Journal of Organometallic Chemistry, 131 (1977) 105—111
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ELECTROPHILIC SUBSTITUTION OF METHOXYBENZENES BY PENTADIENYLTRICARBONYLIRON CATIONS

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(Received September 27th, 1976)

Summary

The kinetics of reactions of some open-chain pentadienyltricarbonyliron cations with 1,3-dimethoxy- and 1,3,5-trimethoxybenzene, for which observable equilibria are found, are discussed. These reactions contrast with those previously reported, which go essentially to completion.

Introduction

Previously we reported kinetic studies of the attack of several open-chain pentadienyltricarbonyliron cations (I) on 1,3-dimethoxybenzene [1]. We obtained evidence that the reactions proceed via an active intermediate, which we suggest is the *trans* cation II. Kane-Maguire and coworkers have studied similar electrophilic aromatic substitutions by the cyclohexadienyltricarbonyliron cation [2,3,4]. This species reacts more slowly than the acyclic cations, probably because it cannot form a *trans* ion intermediate.

Results and discussion

In contrast to the reactions of other open-chain pentadienyltricarbonyliron cations previously reported [1], which go to completion, the reaction of 1,5-diphenylpentadienyltricarbonyliron tetrafluoroborate (Ia) with an excess of 1,3-dimethoxybenzene in nitromethane tends to an equilibrium position. Approximate values of the pseudo-first order rate constants for the forward reaction $(k_f)_{obs}$ were obtained by plotting $\ln a/(a-x)$ against time for the cation, and taking the initial slope, that is, when the effect of the back reaction is insignificant. Good agreement was obtained with the values of $(k_f)_{obs}$ calculated using the integrated form of the rate equation for a reversible reaction of the type $A \underset{k_b}{\overset{(k_f)_{obs}}{\rightleftharpoons}} B + C$ [5],

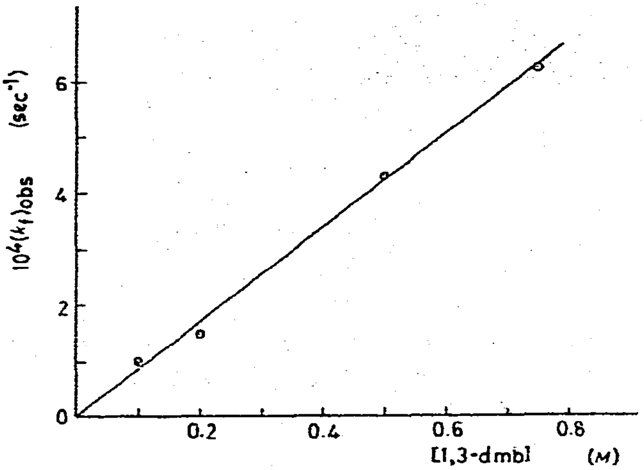


Fig. 1. Reaction of 1,5-diphenylpentadienyltricarbonyliron tetrafluoroborate (Ia) with 1,3-dimethoxybenzene in nitromethane at 25.0 ± 0.1°C.

i.e.

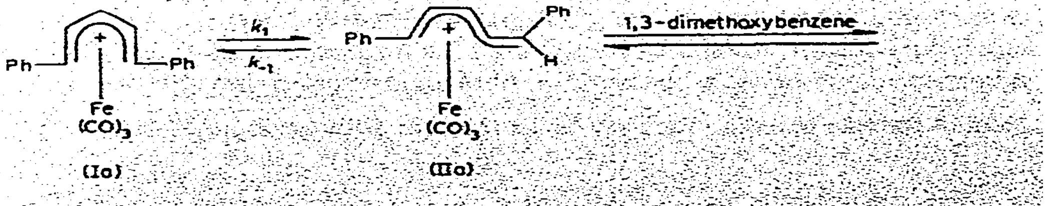
$$\ln\frac{A_0^2 - A_eA}{(A - A_e)A_0} = (k_f)_{obs}\left(\frac{A_0 + A_e}{A_0 - A_e}\right)\cdot t, \qquad (1)$$

