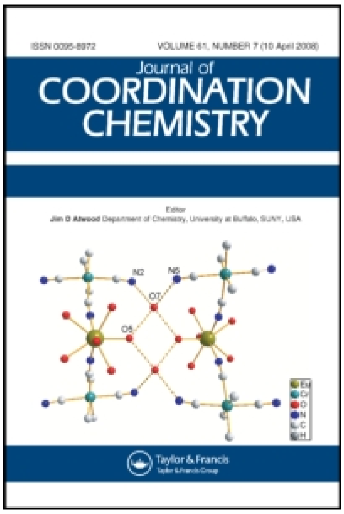

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# KINETICS OF NUCLEOPHILIC ATTACK ON COORDINATED ORGANIC MOIETIES. PART 32.* SYNTHETIC AND MECHANISTIC STUDIES OF THE REACTION OF IODINE ION WITH [($\eta^5$-DIENYL)Fe(CO)$_3$] CATIONS (DIENYL = $C_6H_7$, 2-MeO$C_6H_6$, $C_7H_9$)

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# KINETICS OF NUCLEOPHILIC ATTACK ON COORDINATED ORGANIC MOIETIES. PART 32.* SYNTHETIC AND MECHANISTIC STUDIES OF THE REACTION OF IODIDE ION WITH $[(\eta^5\text{-DIENYL})Fe(CO)_3]^+$CATIONS (DIENYL = $C_6H_7$, 2-MeO$C_6H_6$, $C_7H_9$)

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The reactions between $I^-$ and the cations $[(\eta^5\text{-dienyl})Fe(CO)_3)]^+$ (dienyl = $C_6H_7$, 2-MeO$C_6H_6$, or $C_7H_9$) provide a rare example in which attack occurs at each of the hydrocarbon, carbonyl and metal centres. In the case of the $C_6H_7$ and 2-MeO$C_6H_6$ complexes ring adduct formation predominates, whereas with the more sterically crowded $C_7H_9$ substrate the dominant pathway is CO ligand substitution. A minor organometallic product formed in $CH_3NO_2$ and acetone solvents is believed to be the novel acyl iodide adduct $[(\eta^5\text{-dienyl})Fe(CO)_2(COI)]$. However, in $CH_3CN$ this latter species is not observed.

Concomitant formation of molecular iodine occurs, which is converted to $I_3^-$ in the presence of the large excess of $I^-$ employed. This suggests that a single electron transfer (SET) mechanism is operating, involving initial transfer of one electron from the $I^-$ to the dienyl cations and the formation of iodine radicals. Kinetic studies in various solvents, showing the general rate law Rate = k[Fe][$I^-$], are consistent with rate-determining initial electron transfer followed by rapid reaction between the radicals formed to give the observed products.

*Keywords:* Kinetics; mechanism; iodide attack; tricarbonyl(dienyl) iron cations

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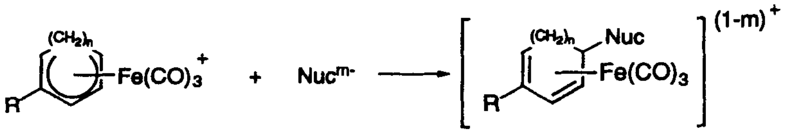
## INTRODUCTION

Attack by nucleophiles on $[(\pi\text{-hydrocarbon})M(CO)_3]^+$ complexes may in principle occur at the coordinated π-hydrocarbon, the metal, or a carbonyl ligand.[1-3] In the case of the dienyl cations $[(\eta^5\text{-dienyl})Fe(CO)_3]^+$ (**1**; dienyl = $C_6H_7$, 2-$MeOC_6H_6$, or $C_7H_9$) in which the hydrocarbon ligand is relatively electrophilic, the vast majority of nucleophiles (tertiary phosphines and phosphites, primary and secondary amines, anilines, pyridines, imidazoles, aromatic heterocycles, and the anions $H^-$, $CN^-$, $CNS^-$, $NCO^-$, *etc.*) undertake π-hydrocarbon ring addition only (1).[1-4] Detailed kinetic and mechanistic studies have been reported[1,3,5] for a range of such ring addition reactions, supporting direct addition of the nucleophiles to the dienyl ring.



**1**

(1)

However, with alkoxide[6] and hydroxide[7] ions as nucleophiles, the kinetically favoured site for initial attack has been shown to be a carbonyl ligand, and under appropriate conditions $[(\eta^5\text{-dienyl})Fe(CO)_2(COOR)]$($R = H$, Me, Et) species have been isolated as initial products. These rapid carbonyl additions are reversible and at longer reaction times ring addition products are formed, as in (1). Recently, the related acyl complex $[(\eta^5\text{-}C_6H_7)$ $Fe\text{-}(CO)_2(COPh)]$ has also been isolated from the reaction of *o*-$MeOCH_2$-$C_6H_4Li$ with (**1**; dienyl = $C_6H_7$) in dimethoxyethane solvent.[8]

The only reported example in which nucleophilic attack at the iron centre occurs for type (**1**) complexes is reaction (2), which is the synthetic route described[9] for the preparation of $[(\eta^5\text{-dienyl})Fe(CO)_2I]$ (**2**; dienyl = $C_6H_7$, $C_7H_9$) compounds.

$$\underset{\mathbf{1}}{[(\eta^5\text{-dienyl})Fe(CO)_3]^+} + I^- \longrightarrow \underset{\mathbf{2}}{[(\eta^5\text{-dienyl})Fe(CO)_2I]} + CO \qquad (2)$$

We have recently employed the latter route to $[(\eta^5\text{-dienyl})Fe(CO)_2I]$ complexes as part of a synthetic strategy aimed at developing polymer-supported (dienyl)iron complexes.[10] Preliminary investigations in our laboratories revealed[11] that the reaction of iodide ion with $[(\eta^5\text{-dienyl})$-$Fe(CO)_3]^+$ cations is considerably more complex than previously reported.

For example, the reaction of $[(\eta^5\text{-}C_6H_7)Fe(CO)_3)]^+$ (**1a**) with KI in acetone yielded not only the reported $[(\eta^5\text{-}C_6H_7)Fe(CO)_2I]$ (**2a**), but also the ring adduct $[(\eta^4\text{-}C_6H_7.I)Fe(CO)_3]$ (**3a**). In addition, IR spectroscopic studies in acetone revealed the presence of a third ironcarbonyl product, believed to be the acyl derivative $[(\eta^5\text{-}C_6H_7)Fe(CO)_2(COI)]$ (**4a**) arising from nucleophilic attack on a carbonyl ligand.

The reaction of $I^-$ ion with $[(\eta^5\text{-dienyl})Fe(CO)_3]^+$ (**1**) cations therefore appears to provide a rare example exhibiting each of the possible pathways for attack on a $[(\pi\text{-hydrocarbon})M(CO)_3]^+$ substrate. We report here detailed synthetic, spectroscopic and kinetic studies of these reactions. These reveal a strong dependence of the reaction pathway on the nature of the dienyl ligand and the solvent employed. In addition, the reaction is shown not to involve classical nucleophilic attack (two electron donation) by $I^-$, but rather a single electron transfer (SET) mechanism involving initial transfer of one electron from the $I^-$ to the dienyl ligands as the rate-determining step.

## EXPERIMENTAL

### Materials

The dienyl iron complexes $[(\eta^5\text{-}C_6H_7)Fe(CO)_3)][BF_4]$ (**1a**), $[(\eta^5\text{-}2\text{-}MeOC_6H_6)Fe(CO)_3][PF_6]$ (**1b**) and $[(\eta^5\text{-}C_7H_9)Fe(CO)_3][BF_4]$ (**1c**) were synthesized and purified as described previously.[4,9] Tetraethylammonium iodide, tetra-*n*-butylammonium iodide and sodium iodide were used directly as obtained from Aldrich Chemical Co. Acetonitrile and nitromethane solvents (Aldrich Chemical Co.) were distilled under dinitrogen and stored over molecular sieves (4 Å). Acetone was analytical grade from Aldrich Chemical Co. All solvents were deoxygenated by passing through a stream of dinitrogen for 30 min prior to use.

