}$ = 5.0 Hz), 5.18 (dt, 1H, diene $H^{5'}$, $J_{5',6'}$ = 11.2, $J_{5',4}$ = $J_{5',6}$ = 3.4 Hz), 3.34 (m, 1H, diene H^1, overlaps with neutral adduct H^1), 3.24 (m, 1H, diene H^4, $J_{4,3}$ = 5.8, $J_{4,5'}$ = 3.7, $J_{4,6'}$ = 1.1 Hz), 2.82 (m, diene $H^{6'}$, masked by Me of Im), 2.82 (s, 3H, Me of Im), 1.89 (br d, 1H, diene H^6, $J_{6,6'}$ = 16.0 Hz). ^1H n.m.r. (CD_3CN/2 drops TFA): δ 7.24 (m, Im), 5.82 (diene H^2, masked by free **Ia** peak), 5.69 (t, 1H, diene H^3, $J_{3,2} \sim J_{3,4} \sim 4.5$ Hz), 4.82 (dt, 1H, diene $H^{5'}$, $J_{5',6'}$ = 11.0, $J_{5',4}$ = $J_{5',6}$ = 3.4 Hz), 3.22 (br m, 1H, diene H^1), 2.99 (br t, 1H, diene H^4, $J_{4,3} \sim J_{4,5'} \sim 4.5$ Hz), 2.64 (septet, 1H, diene $H^{6'}$, $J_{6',6}$ = 16.1, $J_{6',5'}$ = 11.0, $J_{6',1}$ = 3.5 Hz), 2.52 (s, 3 H, Me of Im), 1.65 (d, 1H, diene H^6, $J_{6,6'}$ = 16 Hz).

*Tricarbonyl(1-4-η-5-N-methylimidazoliocyclohexa-1,3-diene)iron tetrafluoroborate (***IIIc**)

A similar procedure to the above using *N*-methylimidazole gave this

cationic adduct as a pale yellow microcrystalline product (78% yield). Calc. for $C_{13}H_{13}N_2O_3FeBF_4$: C, 40.2; H, 3.3; N, 7.2%. Found: C, 38.8; H, 3.3; N, 7.0%. I.r.: ν(CO) (acetone): 2056, 1984 cm^{-1}. Electrospray MS (m/z): 301 ($[M]^+$), 219 ($[M\text{-}MeIm]^+$). ^1H n.m.r. (CD_3COCD_3): δ 9.08 (s, 1H, H^2 of Im), 7.73 (t, 1H, H^4 of Im, $J_{4,5}$ = 1.8 Hz), 7.69 (t, 1H, H^5 of Im, $J_{5,4}$ = 1.6 Hz), 5.98 (br t, 1H, diene H^2, $J_{2,1} = J_{2,3}$ = 5.2 Hz), 5.88 (br t, 1H, diene H^3, $J_{3,2} \sim J_{3,4} \sim 5$ Hz), 5.20 (dt, 1H, diene $H^{5'}$, $J_{5',6'}$ = 10.8, $J_{5',4} = J_{5',6}$ = 3.4 Hz), 4.03 (s, 3H, Me of Im), 3.31 (octet, 1H, diene H^1, $J_{1,2}$ = 7.6, $J_{1,6'}$ = 4.1, $J_{1,6}$ = 2.4 Hz), 3.26 (m, 1H, diene H^4, $J_{4,3}$ = 6.0, $J_{4,5'}$ = 3.6, $J_{4,6'}$ = 1.2 Hz), 2.77 (m, 1H, diene $H^{6'}$, $J_{6',6}$ = 15.6, $J_{6',5'}$ = 10.8, $J_{6',1}$ = 4.3 Hz), 1.89 (m, 1H, diene H^6, $J_{6,6'}$ = 16.3, $J_{6,1}$ *ca* 2.0, $J_{6,4}$ *ca* 1.2 Hz). ^1H n.m.r. (CD_3CN)/2 drops TFA: δ 7.37– 8.5 (Im), 5.82 (diene H^2, masked by free **Ia** peak), 5.70 (t, 1H, diene H^3, $J_{3,2} = J_{3,4}$ = 4.7 Hz), 4.93 (br dt, 1H, diene $H^{5'}$, $J_{5',6'}$ = 10.8, $J_{5',4} = J_{5',6}$ = 3.2 Hz), 3.77 (s, 3H, Me of Im), 3.19 (br m, 1H, diene H^1), 3.04 (br m, 1H, diene H^4), 2.64 (septet, 1H, diene $H^{6'}$, $J_{6',6}$ = 15.7, $J_{6',5'} \sim 11$, $J_{6',1} \sim 4$ Hz), 1.65 (d, 1H, diene H^6, $J_{6,6'}$ = 16.3 Hz).

*Tricarbonyl(1-4-η-5-N-tritylimidazoliocyclohexa-1,3-diene)iron tetrafluoroborate (***IIId**)

A similar procedure to the above using *N*-tritylimidazole (**II**, $R^1 = CPh_3$, $R^2 = R^4$ = H) gave adduct (**IIId**) as a pale yellow solid (yield = 83%). Calc. for $C_{31}H_{25}N_2O_3FeBF_4$: C, 60.4; H, 4.1; N, 4.5%. Found: C, 59.1; H, 4.1; N, 4.0%. I.r.: ν(CO) (acetone): 2056, 1985 cm^{-1}. Electrospray MS (m/z): 529 ($[M]^+$), 311 ($[Ph_3C.Im]^+$), 243 ($[Ph_3C]^+$), 219 ($[M\text{-}CPh_3.Im]^+$). ^1H n.m.r. (CD_3COCD_3): δ 9.17 (H^2 of Im), 7.92 (H^4 of Im), 7.80 (H^5 of Im), 7.2–7.6 (Ph_3C), 5.97 (t, 1H, diene H^2, $J_{2,1} = J_{2,3}$ = 5 Hz), 5.86 (br m, 1H, diene H^3), 5.31 (m, 1H, diene $H^{5'}$), 3.30 (br m, 1H, diene H^1), 3.24 (br m, 1H diene H^4), 2.8 (diene $H^{6'}$, masked by H_2O), 1.96 (m, 1H, diene H^6).