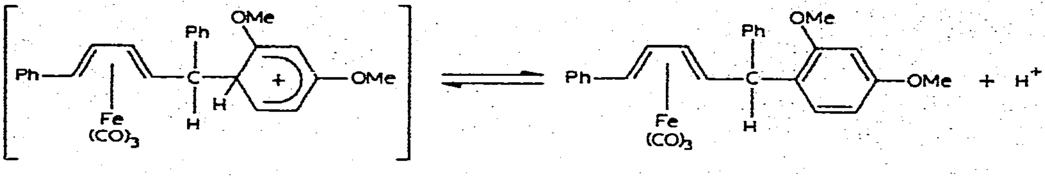
where A_0 and A_e are the concentrations of A initially and at equilibrium respectively and A its concentration after time t. A computer program was used which varied iteratively the position of equilibrium to give the best least squares fit for a linear plot of the left hand side of eq. 1 against time. The equilibrium positions found by this method were close to those observed experimentally.

A plot of the pseudo first order rate constants $(k_f)_{obs}$ against the concentration of 1,3-dimethoxybenzene (1,3-dmb) is shown in Fig. 1. The linear relationship indicates that the forward reaction obeys overall second order kinetics, first order in each reactant with $(k_2)_f = 8.7 \pm 1.0 \times 10^{-4}$ dm^3 mol^{-1} sec^{-1}.

The ^{1}H NMR spectrum of the product from this reaction is consistent with a *trans-trans*-structure [6]. Although the form of the rate equation in this case does not allow one to distinguish between direct attack by the *cis* cation Ia followed by isomerisation of the product and a pathway via a *trans* intermediate IIa, we consider the latter to be more likely. Reaction of Ia with methanol gives a methyl ether VI which has a similar NMR spectrum to that of IVa. In all known cases the products obtained by attack of methanol on open-chain pentadienyltricarbonyliron cations have the *trans-trans* structure, formed, it is proposed, via a *trans* ion intermediate [7].

The following mechanism is therefore suggested:





(IIIa) (IVa)

The tertiary carbon atom in IVa is attached to three strongly charge stabilising groups; 2,4-dimethoxyphenyl, phenyl and (diene)tricarbonyliron. Whereas the analogous reactions of 1,5-dimethyl- and 1-methyl,5-phenylpentadienyltricarbonyliron tetrafluoroborates with 1,3-dmb go essentially to completion [1], replacement of methyl by phenyl at the reaction centre enhances the reverse reaction, so that an equilibrium is now observed.

The reactions of 1-methyl-5-phenyl-, 1-methyl-5-*p*-methoxyphenyl-, and 1,5-dimethylpentadienyltricarbonyliron tetrafluoroborates (Ib, Ic and Id respectively) with 1,3,5-trimethoxybenzene (tmb) were also found to give observable equilibria, in contrast to the reaction of these salts with 1,3-dimethoxy- and 1,2,4-trimethoxybenzenes [8,9]. For Ib and Id in nitromethane at 25°C the equilibrium position is reached within 10—15 min; in the latter case reliable kinetic data were not obtained, because the reaction was too fast. For Ib and Ic the results were calculated as described above. In each case the pseudo first order rate constant for the forward reaction does not vary linearly with the concentration of 1,3,5-tmb, but tends to a limit at high tmb concentration (Fig. 2). This implies the formation of a reactive intermediate, the *trans* ion, the rate of formation of which from the *cis* ion is comparable with the rate at which it reacts with the aromatic compound [1].