### Synthetic Studies

### *Reaction of $[(\eta^5\text{-}C_6H_7)Fe(CO)_3][BF_4]$ (1a) with Iodide Ion*

Potassium iodide (0.94 g, 5.66 mmol) was added to a pale orange-yellow solution of tricarbonyl($\eta^5$-cyclohexadienyl)iron tetrafluoroborate (**1a**; 1.15 g, 3.76 mmol) in acetone (120 cm$^3$). The mixture, which turned dark brown immediately, was stirred at 28–30°C for 3 hr. Rotary evaporation of the mixture gave a dark brown, oily solid (1.99 g). Purification of this crude solid by column chromatography on silica gel (70–230 mesh) using benzene-hexane (1 : 1) as eluent gave two fractions.

The first fraction (colourless band) yielded tricarbonyl($\eta^4$-5-iodo-1,3-cyclohexadiene)iron (**3a**) as a colourless liquid (0.15 g, 9% yield). $\nu$(CO)($CH_2Cl_2$): 2040, 1965 $cm^{-1}$; $\nu$(CO)($CH_3CN$): 2044, 1967 $cm^{-1}$; UV-visible: no peak above 300 nm ($\epsilon_{360} = 90\,M^{-1}\,cm^{-1}$); $^1H$ NMR ($d_6$-acetone): $\delta$ 5.48 (dd, $J_{2,3} = 5.2$ Hz, $J_{1,2} = J_{3,4} = 2.6$ Hz, 2H, $H^2$ and $H^3$), 3.34 (m, $H^1$ and $H^4$), 2.10 (m, 1H, $H^{5'}$), 1.71 (dt, $J_{1,6'} = 2.3$ Hz, $J_{5',6'} = 9.9$ Hz, $J_{6,6'} = 11.5$ Hz, 1H, $H^{6'}$), 1.61 (d, $J_{6,6'} = 11.5$ Hz, 1H, $H^6$); CI MS (+ve): *m*/*z* 220 ($[M-I+H]^+$, 2%), 192 ($[M-I-CO+H]^+$, 20%), 164 ($[M-I-2CO+H]^+$, 25%).

The second fraction (brown band) gave dicarbonyliodo($\eta^5$-cyclohexadienyl)iron (**2a**) as a dark brown, crystalline solid (0.91 g, 78% yield). $\nu$(CO)($CH_2Cl_2$): 2036, 1994 $cm^{-1}$ [lit.[9] $\nu$(CO)(KCl): 2041, 1992 $cm^{-1}$]; UV-visible: $\lambda_{max}^{acetone}$ 490 (420), 340sh (4020) ($\epsilon_{360} = 3400\,M^{-1}\,cm^{-1}$); $^1H$ NMR ($d_6$-acetone): $\delta$ 7.21 (t, $J_{2,3} = J_{3,4} = 6.3$ Hz, 1H, $H^3$), 5.49 (t, $J_{1,2} = J_{2,3} = J_{3,4} = J_{4,5} = 6.3$ Hz, 2H, $H^2$ and $H^4$), 3.29 (t, $J_{1,6'} = J_{5,6'} = 6.3$ Hz, 2H, $H^1$ and $H^5$), 2.84 (dt, $J_{1,6'} = J_{5,6'} = 6.3$ Hz, $J_{6,6'} = 14.2$ Hz, 1H, $H^{6'}$), 2.13 (d, $J_{6,6'} = 14.2$ Hz, 1H, $H^6$); ES MS (+ve, $CH_3CN$): *m*/*z* 317 ($[M]^+$, 34%), 289 ($[M-CO]^+$, 62%), 163 ($[M-2CO-I]^+$, 90%); ES MS (−ve, $CH_3CN$): *m*/*z* 127 ($[I]^-$, 100%).

### *Reaction of* $[(\eta^5\text{-}2\text{-}MeOC_6H_6)Fe(CO)_3][PF_6]$ *(1b) with Iodide Ion*

A similar procedure to that described above was employed, except that tricarbonyl($\eta^5$-2-methoxycyclohexadienyl)iron hexaflurophosphate (**1b**) was used instead of (**1a**). A dark brown solid was obtained and purification by column chromatography on silica gel (70–230 mesh) using benzene-hexane (1 : 1) as eluent gave two fractions.

The first fraction (colourless band) gave tricarbonyl($\eta^4$-5-iodo-2-methoxy-1,3-cyclohexadiene)iron (**3b**), which was isolated as a colourless liquid (32 mg, 8% yield). $\nu$(CO)($CH_2Cl_2$): 2042, 1965 $cm^{-1}$; $\nu$(CO)($CH_3CN$): 2041, 1965 $cm^{-1}$; $\nu$(CO)(hexane): 2046, 1976 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 400 MHz): $\delta$ 5.09 (dd, $J_{1,3} = 2.1$ Hz, $J_{3,4} = 6.4$ Hz, 1H, $H^3$), 3.61 (s, 3H, MeO), 3.46 (d, $J_{1,6'} = 2.4$ Hz, 1H, $H^1$), 2.76 (br t, $J_{4,5'} = J_{5',6} = 3.6$ Hz, 1H, $H^{5'}$), 1.71 (dt, $J_{4,5'} = 3.6$ Hz, $J_{3,4} = 6.4$ Hz, 1H, $H^4$), 1.58 (dt, $J_{5',6} = 3.6$ Hz, $J_{5',6'} = 10.0$ Hz, $J_{6,6'} = 12.8$ Hz, 1H, $H^{6'}$), 1.50 (dt, $J_{1,6} = 2.4$ Hz, $J_{6,6'} = 12.8$ Hz, 1H, $H^6$); CI MS (+ve): *m*/*z* 250 ($[M-I+H]^+$, 5%), 222 ($[M-I-CO+H]^+$, 100%), 194 ($[M-I-2CO+H]^+$, 15%).

The second fraction (brown band) gave dicarbonyliodo($\eta^5$-2-methoxy-cyclohexadienyl)iron (**2b**) as a dark brown, crystalline solid (300 mg, 83%

yield). Anal. Calcd. for $C_9H_7O_3FeI$: C, 31.1; H, 2.6; I, 36.5; Found: C, 30.6; H, 2.7; I, 36.5%. $\nu$(CO)($CH_2Cl_2$): 2033, 1989 $cm^{-1}$; $\nu$(CO)($CH_3CN$): 2031, 1985 $cm^{-1}$; $^1H$ NMR ($d_6$-acetone): $\delta$ 7.04 (d, $J_{3,4}=6.3$ Hz, 1H, $H^3$), 5.60 (t, $J_{3,4}=J_{4,5}=6.3$ Hz, 1H, $H^4$), 3.66 (s, 3H, MeO), 3.37 (t, $J_{4,5}=J_{5,6'}=6.3$ Hz, 1H, $H^5$), 2.99 (d, $J_{1,6'}=6.3$ Hz, 1H, $H^1$), 2.79 (dd, $J_{1,6'}=J_{5,6'}=6.3$ Hz, $J_{6,6'}=12.6$ Hz, 1H, $H^{6'}$), 2.13 (d, $J_{6,6'}=12.6$ Hz, 1H, $H^6$); $^{13}C$ NMR ($CDCl_3$): $\delta$ 212.0 (CO), 140.0 (C), 72.9 (CH), 67.6 (CH), 55.3 (MeO), 54.2 (CH), 50.8 (CH), 25.6 ($CH_2$); ES MS (+ve, $CH_3CN$): $m/z$ 293 ($[M+H-2CO]^+$, 5%), 165 ($[M-2CO-I]^+$, 50%); ES MS (−ve, $CH_3CN$): $m/z$ 127 ($[I]^-$, 100%).