*Tricarbonyl(1-4-η-5-N-methylethyletherimidazoliocyclohexa-1,3-diene)iron hexafluorophosphate (***IIIe**)

A similar procedure to the above using *N*-methylethyletherimidazole (**II**, $R^1 = CH_2OEt$, $R^2 = R^4$ = H) gave an oil which could not be crystallised from acetone/diethylether. The oil was redissolved in water and NH_4PF_6 (0.07 g) added to give a pale yellow precipitate. A further reprecipitation from aqueous NH_4PF_6 gave the product as a mixture of its PF_6^- and BF_4^-

salts (as evidenced by ESMS). Electrospray MS (m/z): +ve, 345 ($[M]^+$), 219 ($[M\text{-}CH_2OEt.Im]^+$); -ve, 145 ($[PF_6]^-$), 87 ($[BF_4]^-$) {PF_6^-/BF_4^- ratio = 1:1}. ^1H n.m.r. (CD_3COCD_3): δ 9.32 (s, 1H, H^2 of Im), 7.88 (t, 1H, H^4 of Im, $J_{4,5}$ = 1.8 Hz), 7.84 (t, 1H, H^5 of Im, $J_{5,4}$ = 1.8 Hz), 6.00 (br t, 1H, diene H^2, $J_{2,3}$ = $J_{2,1}$ = 5.4 Hz), 5.89 (br t, 1H, diene H^3, $J_{3,2}$ = $J_{3,4}$ = 5.0 Hz), 5.28 (dt, 1H, diene $H^{5'}$, $J_{5',6'}$ = 11.1, $J_{5',4}$ = $J_{5',6}$ = 3.4 Hz), 3.66 (q, 2H, OCH_2 of Im, J = 6.9 Hz), 3.32 (octet, 1H, diene H^1, $J_{1,2}$ = 8.0, $J_{1,6'}$ = 4.0, $J_{1,6}$ = 2.0 Hz), 3.29 (octet, 1H, diene H^4, $J_{4,3}$ = 6.1, $J_{4,5'}$ = 3.8, $J_{4,6'}$ = 1.2 Hz), 2.83 (s, 2H, *N*-CH_2 of Im), 2.79 (m, diene $H^{6'}$, masked by Im *N*-CH_2), 1.93 (br d, 1H, diene H^6, $J_{6,6'}$ *ca* 16 Hz), 1.17 (t, 3H, -OCH_2CH_3 of Im, J = 7.0 Hz).

*Tricarbonyl(1-4-η-2-methoxy-5-imidazoliocyclohexa-1,3-diene)iron hexafluorophosphate (***IIIf**)

This pale yellow complex was prepared in a similar fashion to (**IIIa**) *via* the reaction of imidazole with an equimolar amount of the dienyl salt $[Fe(CO)_3(2\text{-}MeOC_6H_6)]PF_6$ (**Ib**) in acetone (yield = 82%). Electrospray MS (m/z): 317 ($[M]^+$), 249 ($[M\text{-}Im]^+$). I.r.: ν(CO) (acetone): 2055, 1985 cm^{-1}. ^1H n.m.r. (CD_3COCD_3): δ 7.3–8.1 (Im), 5.64 (dd, 1H, diene H^3, $J_{3,4}$ = 6.2, $J_{3,1}$ = 2 Hz), 4.81 (dt, 1H, diene $H^{5'}$, $J_{5',6'}$ = 10.8, $J_{5',4} \sim J_{5',6'} \sim 2.8$ Hz), 3.81 (s, 3H, diene MeO), 3.43 (m, 1H, diene H^1), 2.81 (m, 1H, diene H^4), 2.68 (septet, 1H, diene $H^{6'}$, $J_{6',6}$ = 15.3, $J_{6',5'}$ = 10.8, $J_{6',1}$ = 3.8 Hz), 1.8 (d, 1H, diene h^6, $J_{6,6'} \sim 14.5$ Hz).

*Tricarbonyl(1-4-η-2-methoxy-5-2-methylimidazoliocyclohexa-1,3-diene)iron hexafluorophosphate (***IIIg**)

A similar procedure reacting (**Ib**) with 2-methylimidazole gave a yellow solid which could not be crystallised from acetone/diethyl ether. Precipitation from aqueous NH_4PF_6 as described above for (**IIIe**) gave the adduct as a mixture of its PF_6^- and BF_4^- salts. I.r.: ν(CO) (acetone): 2055, 1983 cm^{-1}. Electrospray MS (m/z): 331 ($[M]^+$), 249 ($[M\text{-}MeIm]^+$). Its ^1H n.m.r. spectrum in d^6-acetone indicated partial deprotonation of the cationic adduct (**IIIg**) to give an *ca* 1/2 mixture of (**IIIg**) and the neutral adduct (**IVg**). ^1H n.m.r. of the cationic adduct (CD_3COCD_3): δ 7.67 (m, 2H, H^4 and H^5 of Im), 5.74 (dd, 1H, diene H^3, $J_{3,1} \sim 2.4$ Hz, overlaps with neutral adduct H^3), 5.03 (dt, 1H, diene $H^{5'}$, $J_{5',6'}$ = 11.0, $J_{5',4}$ = $J_{5',6} \sim 3.2$ Hz), 3.84 (s, 3H, diene OMe), 3.50 (dt, 1H, diene H^1, $J_{1,6'}$ = 4, $J_{1,6}$ = $J_{1,4}$ = 2 Hz), 2.89 (dd, 1H, diene H^4, $J_{4,3} \sim 6.4$, $J_{4,5'} \sim$

3.8 Hz, overlaps with neutral adduct H^4), 2.80 (m, 3H, Me of Im), 2.76 (m, $H^{6'}$, partly masked by Me and by neutral adduct $H^{6'}$), 1.98 (br dt, 1H, H^6, $J_{6,6'}$ = 15.6 Hz).