It is possible that, in addition, some direct attack by the *cis* cation on the reactive substrate 1,3,5-tmb occurs. Only one product, however, was isolated from the reaction of Ib with 1,3,5-tmb in dichloromethane in the presence of sodium

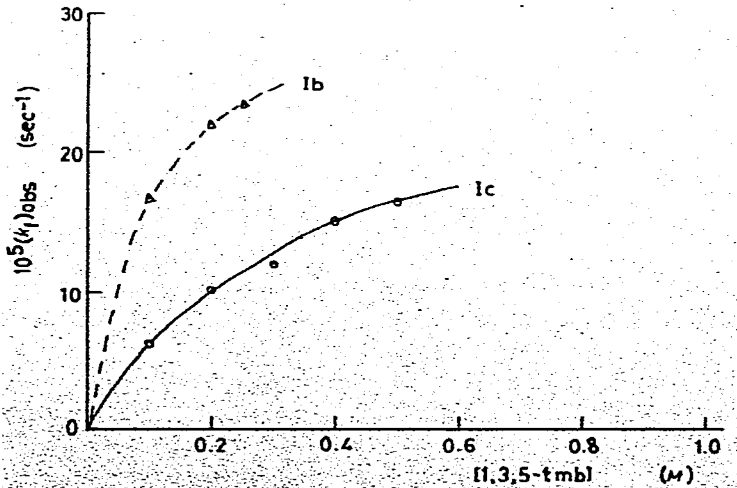


Fig. 2. Reactions of Ib (Δ) and Ic (○) with 1,3,5-trimethoxybenzene in nitromethane at 25.0 ± 0.1°C.

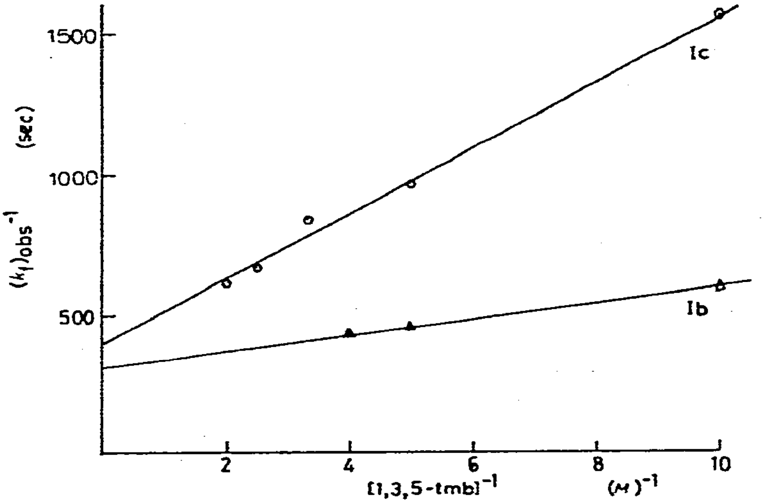
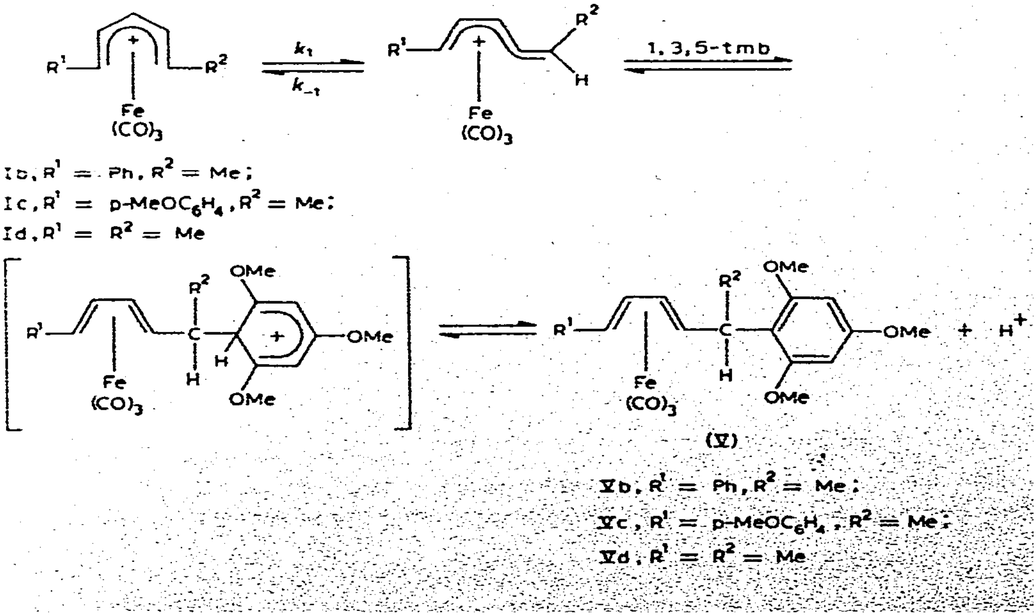