### *Reaction of [($\eta^5$-$C_7H_9$)Fe(CO)$_3$][$BF_4$] (1c) with Iodide Ion*

A similar procedure to that described above was employed, except that tricarbonyl($\eta^5$-cycloheptadienyl)iron tetrafluoroborate (**1c**) was used instead of (**1a**). A dark brown solid was obtained and purification by column chromatography on silica gel (70–230 mesh) using benzene-hexane (1:1) as eluent gave two fractions.

The first fraction (colourless band) gave tricarbonyl($\eta^4$-5-iodo-1,3-cycloheptadiene)iron (**3c**) as a colourless liquid (60 mg, 5% yield). $\nu$(CO) ($CH_2Cl_2$): 2040, 1965 $cm^{-1}$; $\nu$(CO)($CH_3CN$): 2045, 1970 $cm^{-1}$; $^1H$ NMR ($CDCl_3$): $\delta$ 5.28 (m, 2H, $H^2$ and $H^3$), 3.12 (m, $H^4$), 2.78 (m, 1H, $H^1$), 2.32 (m, 1H, $H^{5'}$), 1.95 (m, 2H, $H^{6'}$ and $H^{7'}$), 1.26 (m, 2H, $H^6$ and $H^7$); CI MS (+ve): $m/z$ 220 ($[M-I+H]^+$, 2%), 192 ($[M-I-CO+H]^+$, 20%), 164 ($[M-I-2CO+H]^+$, 25%); CI MS (+ve): $m/z$ 234 ($[M-I+H]^+$, 3%), 206 ($[M-I-CO+H]^+$, 5%), 178 ($[M-I-2CO+H]^+$, 8%).

The second fraction (brown band) upon evaporation gave dicarbonyliodo($\eta^5$-cycloheptadienyl)iron (**2c**) as a dark brown, crystalline solid (1.02 g, 86% yield). $\nu$(CO) ($CH_2Cl_2$): 2034, 1993 $cm^{-1}$; $\nu$(CO)($CH_3CN$): 2032, 1989 $cm^{-1}$ [lit.[9] $\nu$(CO) (KCl): 2041, 1992 $cm^{-1}$]; $^1H$ NMR ($d_6$-acetone): $\delta$ 7.08 (t, $J_{2,3}=J_{3,4}=6.3$ Hz, 1H, $H^3$), 5.73 (t, $J_{1,2}=J_{2,3}=J_{3,4}=J_{4,5}=6.3$ Hz, 2H, $H^2$ and $H^4$), 3.97 (br s, 2H, $H^1$ and $H^5$), 2.42 (dt, $J_{6,7}=J_{6',7'}=3.6$ Hz, $J_{6,6'}=J_{7,7'}=9.6$ Hz, 2H, $H^{6'}$ and $H^{7'}$), 1.45 (d, $J_{6,6'}=J_{7,7'}=9.6$ Hz, 2H, $H^6$ and $H^7$); ES MS (+ve, $CH_3CN$): $m/z$ 332 ($[M]^+$, 5%), 304 ($[M-CO]^+$, 22%); ES MS (−ve, $CH_3CN$): $m/z$ 127 ($[I]^-$, 100%).

### *Bis{1,1-[tricarbonyl($\eta^4$-2,4-cyclohexadiene)]}diiron (6)*

This compound was prepared according to the literature procedure.[9] A mixture of tricarbonyl($\eta^5$-cyclohexadienyl)iron tetrafluoroborate (**1a**);

(92 mg, 0.30 mmol) and zinc powder (42 mg, 0.64 mmol) in THF (5 mL) was stirred for 5 days and then filtered. The filtrate was evaporated *in vacuo* to give the title compound as a light yellow solid (97 mg, 74% yield). $\nu(CO)(CH_2Cl_2)$: 2039, 1970 cm$^{-1}$; $\nu(CO)(CH_3CN)$: 2039, 1970 cm$^{-1}$; $^1H$ NMR ($CDCl_3$): $\delta$ 5.31 (m, 2H, $H^3$ and $H^4$), 3.08 (dt, $J_{1',2} = 3.3$ Hz, 1H, $H^2$), 3.00 (m, 1H, $H^5$), 1.87 (d, $J_{1',6'} = 9.0$ Hz, 1H, $H^{1'}$), 1.26 (br s, 1H, $H^{6'}$), 1.08 (d, $J_{6,6'} = 13.8$ Hz, 1H, $H^6$); ES MS (+ve, $CH_3CN$): *m/z* 219 {$[(C_6H_7)Fe(CO)_3]^+$, 100%}.

## Spectroscopic Studies

Infrared spectra were recorded in a $CaF_2$ liquid cell using a Biorad FTS-5 or a Bomem Gram-Michelson Fourier transform spectrophotometer. Electronic spectra of reaction mixtures were recorded under a dinitrogen atmosphere using a Shimadzu UV-265 spectrophotometer. $^1H$ NMR spectra were measured on a Varian Unity 400 MHz spectrometer. Signals are described in terms of chemical shift ($\delta$) in ppm from TMS. The assignments for most of the $^1H$ NMR spectra were confirmed by their related COSY NMR spectra. Electrospray (ES) mass spectra (in $CH_3CN$ solution) and chemical ionization (CI) mass spectra (methane reagent gas) were recorded on a VG Quattro Triple Quadrupole mass spectrometer.

## Kinetic Studies

### *Slow Reactions*

The relatively slow reactions of the dienyl salts with iodide ion in acetonitrile and nitromethane were studied by an IR sampling technique. A solution of the iodide nucleophile in the appropriate solvent was thermostatted for 20 min in a constant temperature (±0.1°C) bath and then rapidly mixed with the solid dienyl complex to give the reaction solution of the desired concentration. The reaction flask was rapidly flushed with dinitrogen, sealed with a Subaseal and wrapped in aluminium foil to exclude light. Samples were then withdrawn via syringe for IR analysis between 2200 and 1800 cm$^{-1}$.

During the reactions the $\nu(CO)$ bands of the original dienyl cations at 2100 and 2060 cm$^{-1}$ gradually decreased in intensity, being replaced by bands associated with $[(\eta^4\text{-diene.I})Fe(CO)_3]$, $[(\eta^5\text{-dienyl})Fe(CO)_2I]$ and $[(\eta^5\text{-dienyl})Fe(CO)_2(COI)]$ products. The reactions were followed by monitoring the disappearance of the 2110 cm$^{-1}$ band of the dienyl starting materials, which was well separated from the product $\nu(CO)$ bands. All reactions were carried out under *pseudo*-first-order conditions using a large excess of iodide nucleophile ([Fe] $= 0.8-3.0 \times 10^3$ mol dm$^{-3}$, [I$^-$] $= 0.55-6.0 \times 10^{-2}$ mol dm$^{-3}$). *Pseudo*-first-order rate constants, $k_{obs}$, were obtained from the slopes of plots of $\ln A_t$ *vs* time (using a least-squares program), where $A_t$ = absorbance of the reaction solution at 2110 cm$^{-1}$ at time t. Such kinetic plots were generally linear for at least two half lives. Least squares analyses of plots of $k_{obs}$ *vs* [I$^-$] were used to obtained the second order rate constants (k).

Enthalpies of activation ($\Delta H^\ddagger$) for the reactions of the [($\eta^5$-dienyl)Fe(CO)$_3$]$^+$ cations with [Et$_4$N][I] in $CH_3NO_2$ solvent were calculated from a least-squares analysis of the Eyring equation using the second order rate constants (k). Errors quoted are the standard errors of estimate from these analyses. Entropies of activation ($\Delta S^\ddagger$) were also calculated by standard procedures using the second order rate constants.