*Tricarbonyl(1-4-η-2-methoxy-5-N-methylimidazoliocyclohexa-1,3-diene)iron hexafluorophosphate (***IIIh**)

A similar procedure to the above gave this solid adduct as a pale yellow mixture of its PF_6^- and BF_4^- salts. I.r.: ν(CO) (acetone): 2054, 1981 cm^{-1}. Electrospray MS (m/z): + ve, 331 ($[M]^+$), 249 ([M-MeIm]$^+$); -ve, 145 ($[PF_6]^-$), 87 ($[BF_4]^-$) {PF_6^-/BF_4^- ratio = 6:1}. ^1H n.m.r. (CD_3COCD_3): δ 9.07 (s, 1H, H^2 of Im), 7.70 (overlapping signals, H^4 and H^5 of Im), 5.72 (dd, 1H, diene H^3, $J_{3,4}$ = 6.2, $J_{3,1}$ = 2.2 Hz), 5.06 (dt, 1H, diene $H^{5'}$, $J_{5',6'}$ = 10.8, $J_{5',4}$ = $J_{5',6}$ = 3.6 Hz), 4.01 (s, 3H, Me of Im), 3.82 (s, 3H, diene OMe), 3.45 (m, 1H, diene H^1, $J_{1,6'}$ = 4.0, $J_{1,6}$ = $J_{1,4}$ = 2.0 Hz), 2.91 (dd, 1H, diene H^4, $J_{4,3}$ = 6.0, $J_{4,5'}$ = 3.6 Hz), 2.76 (m, 1H, diene $H^{6'}$, $J_{6',6}$ = 15.5, $J_{6',5'}$ = 11.0, $J_{6',1}$ = 4.3 Hz), 1.99 (br dt, 1H, H^6, $J_{6',6}$ = 15.6, $J_{6,1}$ = $J_{6,4}$ = 2.5 Hz).

*Tricarbonyl(1-4-η-5-imidazoliocyclohepta-1,3-diene)iron hexafluorophosphate (***IIIi**)

A mixture of the cycloheptadienyl cation (**Ic**; 0.10 g, 0.31 m mol) and imidazole (0.021 g, 0.31 mmol) in acetone (10 cm^3) was stirred under dinitrogen for 5 minutes, at which stage i.r. analysis showed reaction to be complete. The mixture was rotary evaporated to dryness, giving an orange oil. This was dissolved in water and NH_4PF_6 (0.051 g, 0.31 mmol) added. After cooling in ice for 30 mins, the product was collected and washed with diethylether (0.070 g). A further reprecipitation from aqueous NH_4PF_6 gave the pale yellow solid (**IIIi**; 0.041 g), whose negative ion electrospray (ES) mass spectrum indicated it to be a mixture of the PF_6^- and BF_4^- salts (ratio 5:1). ESMS (+ ve ion): m/z 301 ($[M]^+$), 233 ([M-Im]$^+$). I.r.: ν(CO) (acetone): 2052, 1981 cm^{-1}. Its ^1H n.m.r. spectrum in either d^6-acetone or CD_3CN indicated partial deprotonation of the cationic adduct (**IIIi**) to give an *ca* 30/70 mixture of (**IIIi**) and the neutral adduct (**IVi**). ^1H n.m.r. of the cationic adduct (CD_3COCD_3): δ 7.4–9.3 (m, Im), 5.82 (t, 1H, diene H^2, $J_{2,3}$ = $J_{2,1}$ = 6 Hz), *ca* 5.7 (diene H^3, masked by neutral adduct H^3), 5.10 (br m, 1H, diene $H^{5'}$, $J_{5',6'}$ = 12 Hz), 3.39 (br t, 1H, diene H^1, $J_{1,2}$ = 7 Hz), 3.05 (br d, 1H, H^4, $J_{4,3}$ = 7 Hz), 2.34 (m, 1H, diene $H^{7'}$), 2.18 (m, 1H, diene $H^{6'}$), 1.91 (m, 1H,

diene H^7), 1.72 (m, 1H, diene H^6). ^1H n.m.r. (CD_3CN): δ 7.3–8.6 (Im), 5.65 (t, 1H, diene H^2, $J_{2,3} = J_{2,1} = 5$ Hz), 5.55 (m, 1H, diene H^3), 4.79 (dd, 1H, diene $H^{5'}$, $J_{5',6'} = 12.3$, $J_{5',4} = 3.2$ Hz), 3.26 (t, 1H, diene H^1, $J_{1,2} = 6.9$ Hz), 2.81 (t, 1H, diene H^4, $J_{4,3} = 7.3$ Hz), 2.26 (m, 1H, diene $H^{7'}$), 2.13 (m, 1H, diene $H^{6'}$), 1.72 (m, 1H, diene H^7), 1.51 (m, 1H, diene H^6).

(ii) Neutral Adducts

Upon dissolution in acetone, the above solid cationic adducts (**III**) gave equilibrium mixtures of (**III**) and the corresponding neutral adducts (**IV**), which were characterised from their ^1H n.m.r. spectra in d^6-acetone. The neutral adducts could also be produced quantitatively *in situ, via* deprotonation of the cationic adducts (**III**) in CD_3CN using Pr^i_2EtNH.