Fig. 3. Reciprocal plot of pseudo first order rate constants for the forward reactions of Ib (△) and Ic (○) with 1,3,5-trimethoxybenzene.

bicarbonate. This was shown to have the *trans-trans* structure. If the reactions go entirely via the *trans* ion there will be a limiting maximum rate, independent of the strength of the nucleophile, which is the rate of formation of the *trans* ion from the *cis*. This can be evaluated from the intercept in the plot of $1/(k_f)_{obs}$ vs $1/c_{ArH}$, which is equal to $1/k_1$, where k_1 is the rate constant for this process (Fig. 3). The values of k_1 for Ib have been found to be 2.5×10^{-3} sec^{-1}, and for Ic 1.6×10^{-3} sec^{-1} [9], in fair agreement with those obtained (3.1×10^{-3} sec^{-1} and 2.4×10^{-3} sec^{-1} respectively) from these reciprocal plots for the 1,3,5-tmb reactions. Semi-quantitative measurements also indicate that methanol attacks Ib at about this limiting rate.



Ib, R^1 = Ph, R^2 = Me;
Ic, R^1 = p-MeOC$_6$H$_4$, R^2 = Me;
Id, R^1 = R^2 = Me

+ H$^+$

(V)

Vb, R^1 = Ph, R^2 = Me;
Vc, R^1 = p-MeOC$_6$H$_4$, R^2 = Me;
Vd, R^1 = R^2 = Me

Experimental

Purification of reagents and solvents

Nitromethane (B.D.H.) was purified by the method of Olah [10]. 1,3-Dimethoxybenzene (Aldrich) was refluxed over sodium metal for 2 h and distilled under reduced pressure through a 25 cm Vigreux column, b.p. 85°C/6.5 mmHg. 1,3,5-Trimethoxybenzene (Aldrich) was dissolved in diethyl ether and the solution shaken with aqueous sodium hydroxide. The ether solution was dried ($MgSO_4$) the ether removed and the residue crystallised from petroleum ether (b.p. 40—60°C), m.p. 55°C (Lit. [11] 54—55°C).

Kinetic procedure

Method A was used for reactions of half-life less than about 30 min, method B when the half-life was significantly longer. Care was taken throughout to exclude moisture.

Method A. Fresh solutions of the reactants were prepared in dry nitromethane. An aliquot (4 cm^3) of each reactant was pipetted into a separate reaction vessel. The reaction vessel consisted of a boiling tube with a Subaseal stopper and having a side arm closed by a greaseless (Rotaflow) tap. The reactant solutions were degassed by several freeze, pump, thaw cycles, placed in the thermostat bath and dry nitrogen admitted. When the solutions had attained thermal equilibrium they were mixed under nitrogen using an all glass syringe fitted with an 18 cm long stainless steel needle. The whole of the arene solution was drawn into the syringe by placing the tip of the needle into a small indentation at the base of the vessel. This solution was injected into the vessel containing the iron complex and the contents thoroughly mixed. A portion of this solution (ca. 4 cm^3) was used to rinse out the first vessel which had contained the arene. The mixing was usually complete within 90 sec. A portion of the reaction mixture was then transferred to a constant temperature infra-red cell (Beckmann-RIIC FHO 1) fitted with calcium fluoride windows. (KBr plates cannot be used as they react with pentadienyltricarbonyliron tetrafluoroborates). This cell was placed in a stainless steel jacket through which water was circulated from a constant temperature bath, set so that the temperature of the cell was 25.0 ± 0.1°C (determined by a thermistor). The whole jacket was insulated by a 20 cm layer of polystyrene foam. To prevent excessive heating of the cell contents by radiation, a calcium fluoride filter was attached to the front of the unit. The cell was filled through stainless steel tubes (22 gauge) with Luer fittings which could be attached directly to a syringe.