### *Rapid Reactions*

The rapid reaction of [($\eta^5$-C$_6$H$_7$)Fe(CO)$_3$][BF$_4$] (**1a**) with tetrabutylammonium iodide in acetone solvent was studied using a thermostatted (±0.1°C) stopped-flow spectrophotometer. The reaction was monitored at 400 nm, at which wavelength a large increase in absorbance occured during the reaction due to the formation of $I_3^-$. These rapid reactions were studied under *pseudo*-first-order conditions using a large excess of iodide nucleophile ([Fe] $= 5.0 \times 10^{-4}$ mol dm$^{-3}$, [I$^-$] $= 1.5-20.0 \times 10^{-2}$ mol dm$^{-3}$). *Pseudo*-first order rate constants, $k_{obs}$, were calculated from the slopes of plots of $\ln(A_\infty - A_t)$ *vs* time using a least-squares program. These plots were generally linear for two half lives. Each $k_{obs}$ quoted is the average of at least three separate runs, with an average reproducibility of ± 7%. Least-squares analyses of plots of $k_{obs}$ *vs* iodide ion concentration were used to obtain the second order rate constants (k).

## RESULTS AND DISCUSSION

### Nature of the Reactions

### *Spectroscopic Studies*

All reactions were carried out in the dark under an atmosphere of argon. The reaction of [($\eta^5$-C$_6$H$_7$)Fe(CO)$_3$][BF$_4$] (**1a**) ([Fe] $= 3 \times 10^{-3}$ mol dm$^{-3}$) with [Et$_4$N][I] ([I] $= 1.5 \times 10^{-2}$ mol dm$^{-3}$) was initially monitored in $CH_3NO_2$ solvent. At the completion of the reaction (as evidenced by the complete disappearance of the initial dienyl salt $\nu$(CO) bands at 2110 and

2060 cm$^{-1}$) three $\nu$(CO) bands were observed at 2080, 2040 and 1967 cm$^{-1}$, together with weak shoulders at 2030 and 1987 cm$^{-1}$. Significantly, there was only a small amount ( < 5%) of the reported[9] carbonyl-displaced product [($\eta^5$-$C_6H_7$)Fe(CO)$_2$I] (**2a**) ($\nu$(CO) in $CH_3NO_2$: 2030, 1987 cm$^{-1}$, see Table I), despite the substantial amount (78%) of this product from the synthetic scale reaction in acetone above.

The $\nu$(CO) bands at 2040 and 1967 cm$^{-1}$ are typical of neutral tricarbonyl($\eta^4$-diene)iron complexes and match those of the ring adduct [($\eta^4$-$C_6H_7$.I)Fe(CO)$_3$] (**3a**) isolated from the synthetic reaction above. Brown *et al.*[2] have also reported (**3a**) as a major product from the reaction of the salt (**1a**) with KI in $CH_2Cl_2/H_2O$ solvent.

The remaining $\nu$(CO) product bands in $CH_3NO_2$ have been tentatively assigned to the novel acyl iodide complex [($\eta^5$-$C_6H_7$)Fe(CO)$_2$(COI)] (**4a**). Support for this assignment comes from the presence of a medium intensity band at *ca* 1715 cm$^{-1}$ observed for the solid product mixture isolated from an analogous preparative procedure. This band is attributed to the COI ligand, being very similar to the peak at 1715 cm$^{-1}$ reported[12] for an acyl iodide intermediate in the reaction of Fe(CO)$_5$ with iodine. Exposure of the product mixture (either solid or in $CH_3NO_2$) to normal laboratory light resulted in the disappearance within minutes of the $\nu$(CO) bands associated with (**4a**). This was not accompanied by the growth of any other $\nu$(CO) bands. The instability of (**4a**) to the light parallels that of organic acyl iodides which are known[13] to undergo CO dissociation upon irradiation (3). The failure to regenerate any [($\eta^5$-$C_6H_7$)Fe(CO)$_2$I] (**2a**) from exposure of (**4a**) to light may arise from rapid decomposition subsequent to CO release,

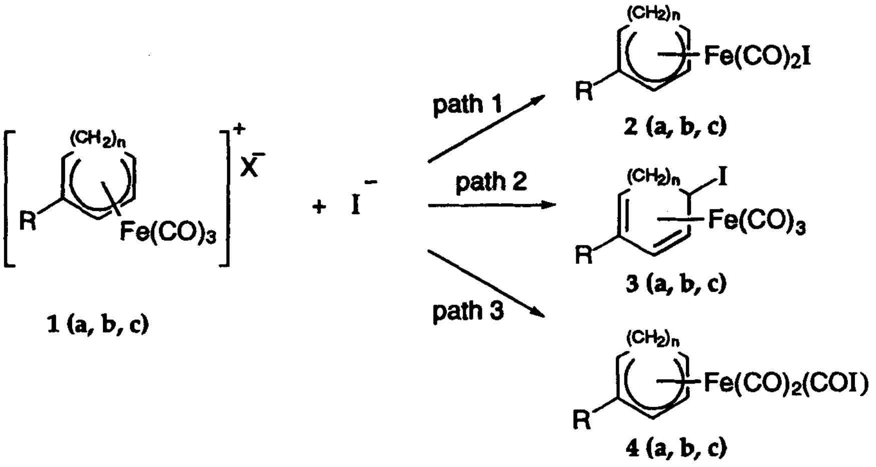
TABLE I IR spectroscopic data for the starting dienyl complexes and the products from their reactions with iodide ion

| *Type* | *Compound* | $\nu$(*CO*) cm$^{-1}$ | | |
|---|---|---|---|---|
| | | $CH_3NO_2$ | $CH_3CN$ | *Acetone* |
| Starting dienyl cations | (**1a**) | 2110, 2060 | 2113, 2065 | 2113, 2063 |
| | (**1b**) | 2112, 2062 | 2111, 2062 | 2110, 2057 |
| | (**1c**) | 2112, 2064 | 2111, 2063 | 2110, 2066 |
| Neutral dicarbonyl iodide products | (**2a**) | 2030, 1987 | 2033, 1989 | 2030, 1985 |
| | (**2b**) | 2031, 1986 | 2031, 1985 | 2029, 1983 |
| | (**2c**) | 2030, 1989 | 2032, 1989 | 2030, 1989 |
| Neutral ring adducts | (**3a**) | 2040, 1967 | 2045, 1970 | 2045, 1969 |
| | (**3b**) | 2047, 1971 | 2041, 1965 | 2040, 1966 |
| | (**3c**) | 2045, 1972 | 2045, 1970 | 2041, 1971 |
| Neutral dienyl acyl iodide products | (**4a**) | 2080, 2030 | | 2073, 2017 |
| | (**4b**) | 2078, 2026 | | 2072, 2014 |
| | (**4c**) | 2078, 2032 | | 2073, 2020 |

before attachment of $I^-$ to the vacated metal site can occur.

$$\mathrm{RCOI} \xrightarrow{h\nu} \mathrm{RI} + \mathrm{CO} \qquad (3)$$

These initial *in situ* IR spectroscopic studies were extended to the reactions of cation (**1a**) with a range of other iodide salts ($[Bu_4N][I]$, NaI and KI) in various solvents ($CH_3NO_2$, $CH_3CN$ and acetone). Similar, but less extensive, studies were made on the related $[(\eta^5\text{-}2\text{-}MeOC_6H_6)Fe(CO)_3]^+$ (**1b**) and $[(\eta^5\text{-}C_7H_9)Fe(CO)_3]^+$ (**1c**) cations. In each case, except in $CH_3CN$ solvent where no acyl iodide species were observed, analogous products were detected, as shown in Scheme 1 (a, R = H, n = 1; b, R = OMe, n = 1; c, R = H, n = 2). Their characteristic $\nu$(CO) bands are summarised in Table I. The ratio of the three types of organometallic product was found to vary significantly with the nature of the solvent and the dienyl salt substrate, but to be relatively insensitive to the nature of the iodide salt employed (Tables II and III).