Tricarbonyl(1-4-η-5-imidazoliocyclohexa-1,3-diene)iron (**IVa**)

^1H n.m.r. (CD_3COCD_3): δ 6.9–7.6 (m, 3H, H^2, H^4 and H^5 of Im), 5.78 (t, 1H, diene H^2, $J_{2,3} = J_{2,1} = 5.2$ Hz), 5.63 (t, 1H, diene H^3, $J_{3,2} = J_{3,4} = 4.6$ Hz), 4.84 (dt, 1H, diene $H^{5'}$, $J_{5',6'} = 10.8$ Hz), 3.17 (br m, 1H, diene H^1), 3.05 (m, 1H, diene H^4), 2.55 (m, 1H, diene $H^{6'}$, $J_{6',6} = 14.8$, $J_{6',5'} = 11.2$, $J_{6',1} = 3.5$ Hz), 1.64 (d, 1H, diene H^6, $J_{6,6'} = 15.9$ Hz). I.r.: ν(CO) (acetone): 2050, 1979 cm^{-1}. ^1H n.m.r. (CD_3CN/1 drop Pr^i_2EtNH): δ 6.9-8.6 (Im), 5.78 (t, 1H, diene H^2, $J_{2,3} = J_{2,1} = 5.2$ Hz), 5.63 (t, 1H, diene H^3, $J_{3,2} = J_{3,4} = 4.6$ Hz), 4.77 (br dt, 1H, diene $H^{5'}$, $J_{5',6'} = 10.8$ Hz), 3.17 (br m, 1H, diene H^1), *ca* 3.0 (diene H^4, masked by Pr^i_2EtNH), 2.56 (septet, 1H, diene $H^{6'}$, $J_{6',6} = 15.2$, $J_{6',5'} = 11.2$, $J_{6',1} = 3.6$ Hz), 1.64 (d, 1H, diene H^6, $J_{6,6'} = 15.9$ Hz).

Tricarbonyl(1-4-η-5-2-methylimidazoliocyclohexa-1,3-diene)iron (**IVb**)

^1H n.m.r. (CD_3COCD_3): δ 7.61 (m, 2H, H^4 and H^5 of Im), 5.96 (t, 1H, diene H^2, $J_{2,3} = J_{2,1} = 5.4$ Hz), 5.87 (t, 1H, diene H^3, $J_{2,3} = J_{3,2} = 4.8$ Hz), 5.15 (t, 1H, diene $H^{5'}$, $J_{5',6'} \sim 12$, $J_{5',4} \sim J_{5',6} \sim 2.8$ Hz), 3.31 (m, 1H, diene H^1, overlaps with cationic adduct H^1), 3.16 (m, 1H, diene H^4), 2.82 (m, diene $H^{6'}$, masked by Me of Im), 2.82 (s, 3H, Me of Im), 1.82 (m, 1H, diene H^6). I.r.: ν(CO) (acetone): 2062, 1995 cm^{-1}. ^1H n.m.r. (CD_3CN/1 drop Pr^i_2EtNH): δ 6.8–7.24 (m, Im), 5.78 (overlap dd, 1H, diene H^2), 5.66 (m, 1H, diene H^3), 4.78 (dt, 1H, diene $H^{5'}$, $J_{5',6'} = 10.5$ Hz), 3.05 (m, 1H, diene H^1), 2.94 (m, 1H, diene H^4), 2.54 (septet, 1H,

diene $H^{6'}$, $J_{6',6}$ = 10.6, $J_{6',1}$ = 4.2 Hz), 2.44 (s, 3H, Me of Im), 1.56 (d, 1H, diene H^6, $J_{6,6'}$ = 16 Hz).

*Tricarbonyl(1-4-η-2-methoxy-5-imidazoliocyclohexa-1,3-diene)iron (***IVf**)

^{1}H n.m.r. (CD_3CN): δ 7.2–8.4 (Im), 5.45 (d, 1H, diene H^3, overlaps with cationic adduct H^3), 4.75 (br d, 1H, diene $H^{5'}$, $J_{5',6'}$ = 11.0 Hz), 3.4 (m, 1H, diene H^1), 2.69 (m, 1H, diene H^4, overlaps with cationic adduct H^4), 2.60 (m, 1H, diene $H^{6'}$, overlaps with cationic adduct $H^{6'}$), 1.75 (d, 1H, diene H^6, $J_{6,6'}$ = 13.5 Hz).

*Tricarbonyl(1-4-η-2-methoxy-5-2-methylimidazoliocyclohexa-1,3-diene)iron (***IVg**)

^{1}H n.m.r. (CD_3COCD_3): δ 7–8 (m, 2H, H^4 and H^5 of Im), 5.70 (dd, 1H, diene H^3, $J_{3,1}$ ~ 2.2 Hz, overlaps with cationic adduct H^3), 4.99 (m, 1H, diene $H^{5'}$, overlaps with cationic adduct $H^{5'}$), 3.81 (s, 3H, diene OMe), 3.46 (m, 1H, diene H^1, $J_{1,6'}$ ~ 6 Hz, overlaps with cationic adduct H^1), 2.82 (dd, 1H, diene H^4, overlaps with diene Me and cationic adduct H^4), 2.72 (m, 1H, diene $H^{6'}$, overlaps with cationic adduct $H^{6'}$), 1.91 (m, 1H, diene H^6, overlaps with cationic H^6). I.r.: ν(CO) (acetone): 2054, 1983 cm^{-1}.