The reactions were followed by scanning the range 2200—1900 cm^{-1} using a Perkin—Elmer 177 double beam spectrometer. The concentration of the pentadienyltricarbonyliron complex was determined directly from the intensity of the 2105 cm^{-1} band. All the iron complexes obeyed Beer's Law. A solution of the arene in nitromethane at the same concentration as in the reaction was used as the reference.

Method B. Method A had the disadvantage that air could leak into the cell over an extended period. For long experiments a sampling technique was used. An aliquot (10 cm^3) of each reactant solution was pipetted into a reaction vessel, degassed, and nitrogen admitted. When the solution had attained thermal equilibrium, samples were removed at intervals by syringe and analysed by infrared spectroscopy in a cell fitted with calcium fluoride windows.

Preparation of complexes

1,5-diphenylpentadienyltricarbonyliron tetrafluoroborate (Ia). $Fe_2(CO)_9$ (20 g) was added to a solution of 1,5-diphenylpenta-2,4-dien-1-ol [12] (10 g) in boiling diethyl ether (150 cm^3) and the mixture refluxed under nitrogen with stirring for 4 h. Ether was removed and the brown residue was dissolved in propanoic anhydride (50 cm^3) and cooled to 0° C. An ice-cold solution of fluoroboric acid (6 cm^3, 40%) in propanoic anhydride (30 cm^3) was added dropwise with stirring. An orange solid separated and more was obtained by addition of diethyl ether. The precipitate was filtered off and recrystallized from nitromethane/ether to give the product (7.1 g, 38%). Found: C, 54.31; H, 3.47. $C_{20}H_{15}BF_4FeO_3$ calcd.: C, 53.87; H, 3.39(%).

1-Methyl-5-phenylpentadienyltricarbonyliron tetrafluoroborate (Ib) was prepared from *ψ-exo*-(6-phenyl-hexa-3,5-dien-2-ol)tricarbonyliron [13] by a modification of the method of Mahler and Pettit [7]. Found: C, 46.76; H, 3.26; B, 2.78. $C_{15}H_{13}BF_4FeO_3$ calcd.: C, 46.92; H, 3.42; B, 2.82(%).

1-Methyl-5-p-methoxyphenylpentadienyltricarbonyliron tetrafluoroborate (Ic). Hexa-2,4-dien-1-al (9.6 g) in diethyl ether (100 cm^3) was added dropwise to a solution of *p*-anisylmagnesium bromide (from 3.0 g Mg and 23.4 g *p*-bromoanisole in 100 cm^3 ether) cooled in ice. After $1\frac{1}{2}$ h saturated ammonium chloride (250 cm^3) was added slowly with stirring. The ether layer was separated and the aqueous layer extracted twice with ether. From the combined, dried ether extracts crude 6-*p*-methoxyphenylhexa-3,5-dien-2-ol was obtained as an orange oil, characterised by ^{1}H NMR. This oil was dissolved in ether (250 cm^3) and treated with $Fe_2(CO)_9$ (20 g) as described above for Ia. By reaction with HBF_4 in propanoic anhydride the desired product (3.0 g) was obtained. Found: C, 46.53; H, 3.85. $C_{16}H_{15}BF_4FeO_3$ calcd.: C, 46.42; H, 3.65(%).