SCHEME 1

### *Influence of Solvent*

As seen from Table II, the *in situ* ratio of the products from the reaction of $[(\eta^5\text{-}C_6H_7)Fe(CO)_3]^+$ (**1a**) with $[Et_4N][I]$ varied as the solvent was changed from $CH_3NO_2$ to $CH_3CN$ to acetone. In each case, the ring adduct complex (**3a**) was the major product ($\geq 80\%$). The maximum yield of (**3a**) was *ca* 95% in acetone solvent. Significantly, the previously reported[9] product from this reaction, namely the carbonyl-displaced complex

TABLE II *In situ* products from the reaction of cation (**1a**) with iodide ion in various solvents. $[I^-] = 0.015$ mol dm$^{-3}$ for $[R_4N][I]$; 0.010 mol dm$^{-3}$ for NaI, KI

| *Solvent* | *Product* (%) | | | |
|---|---|---|---|---|
| | *Iodide salt* | *Dicarbonyl iodide* (**2a**) | *Ring adduct* (**3a**) | *Acyl iodide* (**4a**) |
| $CH_3CN$ | $[Et_4N][I]$ | *ca* 15 | *ca* 85 | |
| $CH_3NO_2$ | $[Et_4N][I]$ | *ca* 5 | *ca* 80 | *ca* 15 |
| Acetone | $[Et_4N][I]$ | trace | *ca* 95 | *ca* 5 |
| | $[Bu_4N][I]$ | *ca* 5 | *ca* 90 | *ca* 5 |
| | NaI | *ca* 5 | $> 85$ | $< 10$ |
| | KI | trace | *ca* 95 | *ca* 5 |

TABLE III *In situ* products from the reaction of $[(\eta^5\text{-dienyl})Fe(CO)_3]^+$ cations with $[Bu_4N][I]$ in acetone ($[Fe] = 3 \times 10^{-3}$ mol dm$^{-3}$, $[I^-] = 1.5 \times 10^{-2}$ mol dm$^{-3}$)

| *Dienyl* | *Product* (%) | | |
|---|---|---|---|
| | *Dicarbonyl iodide* (**2**) | *Ring adduct* (**3**) | *Acyl iodide* (**4**) |
| $C_6H_7$ | *ca* 5 | *ca* 90 | *ca* 5 |
| $2\text{-MeOC}_6H_6$ | *ca* 15 | *ca* 80 | *ca* 5 |
| $C_7H_9$ | $> 90$ | *ca* 5 | *ca* 5 |

$[(\eta^5\text{-}C_6H_7)Fe(CO)_2I]$ (**2a**), was only a minor product in each case (trace to 15%). The maximum yield (*ca* 15%) of the acyl iodide product (**4a**) occurred in $CH_3NO_2$, while this product was absent when reactions were carried out in $CH_3CN$.

### *Influence of Iodide Salt*

In contrast, the results in Table III for the reaction of (**1a**) with various iodide salts in acetone reveal very little dependence on the nature of the counter cation in the iodide salt employed. In each case the ring adduct (**3a**) was again the major *in situ* product (85–95%), while $\leq 5\%$ of each of the other two products (**2a**) and (**4a**) were generally observed.

### *Influence of Dienyl Salt*

The most significant influence on the ratio of the three types of organometallic products is the nature of the dienyl ligand in the initial cationic substrate. As seen in Table III for reactions with $[Bu_4N][I]$ in acetone, the proportion of ring adduct product decreases down the series $C_6H_7 > 2\text{-MeOC}_6H_6 \gg C_7H_9$ (90 : 80 : 5). This is accompanied by an increase in the proportion of the carbonyl-displaced $[(\eta^5\text{-dienyl})Fe(CO)_2I]$ product. The most striking feature is the change from ring adduct formation (path 2) as the major (90%) route with the cyclohexadienyl salt (**1a**) to carbonyl substitution (path 1) as the dominant (90%) route with the cycloheptadienyl complex (**1c**). The proportion of acyl iodide product (path 3) remained constant (*ca* 5%) with each of the dienyl complex substrates.

The ring adduct (**3c**) has been reported previously by Brown *et al.*[2] as a major product from the reaction of the salt (**1c**) with KI in $CH_2Cl_2/H_2O$ solvent. However, the analogous product (**3b**) is reported here for the first time. Its $^1H$ NMR spectrum is characteristic of a ring-substituted ($\eta^4$-1,3-diene) $Fe(CO)_3$ complex. On the basis of earlier configurational assignments for such complexes,[2,5] the $J_{5',6'}$ coupling constant of 10 Hz indicates an *exo*-configuration for the iodo ring substituent.

The reactions of each of the dienyl salts (**1a–1c**) with $I^-$ in the various solvents were accompanied by the development of a deep red colour. This was associated with the growth of an absorption band in the electronic spectrum at 360 nm characteristic of the $I_3^-$ ion. Independent UV-visible spectral studies on the isolated ring adducts (**3**) showed that they did not absorb significantly at this wavelength. The dicarbonyl iodide products (**2**) are moderately absorbing at this wavelength (see Experimental). However, except in the case of the cycloheptadienyl complex (**2c**), they were shown from the above *in situ* infrared studies to be only minor products (5–15%).

The generation of $I_3^-$ in these reactions is most readily explained as arising from one-electron transfer from the $I^-$ reagent to the dienyl salt substrates to give organometallic radical species and the $I^\bullet$ radical (*vide infra*). Coupling of the iodine radicals would give molecular iodine, which in the presence of the excess $I^-$ employed would give rise to the observed $I_3^-$. Using the extinction coefficient determined separately for $I_3^-$ (from mixtures of $I_2$ and $I^-$) in the various solvents, the concentration of $I_3^-$ product in the reactions could be approximately estimated.

For each of the dienyl complex substrates the proportion of the acyl iodide product remains constant at *ca* 5% in acetone solvent. This is not unexpected, since the CO ligand site for iodide radical addition is removed from the steric influence of the dienyl ligand. Classical (two-electron) nucleophilic addition at a CO ligand in $[(\eta^5\text{-dienyl})Fe(CO)_3]^+$ complexes has rarely been observed, the only examples reported to date involving competing attack of alkoxide,[6] hydroxide[7] and aryllithium[8] at dienyl and CO centres.