*Tricarbonyl(1-4-η-5-imidazoliocyclohepta-1,3-diene)iron (***IVi**)

^{1}H n.m.r. (CD_3COCD_3):δ 9.33 (s, 1H, H^2 of Im), 7.9 (m, 2H, H^4 and H^5 of Im), 5.80 (t, 1H, diene H^2, $J_{2,3}$ = $J_{2,1}$ = 6.0 Hz), 5.67 (t, 1H, diene H^3, $J_{3,2}$ = $J_{3,4}$ = 6.2 Hz), 4.99 (br m, 1H, diene $H^{5'}$, $J_{5',6'}$ ~ 11.5 Hz), 3.33 (br t, 1H, diene H^1, $J_{1,2}$ = 6.2 Hz), 3.00 (br d, 1H, diene H^4, $J_{4,3}$ ~ 6.8 Hz), 2.34 (m, 1H, diene $H^{7'}$), 2.18 (m, 1H, diene $H^{6'}$), 1.91 (br d, 1H, diene H^6), 1.72 (m, 1H, diene H^7). ^{1}H n.m.r. (CD_3CN): δ 7.3–8.6 (Im), 5.64 (t, 1H, diene H^2), 5.54 (m, 1H, diene H^3), 4.72 (dd, 1H, diene $H^{5'}$, $J_{5',6'}$ = 12, $J_{5',4}$ = 3.6 Hz), 3.26 (t, 1H, diene H^1, $J_{1,2}$ = 6.9 Hz), 2.81 (t, 1H, diene H^4, $J_{4,3}$ = 7.3 Hz), 2.25 (m, 1H, diene $H^{7'}$), 2.12 (m, 1H, diene $H^{6'}$), 1.71 (m, 1H, H^7), 1.50 (m, 1H, diene H^6).

Spectroscopic Studies

I.r. spectra were recorded on a Biorad FTS-7 Fourier Transform infrared spectrophotometer using matched 0.5 mm CaF_2 solution cells, while ^{1}H

n.m.r. spectra were recorded using either a JEOL GX400 or a Varian Unity 400 MHz n.m.r. spectrometer. Electrospray mass spectra for the imidazolium adducts (**III**) were obtained from CH_3CN solution with a Fisons/VG Biotech Quattro mass spectrometer using a low skimmer voltage (20 V) and procedures described elsewhere.[4]

Kinetic Studies

All of the reactions in Scheme 1 were rapid in CH_3CN and were conveniently monitored at 390 nm using a thermostatted (± 0.1°C), stopped-flow spectrophotometer. At this wavelength a large decrease in absorbance was observed. The reactions were studied under *pseudo*-first-order conditions using a large excess of amine nucleophile ([Fe] = 1 – 1.5 × 10^{-3} mol dm^{-3}, [amine] = 5 – 80 × 10^{-3} mol dm^{-3}).

Pseudo-first-order rate constants, k_{obs}, were calculated from the slopes of plots of log $(A_t - A_\infty)$ *vs* time. Such plots were generally linear for more than two half-lives, except in a few cases where [amine]/[Fe] < 10. Each k_{obs} value was the average of results of at least three separate runs with an average reproducibility of ± 4%. The enthalpy of activation and the associated error of estimate for the addition of imidazole to cation (**Ib**) were calculated from at least squares analysis of ln k_1 *vs* T^{-1}. The entropy of activation was calculated by standard procedures using the second order rate constants, k_1.

RESULTS AND DISCUSSION

Nature of the Reactions

Each of the cationic adducts (**IIIa–d**) (amine = Im, 2-MeIm, *N*-MeIm, *N*-trityl.Im) have been isolated in good yield from the reaction of the cyclohexadienyl salt (**Ia**) with an equimolar amount of the appropriate amine in acetone solvent, and fully characterised from elemental analyses, electrospray mass spectrometry and ^1H n.m.r. and i.r. spectroscopy. The analogous imidazolium adducts (**IIIf-IIIi**) from the related dienyl salts (**Ib**) and (**Ic**) were similarly isolated, but as mixtures of their PF_6^- and BF_4^- salts which were characterised spectroscopically (ESMS, n.m.r., i.r.). For the imidazole and 2-methylimidazole adducts, ν(NH) bands were observed in their Nujol mull i.r. spectra at *ca* 3350 cm^{-1}, while the presence of the PF_6^- and BF_4^- anions in each adduct was confirmed from

negative ion electrospray mass spectrometry and the presence of characteristic ν(PF) and ν(BF) bands in their i.r. spectra.

The ^{1}H n.m.r. spectra of each of the adducts with imidazole and 2-methylimidazole showed that they undergo partial deprotonation in d^6-acetone or CD_3CN solvent to give a mixture of the cationic and neutral adducts (**III**) and (**IV**), respectively (see Experimental). The distinct ^{1}H n.m.r. spectra of adducts (**III**) and (**IV**) could be generated by adding either 1 drop of trifluoroacetic acid (TFA) or diisopropylethylamine, respectively, to these mixtures. A large excess of the appropriate imidazole reagent could alternatively be used to generate the neutral adducts (**IV**) in solution.

In the related reactions of *N*-methylimidazole and *N*-tritylimidazole with the dienyl cations (**Ia**) and (**Ib**), reaction proceeded only to the cationic adducts (**III**), even in the presence of excess amine, due to the absence of an imidazole ring N-H proton for deprotonation.