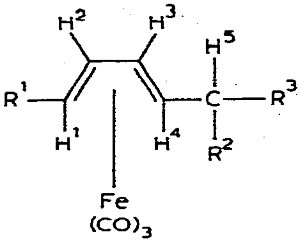
1-(2,4-dimethoxyphenyl),1,5-diphenyl-trans,trans-penta-2,4-diene tricarbonyliron (IVa). 1,5-Diphenylpentadienyltricarbonyliron tetrafluoroborate (1.0 g, 2.2 mmol) was added to a solution of 1,3-dimethoxybenzene (0.3 g, 2.2 mmol) in dichloromethane (25 cm^3). Sodium hydrogen carbonate (1.0 g) was added and the mixture degassed. The suspension was stirred for 6 days in the dark under nitrogen and then filtered. The filtrate was evaporated to leave a solid which was washed with cold pentane (20 cm^3) and recrystallised from petroleum ether/benzene (2 : 1). Yield 0.60 g. (55%), m.p. 160°C dec. Found: C, 67.55; H, 5.11. $C_{28}H_{24}FeO_5$ calcd.: C, 67.75; H, 4.87 (%).

1-Methoxy-1,5-diphenyl-trans,trans-penta-2,4-dienetricarbonyliron (VI). Ia (1.08 g) was added to Analar methanol (30 cm^3) in the presence of excess sodium hydrogen carbonate (ca. 1 g). After 5 min the sodium salts were filtered off and the filtrate evaporated to dryness. The residue was extracted with hot cyclohexane, filtered and evaporated to give yellow needles, (0.67 g, 71%) m.p. 99.5—100.5°C. Found: C, 64.09; H, 4.88. $C_{21}H_{18}FeO_4$ calcd.: C, 64.64; H, 4.65(%).

2-(1,3,5-trimethoxyphenyl)-6-phenyl-trans,trans-hexa-3,5-diene tricarbonyliron (Vb). This was prepared similarly to IVa from Ib (1.88 g, 4.9 mmol) and 1,3,5-trimethoxybenzene (0.80 g, 4.9 mmol). The crude reaction product (1.7 g) had m.p. 138—145°C, and its ^{1}H NMR spectrum showed it to be essentially pure. It showed only one spot on TLC on silica gel (10% ether in cyclohexane). After recrystallization from petroleum ether/benzene (3 : 1) 1.45 g. (66%), m.p. 154—5°C were isolated. Found: C, 62.10; H, 5.22. $C_{24}H_{24}FeO_6$ Calcd.: C, 62.08; H, 5.21(%).

TABLE 1

^{1}H NMR CHEMICAL SHIFTS (δ) FOR SUBSTITUTED DIENE TRICARBONYLIRON COMPLEXES [a]



Compound b	R^1	H^1	H^2	H^3	H^4	H^5	R^2	R^3
IVa	7.3m	2.16d	5.72dd	5.50dd	1.96dd	4.33d	7.3m	6.5s(2H) 7.3s(1H) 3.88s(OCH_3)
VI	7.45s	2.15d	5.7m	5.7m	1.62dd	4.06d	7.25s	3.25(OCH_3)
Vb	7.33s	2.05d	5.71dd	5.33dd	2.1m	3.40m	1.47d(CH_3)	6.25s(2H) 3.83s(OCH_3)

[a] Coupling constants $J(1,2)$ 9—10, $J(2,3)$ 5, $J(3,4)$ 8—9, $J(4,5)$ 7—8 Hz in all cases. [b] IVa, R^1 = Ph, R^2 = Ph, R^3 = 2,4-dimethoxyphenyl; VI, R^1 = Ph, R^2 = Ph, R^3 = OMe; Vb, R^1 = Ph, R^2 = Me, R^3 = 2,4,6-trimethoxyphenyl.

^{1}H NMR spectra, given in Table 1, were measured at 100 MHz in deuterochloroform using a Varian HA 100 spectrometer.

Acknowledgements

We thank the S.R.C. for support and for the award of a maintenance grant (to K.A.H.).

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