## Kinetics and Mechanism

In $CH_3NO_2$ and $CH_3CN$ as solvents, the reactions were slow enough to monitor by conventional IR sampling techniques and the kinetics of the reactions of each of the dienyl cations (**1a**)–(**1c**) with $I^-$ were studied by following the disappearance of the initial dienyl complex $\nu$(CO) bands at *ca* 2110 $cm^{-1}$. IR spectra recorded during a typical reaction of $[(\eta^5\text{-dienyl})Fe(CO)_3]^+$ with $[Et_4N][I]$ in $CH_3NO_2$ are illustrated in Figure 1. This shows the decrease in intensity of the $\nu$(CO) band for the starting dienyl

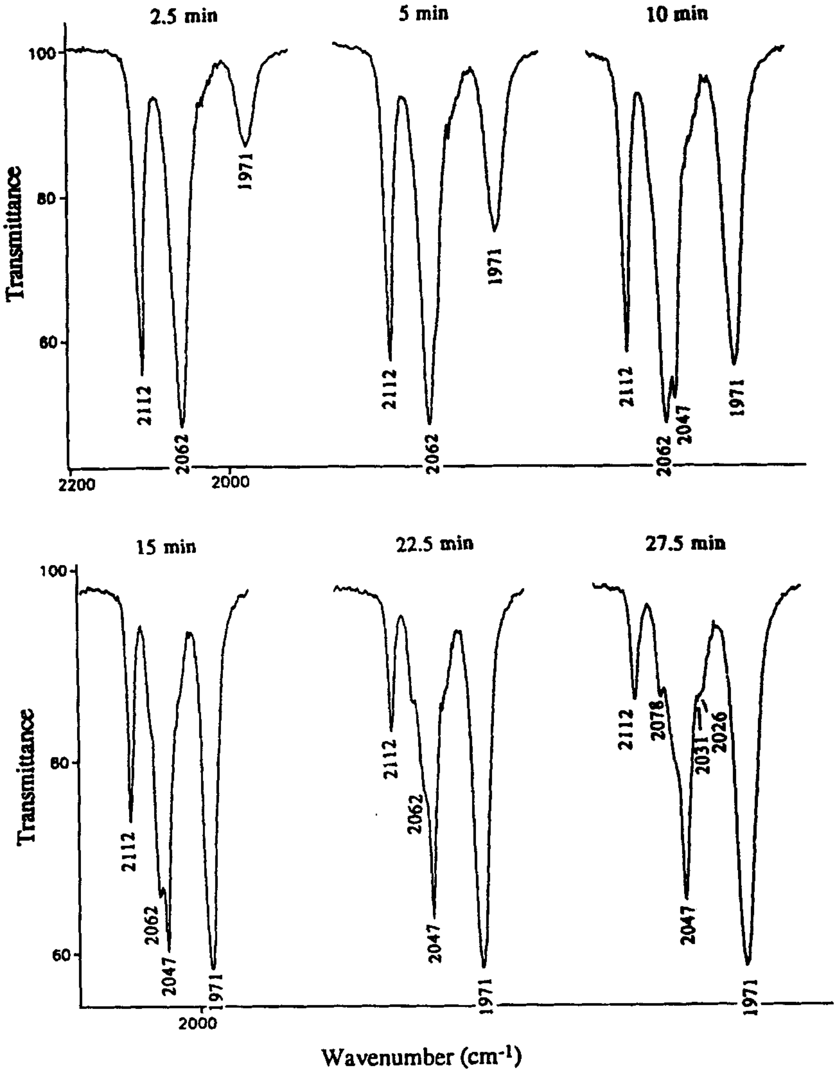
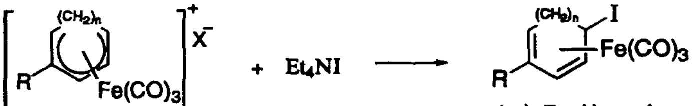


FIGURE 1 *In situ* IR spectra during a typical reaction of (**1b**) with $[Et_4N][I]$ in $CH_3NO_2$ at 25°C (for clarity, not all spectra recorded are shown).

iron complex (**1a**) at 2110 cm$^{-1}$ and the growth in the major product (**3a**) $\nu$(CO) bands at 2040 and 1967 cm$^{-1}$. In a few cases, the kinetics were alternatively measured by following the increase of the $\nu$(CO) band of the ring adduct (3) at 1967 cm$^{-1}$, giving rate constants identical within experimental to those above.

However, the reactions of (**1a**) and (**1b**) were much more rapid in acetone as solvent and required the use of stopped-flow kinetic techniques. The appearance of the $I_3^-$ product was conveniently monitored at 400 nm, where it is strongly absorbing (see above). The major (*ca* 90%) organometallic product, namely the ring adduct (**3a**), does not absorb at this wavelength, while the minor (*ca.* 5%) product [($\eta^5$-$C_6H_7$)Fe$(CO)_2$I] is only weakly absorbing at 400 nm.

The kinetic results are summarised below for each of the solvents in turn. In all solvents the major product ($\geq$80%) occuring for the $C_6H_7$ and 2-MeO$C_6H_6$ substrates (**1a**) and (**1b**) was the ring adduct (**3a**) and (**3b**), respectively (Scheme 2), while for the analogous $C_7H_9$ substrate (**1c**) the carbonyl-substitution process (path 1, Scheme 1) predominated ($\geq$95%).



(**1a**): R = H, n = 1
(**1b**): R = MeO, n = 1

(**3a**): R = H, n = 1
(**3b**): R = MeO, n = 1

SCHEME 2

### *(i) Kinetics in $CH_3NO_2$ and $CH_3CN$ Solvents*

Kinetic results for the reactions between the [($\eta^5$-dienyl)Fe$(CO)_3$]$^+$ cations and [Et N][I] in $CH_3NO_2$ and $CH_3CN$ solvents are summarised in Tables IV and V. In all cases, plots of $k_{obs}$ *vs* [I$^-$] were linear and passed through the origin (*e.g.* Figure 2), indicating that expression (4) is obeyed and the overall rate law (5).

$$k_{obs} = k\,[I^-] \tag{4}$$

$$\text{Rate} = k\,[Fe][I^-] \tag{5}$$

In order to examine the influence of the iodide salt counter cation on these processes, the reactions of each of the dienyl salts (**1a**)–(**1c**) with [$Bu_4N$][I] were also studied in $CH_3NO_2$ solvent. The comparative data in

TABLE IV Kinetic results for the reactions of $[(\eta^5\text{-dienyl})Fe(CO)_3]^+$ cations with $[Et_4N][I]$ in $CH_3NO_2$

| *Dienyl*[a] | *Temp.* (°C) | $10^2$ $[I^-]$ (mol dm$^{-3}$) | $10^4$ $k_{obs}$ (s$^{-1}$) | $10^2$ k (mol$^{-1}$ dm$^3$ s$^{-1}$) |
|---|---|---|---|---|
| $C_6H_7$ | 25.0 | 1.00 | 1.44 | |
| **(1a)** | | 1.50 | 2.95 | |
| | | 2.00 | 4.20 (3.70)[b] | |
| | | 3.00 | 6.24 | |
| | | 4.00 | 7.82 | |
| | | 5.00 | 10.5 | 2.13 (0.09) |
| | 22.5 | 1.50 | 1.97 | |
| | 25.0 | 1.50 | 2.95 | |
| | 27.6 | 1.50 | 4.04 | |
| | 30.0 | 1.50 | 6.04 | |
| | 35.0 | 1.50 | 9.80 | |
| | 40.0 | 1.50 | 15.9 | |
| 2-$MeOC_6H_6$ | 25.0 | 1.50 | 1.82 | |
| **(1b)** | | 2.00 | 2.30 (2.57)[b](2.24)[c] | |
| | | 3.00 | 3.70 | |
| | | 4.00 | 5.00 | |
| | | 5.00 | 5.50 (5.23)[c] | |
| | | 5.50 | 6.57 | |
| | | 6.00 | 8.62 | 1.23 (0.08) |
| | 20.0 | 1.50 | 1.13 | |
| | 30.0 | 1.50 | 3.49 | |
| | 35.0 | 1.50 | 5.73 | |
| | 40.0 | 1.50 | 12.0 | |
| $C_7H_9$ | 25.0 | 0.55 | 0.55 | |
| **(1c)** | | 0.75 | 0.75 | |
| | | 1.00 | 0.80 | |
| | | 1.50 | 1.37 | |
| | | 2.00 | 1.82 (1.64)[b] | 0.884 (0.068) |

[a] [Fe] for **(1a)** and **(1b)** is 2.0 × $10^{-3}$ mol dm$^{-3}$, and for **(1c)** is 0.8–2.0 × $10^{-3}$ mol dm$^{-3}$. [b] $k_{obs}$ values in brackets obtained using $[Bu_4N][I]$. [c] Calc. from growth of product **(3b)** band at 1967 cm$^{-1}$.