The ^{1}H n.m.r. spectra of the cationic adducts (**IIIa–IIIi**) are characteristic of (5-substituted-1,3-diene)$Fe(CO)_3$ complexes[5] and are very similar to those observed[6,7] for the analogous pyridinium adducts. Discrete resonances are observed for each of the diene ring protons. In particular, the $H^{5'}$ proton appears as a characteristic double triplet (Figure 1), from which coupling constants of $J_{5',6'} \sim 11$ Hz and $J_{5',4} \sim 3$ Hz are estimated for each cationic adduct. The small value of $J_{5',4}$ allows the unequivocal assignment of an *exo*-configuration to the imidazole substituent in each case, as has been demonstrated previously[8,9] for related phosphonium and other adducts. For the alternative *endo*-isomers molecular models predict $J_{5',4} > 5$ Hz on the basis of the Karplus equation.[10]

Comparison of the ^{1}H n.m.r. spectra of adducts (**IIIa–IIIi**) with those of the appropriate free imidazoles in CD_3COCD_3 shows that the imidazole ring protons are shifted appreciably downfield upon attachment of the $[Fe(CO)_3(dienyl)]^+$ residues to the tertiary nitrogen. The largest shift occurs for the imidazole H^2 proton, which moves downfield by up to 1.57 ppm in the *N*-methylimidazole case. These shifts in H^2 signals are considerably larger than those observed on protonation (*e.g.*, 0.53 ppm for *N*-methylimidazole). The H^4 and H^5 protons, which show only a single averaged peak in the free imidazoles (due to rapid proton exchange between the nitrogen centres), become inequivalent as expected in adducts (**IIIa–IIIi**), and experience somewhat smaller downfield shifts (*ca* 0.6 ppm).

The ν(CO) bands observed for the cationic adducts (**IIIa–IIIi**) in acetone at *ca* 2055 and 1985 cm^{-1} are also characteristic of tricarbonyl-

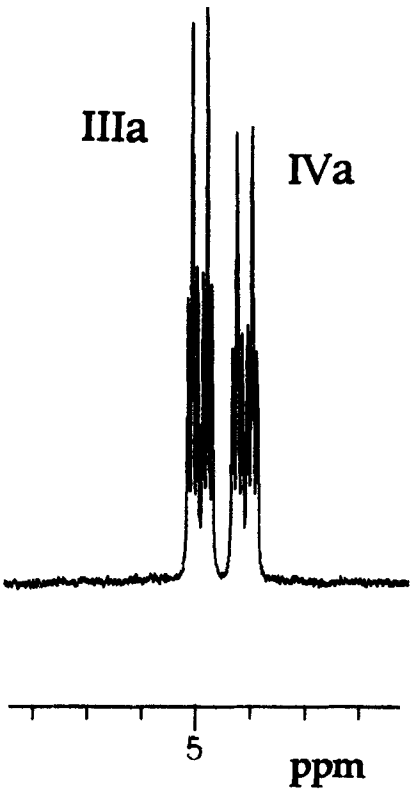


FIGURE 1 $H^{5'}$ n.m.r. signals for *exo*-$[Fe(CO)_3(Im.C_6H_7)]^+$ (IIIa) and the neutral species *exo*-$[Fe(CO)_3(Im.H_{-1}C_6H_7)]$(IVa) in CD_3COCD_3).

(diene)iron complexes and are very similar to those found[6,7] for the analogous pyridinium adducts (2055 and 1980 cm^{-1}). Deprotonation of the cationic adducts containing ring N-H protons *via* the addition of 1 drop of Pr^i_2EtNH in CH_3CN (or excess imidazole) caused a small decrease ($\leq$ 5 cm^{-1}) in the frequency of the ν(CO) bands, as expected for the formation of the neutral adducts (**IV**). A similar small difference of *ca* 10 cm^{-1} has been previously reported[11] between the ν(CO) bands of the related cationic and neutral anilino-derivatives $[Fe(CO)_3(PhNH_2.C_6H_7)]^+$ and $[Fe(CO)_3(PhNH.C_6H_7)]$. These neutral imidazolio-adducts (**IVa–IVi**) were also characterised by their ^1H n.m.r. spectra. As expected, the diene ring protons in the neutral species (**IV**) are shifted slightly upfield (0.02–0.11 ppm) compared with those in the corresponding cationic adducts (**III**).

In contrast, addition of TFA to each of the cationic adducts (III) in acetone or CH_3CN caused partial or complete cleavage of the imidazole substituent and regeneration of the dienyl salts (**I**), as evidenced by changes in their ^1H n.m.r. and i.r. spectra. For example, addition of 2 drops of TFA to (**IIIa**) in CH_3CN resulted in the quantitative conversion over 3 hours to the dienyl salt (**Ia**) {ν(CO) bands at 2112 and 2060 cm^{-1}}. Similarly, addition of 5 drops of TFA to an acetone solution of (**IIIa**) caused complete release of the imidazole substituent to give (**Ia**). Interestingly, acid-promoted cleavage of the imidazole substituent in the analogous cycloheptadiene adduct (**IIIi**) was much less facile. This may be explained in terms of greater steric hindrance to approach by the $H^+(TFA^-)$ electrophile in the case of the 7-membered ring substrate. Similar steric differences have been previously noted[9] for nucleophilic attack by tertiary phosphines at 6- and 7-membered ring dienyl complexes (**Ia**) and (**Ic**).

Kinetics and Mechanism

I.r. spectroscopic studies confirmed that under the kinetic conditions employed in this study ([Fe] = 1–1.5 × 10^{-3} mol dm^{-3}, [amine] = 5 – 80 × 10^{-3} mol dm^{-3}) the reaction of imidazole with cations (**Ia–Ic**) proceeds as in Scheme 1, *i.e.*, initial formation of cationic adducts (**III**) is followed by rapid deprotonation with excess imidazole to yield the neutral products (**IV**). For example, within 1 min. of mixing equimolar (**Ia**) and imidazole ([Fe] = [Im] = 2 × 10^{-3} mol dm^{-3}), the ν(CO) bands of the initial dienyl salt at 2112 and 2060 cm^{-1} were replaced by two intense bands at 2055 and 1984 cm^{-1}, indicating quantitative formation of adduct (**IIIa**). Using higher imidazole concentrations ([Im] > 1 × 10^{-2} mol dm^{-3}) similar to those used in the kinetic studies, the product ν(CO) bands were at slightly lower frequency (2050 and 1979 cm^{-1}), consistent with formation of the neutral adduct (**IVa**).