TABLE V Kinetic results for the reaction of $[(\eta^5\text{-dienyl})Fe(CO)_3]^+$ cations with $[Et_4N][I]$ in $CH_3CN$ ([Fe] = 2.0–3.0 × $10^{-3}$ mol dm$^{-3}$)

| *Dienyl* | *Temp.* (°C) | $10^2$ $[I^-]$ (mol dm$^{-3}$) | $10^4$ $k_{obs}$ (s$^{-1}$) | $10^2$ k (mol$^{-1}$ dm$^3$ s$^{-1}$) |
|---|---|---|---|---|
| $C_6H_7$ | 25.0 | 1.50 | 13.4 | |
| **(1a)** | | 2.00 | 18.0 | |
| 2-$MeOC_6H_6$ | 25.0 | 1.50 | 4.41 | |
| **(1b)** | | 2.00 | 5.35 | |
| | | 2.50 | 6.00 | |
| | | 3.00 | 8.20 | |
| | | 3.50 | 8.76 | |
| | | 4.00 | 11.5 | 2.74 (0.31) |
| | 22.0 | 1.50 | 3.05 | |
| | 30.0 | 1.50 | 7.69 | |
| | 35.0 | 1.50 | 12.1 | |
| | 38.5 | 1.50 | 17.5 | |

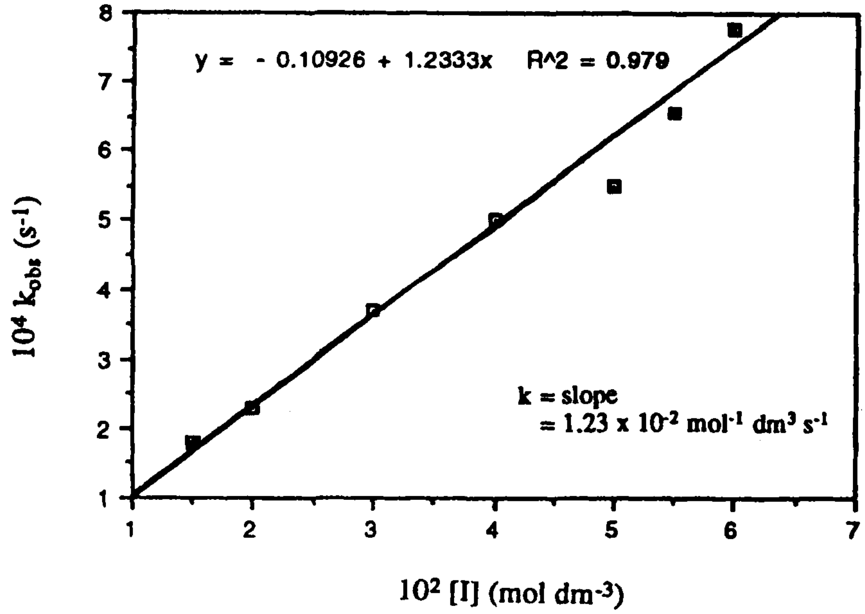


FIGURE 2 A typical plot of $k_{obs}$ *vs* [$I^-$] for the reaction of **1b** with [$Et_4N$][I] in $CH_3NO_2$ at 25°C.

Table IV for [$Et_4N$][I] and [$Bu_4N$][I] as alternative sources of the $I^-$ reactant show that the iodide counter cation has only a very minor influence on the $k_{obs}$ values for the reactions.

Activation parameters ($\Delta H^\ddagger$ and subsequently $\Delta S^\ddagger$ values) calculated from the data in Tables IV and V at different temperatures are summarised in Table VI. The second order rate law (5) and the negative entropies of activation ($\Delta S^\ddagger$) observed for the reactions of the cations (**1a**) and (**1b**) with $I^-$ are consistent with initial transfer of a single electron from the $I^-$ to the dienyl cations as shown in Scheme 3 (*vide infra*). In the case of the $C_7H_9$ complex (**1c**), steric retardation of nucleophilic addition to the dienyl ring is known from previous studies[14,15] to be severe, and in the present case results in the alternative carbonyl-displacement reaction becoming the dominant subsequent pathway.

### *(ii) Kinetics in Acetone Solvent*

The reactions of the cation [($\eta^5$-$C_6H_7$)Fe(CO)$_3$]$^+$ (**1a**) with [$Bu_4N$][I] and NaI in acetone also occur predominantly (*ca* 90%) *via* ring addition (path 2), as shown in Scheme 2. The reactions in acetone, however, are

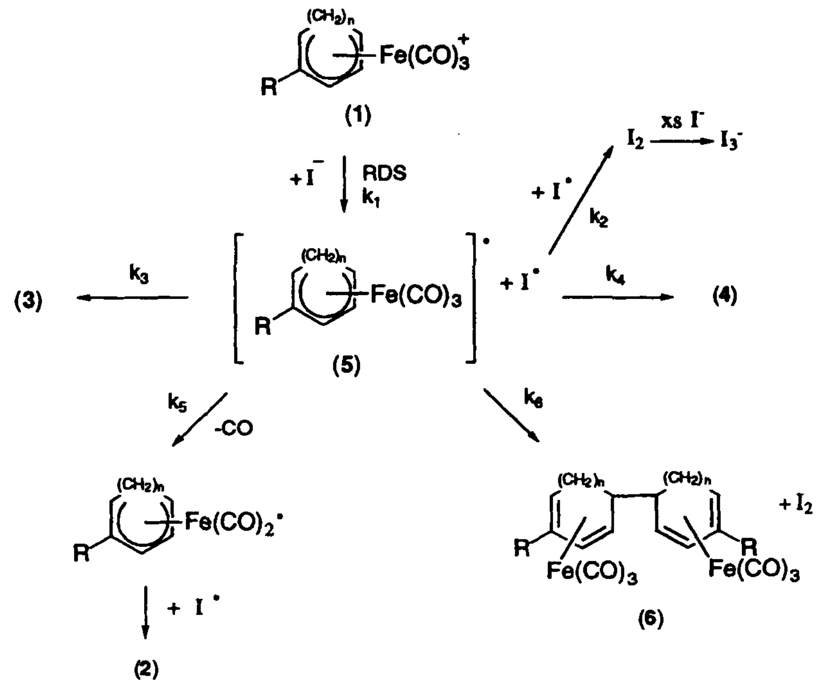
TABLE VI Rate and activation parameters for the reaction of $[(\eta^5\text{-dienyl})Fe(CO)_3]^+$ cations with $[Et_4N][I]$

| *Dienyl* | *Solvent* | $10^2 k_{25.0°C}$ ($mol^{-1} dm^3 s^{-1}$) | $\Delta H^\ddagger$ ($kJ\ mol^{-1}$) | $\Delta S^\ddagger$($J\ K^{-1} mol^{-1}$) |
|---|---|---|---|---|
| $C_6H_7$ | $CH_3NO_2$ | 2.13 | 88.9 (5.9) | −14 (12) |
| 2-$MeOC_6H_6$ | $CH_3NO_2$ | 1.23 | 91.5 (5.2) | −10 (12) |
| | $CH_3CN$ | 2.76 | 80.2 (2.6) | −39 (7) |
| $C_7H_9$ | $CH_3NO_2$ | 0.88 | | |

much more rapid than those reported above in $CH_3NO_2$ and $CH_3CN$. The rapid stopped-flow kinetic results in acetone are summarised in Table VII. Plots of $k_{obs}$ *vs* $[I^-]$ for these reactions of cation (**1a**) with $[Bu_4N][I]$ and NaI are linear and pass through the origin in each case, thereby confirming the rate law (5) as established above in $CH_3NO_2$ and $CH_3CN$ solvents.