In contrast, with *N*-methylimidazole (which contains no ring N-H group), i.r. studies in CH_3CN confirmed only rapid, quantitative formation of the cationic adduct (**IIIc**) from (**Ic**) under the kinetic conditions.

Kinetic results for the reactions of cations (**Ia**), (**Ib**), and (**Ic**) with various imidazoles in CH_3CN are collected in Tables I and II. All the reactions obey the expression (*1*).

$$k_{obs} = k\,[\text{amine}] \qquad (1)$$

These results may be rationalised in terms of the two-step mechanism

TABLE I Kinetic results for the addition of imidazoles to $[Fe(CO)_3(1\text{-}5\text{-}\eta\text{-dienyl})]^+$ cations in CH_3CN at 0.0°C.

Dienyl	*Amine*	10^2[amine] (mol dm^{-3})	k_{obs} (s^{-1})	$k^\dagger$ (mol dm^3 s^{-1})
C_6H_7	imidazole	0.50–4.00		4390[a]
		0.30[b]	29.8[b]	
		0.40[b]	46.3[b]	11,000[b]
	1-methylimidazole	0.50	34.5	7000
		1.00	70.5	
	2-methylimidazole	0.50	44.3	8860
	4-methylimidazole	0.50	42.6	8520
2-$MeOC_6H_6$	imidazole	0.50	2.60	
		1.00	4.33	
		2.00	8.12	375 (28)
		4.00	12.5	
		8.00	31.2	
	1-methylimidazole	0.50	2.46	
		1.00	5.98	
		2.00	11.3	769 (18)
		3.00	21.6	
		4.00	28.4	
		8.00	59.6	
	2-methylimidazole	0.50	3.32	
		1.00	7.48	980 (37)
		2.00	16.2	
		4.00	37.4	
	4-methylimidazole	0.50	3.60	
		1.00	7.48	
		2.00	17.6	1080 (26)
		3.00	32.3	
		4.00	41.6	
		8.00	83.2	
C_7H_9	imidazole	1.00	0.850	81
		2.00	1.54	
		1.00[b]	3.74[b]	374[b]

†Values in parentheses are the standard errors of estimate from a least squares analysis of (*2*). [a]Previous data (ref. 1). [b]Temperature 20.0°C.

shown in Scheme 1. Under the kinetic conditions employed the first ring-addition step (k_1) proceeds effectively to completion, *i.e.*, $k_1 >> k_{-1}$. Provided the subsequent deprotonation step (k_2) is very rapid compared with k_1, the rate constants k determined here may be equated with the second-order rate constants, k_1, for addition of the imidazoles to the dienyl rings of (**Ia**), (**Ib**) and (**Ic**), *(eqn. 2)*. This is consistent with the observation of only a single step in the stopped-flow spectroscopic analysis of the reactions. Also consistent with this bimolecular addition is the large negative $\Delta S_1^\ddagger$ of -72 JK^{-1} mol^{-1} and the low $\Delta H_1^\ddagger$ of 33.2 kJ mol^{-1} found for the reaction of imidazole with (**Ib**).

$$k_{obs} = k_1 [\text{amine}] \qquad (2)$$

TABLE II Temperature dependence data for the reaction of imidazole with $[Fe(CO)_3(1\text{-}5\text{-}\eta\text{-}2\text{-}MeOC_6H_6)]^+$ in CH_3CN; [Fe] = 1.25×10^{-3} mol dm^{-3}.

Temp. (°C)	10^2 *[imidazole]* (mol dm^{-3})	k_{obs} (s^{-1})	k_1 ($mol^{-1} dm^3 s^{-1}$)
0.0	0.5–8.0		390[a]
5.0	1.0	5.55	555
10.0	1.0	7.39	739
15.0	1.0	9.33	933
20.0	1.0	12.2	1220
25.0	1.0	14.4	1440
30.0	1.0	17.2	1720
35.0	1.0	24.7	2470
40.0	1.0	30.7	3070

[a]From Table I; $\Delta H^{\neq}_1$ = 33.2(9) kJ mol^{-1}, $\Delta S^{\neq}_1$ = −72(3) J K^{-1} mol^{-1}

The reactions of cations **(Ia)** and **(Ib)** with *N*-methylimidazole obey expression (*2*) directly, since they only proceed as far as the monocationic adducts **(III)**.

Table III summarises the k_1 values for addition of imidazole to each of the dienyl cations **(Ia)**, **(Ib)** and **(Ic)** at 0°C. The marked decrease in reactivity down the series C_6H_7 > 2-$MeOC_6H_6$ > C_7H_9 (relative rates *ca* 47:4:1) is consistent with direct nucleophilic attack from above the dienyl ring in each case. As discussed in earlier studies[6,7] of pyridine addition to these cations, the electronic influence of the 2-methoxy substituent is expected to retard nucleophilic attack at the dienyl ring, while the cycloheptadienyl cation is expected to be the slowest on steric grounds. Also consistent with direct approach of imidazole from above the dienyl ring is the *exo*-configuration established unequivocally above for adduct **(IIIa)** from ^1H n.m.r. evidence.

TABLE III Comparative rate constants for addition of some tertiary amines to $[Fe(CO)_3(1\text{-}5\text{-}\eta\text{-}dienyl)]^+$ cations in CH_3CN at 0°C.

Amine	*pKa**	k_1 ($mol^{-1} dm^3 s^{-1}$) *Dienyl*			*Ref.*
		C_6H_7	$2MeOC_6H_6$	C_7H_9	
pyridine	5.23	2170	425	140	6
2-methylpyridine	6.20	766	96	22	6
4-methylpyridine	6.02	8340			6
imidazole	6.95	4390	375	81	6 & this work
1-methylimidazole	7.33	7000	769		this work
4-methylimidazole	7.54	8520	1080		this work
2-methylmidiazole	7.86	8860	980		this work

*Of conjugate acid in water

It should be noted that in an earlier paper we reported[1] that imidazole reacted 85 times less rapidly with (**Ib**) than with (**Ia**). A specific H-bonding interaction between the imidazole-NH and the diene-2-methoxy substituent was proposed to explain the anomalously low reactivity of cation (**Ib**). The previous k_1 value for (**Ib**) has now been shown to be erroneous, and the corrected $k_{C_6H_7}/k_2\text{-}MeOC_6H_6$ ratio of *ca* 11 is comfortably in the range found for other neutral nucleophiles.[12]

Steric and Electronic Effects of the Nucleophiles

From Table III, the nucleophilicity order 2-methylimidazole ~ 4-methyimidazole > *N*-methylimidazole > imidazole is seen to be observed towards both cations (**Ia**) and (**Ib**). The relative rates are strongly influenced by the amine basicity, with the second-order rate constant, k_1, increasing with the introduction of electron donating methyl substituents on the imidazole nucleus. Quantitative separation of the electronic and steric effects of these substituents can be made by examination of the Brønsted plot shown in Figure 2. For addition to cation (**Ia**), imidazole, *N*-methylimidazole and 4-methylimidazole obey the Brønsted relation-

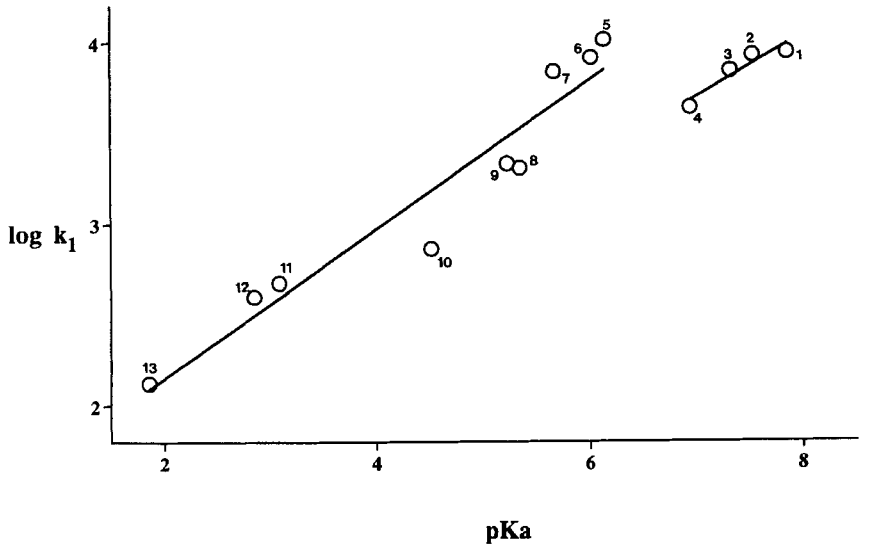
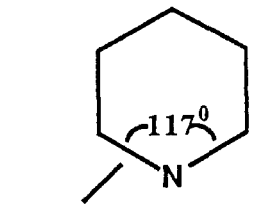


FIGURE 2 Brønsted plot of log k_1 *vs* pKa (H_2O) for the addition of substituted pyridines and imidazoles to $[Fe(CO_3)(1\text{-}5\text{-}\eta\text{-}C_6H_7)]^+$ in CH_3CN at 0°C: 1, 2-MeIm; 2, 4-MeIm; 3, *N*-MeIm; 4, Im 5, 3,5-Me_2py; 6, 4-Mepy; 7, 3-Mepy; 8, 4-Phpy; 9, py; 10, 4-CHOpy; 11, 3-Brpy; 12, 3-CO_2Mepy; 13, 4-CNpy.

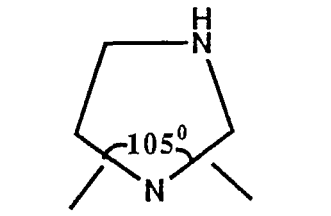
ship (*3*), with a slope, α, of *ca* 0.5. This slope is similar to that recently reported[6,7] for the analogous addition of 3- and 4-substituted pyridines to cation (**Ia**). However, imidazoles are *ca* 5 times less nucleophilic than pyridines of the same basicity, as shown by the separation of *ca* 0.7 log units between the associated Brønsted plots in Figure 2.

$$\log k_1 = \alpha\, pK_a + \text{constant} \qquad (3)$$

The cause of this lower intrinsic reactivity for imidazoles towards $[Fe(CO)_3(dienyl)]^+$ substrates appears to be electronic, rather than steric, in origin. Examination of X-ray crystallographic data[13] for the parent pyridine and imidazole molecules, (**V**) and (**VI**), shows that steric hindrance by groups (H or Me) *alpha* to the tertiary N reaction centre in imidazole will be considerably less than in analogous pyridine species. This is confirmed by the relatively small steric effect shown by a 2-methyl substituent in reaction (*1*). Thus, despite the introduction of a bulky methyl substituent *alpha* to the N reaction centre in 2-methylimidazole, this nucleophile is *ca* twice as reactive towards (**Ia**) as the parent imidazole.



(**V**)



(**VI**)

The steric influence of a 2-methyl substituent in the imidazole nucleophile is quantified by the small negative departure (Δ = 0.15 log units) of 2-methylimidazole from the linear Brønsted plot shown by the other imidazoles (Figure 2). This contrasts with the related additions of pyridines to cation (**Ia**) where 2-methylpyridine is *ca* 3 times *less* reactive than pyridine despite its higher basicity (departure from pyridine Brønsted plot *ca* 1.0 log units).[6] Adherence of 4-methylimidazole to the Brønsted equation (*3*) suggests that this nucleophile employs its non-sterically demanding 5-methyl tautomeric form in addition to (**Ia**).

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