## *General Mechanism for the Reaction of Iodide Ion with Tricarbonyl(Dienyl) Iron Cations*

The above spectroscopic and kinetic results may be rationalised in terms of the single electron transfer (SET) mechanism shown in Scheme 3 below



SCHEME 3

TABLE VII Kinetic results for the reaction of $[(\eta^5\text{-}C_6H_7)Fe(CO)_3][BF_4]$ ($[Fe] = 5 \times 10^{-4}$ mol $dm^{-3}$) with $[Bu_4N][I]$ and NaI in acetone

| *Iodide* | *Temp.* (°C) | $10^2$ $[I^-]$ (mol $dm^{-3}$) | 10 $k_{obs}$ ($s^{-1}$) | k ($mol^{-1}$ $dm^3$ $s^{-1}$) |
|---|---|---|---|---|
| $[Bu_4N][I]$ | 25.0 | 1.5 | 0.38 | |
| | | 2.5 | 0.70 | |
| | | 3.5 | 1.20 | |
| | | 5.0 | 1.45 | |
| | | 7.5 | 2.40 | 3.30 (0.22) |
| NaI | 20.0 | 7.6 | 0.52 | |
| | | 10.1 | 0.78 | |
| | | 15.0 | 1.02 | |
| | | 20.0 | 1.40 | 0.68 (0.06) |

(R = H or MeO, n = 1 or 2). This involves initial rate-determining transfer of one electron from the $I^-$ to the dienyl cations, generating the intermediate organometallic radical (**5**) together with the $I^\bullet$ radical. Several pathways may then be followed, involving either the coupling ($k_2$) of two $I^\bullet$ radicals to give $I_2$ (and thus $I_3^-$ in the presence of excess $I^-$) and/or the reaction of (**5**) (or its dissociation product $[(dienyl)Fe(CO)_2]^\bullet$) with $I^\bullet$ to give the observed organometallic products (**2**)–(**4**).

This mechanism contrasts with the classical nucleophilic attack (two electron donation) observed previously[1–7] for the reactions of a wide range of other nucleophiles with dienyl cations of type (**1**). However, such SET processes have been reported, for example, in the reaction of $H^-$ with the $[(\eta^6\text{-}C_6H_6)Fe(Cp)]^+$ cation.[17]

Assuming this SET mechanism, the calculated second order rate constants, k, in Tables IV to VII refer in each case to the initial rate-determining single electron transfer, $k_1$, between $I^-$ and the initial cations (**1**). The redox potentials of the $[(\eta^5\text{-dienyl})Fe(CO)_3]^+$ cations have been recently shown[18] to be relatively insensitive to the nature of the dienyl ligand, *e.g.*, $Ep^{red} = -0.48$ and $-0.52$ V for (**1a**) and (**1b**), respectively. This SET mechanism is therefore consistent with the similar k values observed for $I^-$ attack on cations (**1a**)–(**1c**) in $CH_3NO_2$ ($C_6H_7 \geq 2\text{-}MeOC_6H_6 \geq C_7H_9$; 2.16 : 1.23 : 0.88; Table V). The activation parameters for the reactions of $I^-$ with the $C_6H_7$ and $2\text{-}MeOC_6H_6$ cations in $CH_3NO_2$ solvent are also very similar (Table VI). In contrast, for classical nucleophilic (two-electron) attack by a range of nucleophiles on these cations, a marked decrease in reactivity was observed[1,14] down the series $C_6H_7 > 2\text{-}MeOC_6H_6 \gg C_7H_9$ (*ca* 60 : 5 : 1), which was explained on the basis of the electronic and steric effects of the dienyl ring substituents.

The negative entropies of activation (−10 to −39 $JK^{-1}$ $mol^{-1}$) calculated for the reactions of (**1a**) and (**1b**) with $I^-$ in $CH_3NO_2$ and $CH_3CN$ solvents

(Table VII) are consistent with the bimolecular one-electron transfer ($k_1$). The enthalpies of activation (80–92 kJ mol$^{-1}$, Table VI) are considerably higher than those previously found[1,5] for nucleophilic (two-electron) addition of various nucleophiles to the same cations. The increase in rate for the reaction of (**1b**) with $I^-$ as the solvent is changed from $CH_3NO_2$ to $CH_3CN$ is seen from Table VII to be enthalpy controlled.

Which subsequent pathway in Scheme 3 dominates will depend on the nature of the individual radical intermediates (**5**). The observed product distribution suggests, for example, that the subsequent addition ($k_3$) of $I^\bullet$ at the dienyl ring for the more sterically hindered $C_7H_9$ complex is slower than the alternative CO substitution ($k_5$). Interestingly, spectroscopic studies failed to detect any of the dimeric product (**6**), which may be expected to arise from the coupling ($k_6$) of two dienyl radical intermediate species (**5**). While the $\nu$(CO) bands for dimer (**6**) (2039, 1970 cm$^{-1}$ in $CH_3CN$) are only slightly different to the iodo ring adduct (**3a**), its $^1H$ nmr spectrum is distinctly different, showing upfield resonances compared to (**3a**) (see Experimental).

Interestingly, in contrast to the *in situ* spectroscopic and kinetic studies, when these reactions were conducted on a synthetic scale (under normal laboratory light), the major product with each of the cations (**1a**)–(**1c**) was the corresponding neutral [($\eta^5$-dienyl)Fe(CO)$_2$I] complex (**2**). The absence of the acyl iodide (**4**) product is not surprising since we have found that it decomposes in the presence of light. A possible explanation for the synthetic results is that ring adduct (**3**) formation (path 2 in Scheme 1) is reversible, in contrast to the slower but irreversible formation of (**2**) (path 1). Upon evaporation of the reaction mixture at the end of the synthetic reaction, a lower solubility for the [($\eta^5$-dienyl)Fe(CO)$_2$I] product compared to the ring adduct could then lead to its enhanced yield. This was confirmed in a separate experiment in which a chromatographed sample of pure (**3**) was dissolved in acetone and rotary evaporated to dryness.

## CONCLUSIONS

The reactions between $I^-$ and the cations [($\eta^5$-dienyl)Fe(CO)$_3$]$^+$ (dienyl = $C_6H_7$, 2-MeOC$_6H_6$, or $C_7H_9$) provide a rare example in which attack at each of the hydrocarbon, carbonyl and iron centres may be observed. In the case of the $C_6H_7$ and 2-MeOC$_6H_6$ complexes ring adduct formation dominates, whereas the greater ring crowding in the $C_7H_9$ substrate causes carbonyl ligand substitution to be the dominant pathway. A minor product in $CH_3NO_2$ and acetone solvents is believed to be the novel acyl iodide adduct $[(\eta^5\text{-dienyl})Fe(CO)_2(COI)]$. However, in $CH_3CN$ this latter species is not observed. Another major influence of solvent is the much more rapid reactions observed in acetone compared with $CH_3NO_2$ and $CH_3CN$ as solvents. Conversely, the nature of the counter cation in the iodide salt reagent has only a very minor effect on the reactions.

Detailed kinetic studies of these reactions in various solvents reveal the general second order rate law, $\text{Rate} = k[Fe][I^-]$, in each solvent. In the case of the reaction of $[Et_4N][I]$ with $[(\eta^5\text{-}C_6H_7)Fe(CO)_3]^+$ and $[(\eta^5\text{-2-MeOC}_6H_6)Fe(CO)_3]^+$ in $CH_3NO_2$ and $CH_3CN$, the activation parameters (including negative $\Delta S^\ddagger$ values) and the rate trend $C_6H_7 > 2\text{-MeOC}_6H_6$ are consistent with rate-determining one-electron transfer from $I^-$ to the dienyl rings.

## *Acknowledgements*

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