

On the Reactivity of Tricarbonyl(1—4- η -cyclohepta-1,3,5-triene)iron Derivatives: C—C Bond Formation of Tricarbonyl(cycloheptatrienide)irons with 2-Chlorotropone

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Tricarbonyl(1—4- η -cyclohepta-1,3,5-triene)iron derivatives $[(RC_7H_7)Fe(CO)_3]$ (R = H, OMe, CN, and Ph) (**4a–d**) have been prepared and a study made of the nucleophilic attack of 2-chlorotropone by their corresponding anions. The tricarbonyl(cycloheptatrienide)iron and tricarbonyl(methoxycycloheptatrienide)iron undergo the reaction to give tricarbonyl[1—4- η -7-(2-oxocyclohepta-1,3,5-trienyl)cyclohepta-1,3,5-triene]iron (**7a**) and tricarbonyl[1—4- η -6-methoxy-7-(2-oxocyclohepta-1,3,5-trienyl)cyclohepta-1,3,5-triene]iron (**7b**), respectively. In contrast, tricarbonyl(cyanocycloheptatrienide)iron reacted with 2-chlorotropone to afford tricarbonyl[1—4- η -6-cyano-7-(2-oxocyclohepta-1,3,5-trienyl)cyclohepta-1,3,5-triene]iron (**7c**) and tricarbonyl[1—4- η -5-cyano-7-(2-oxocyclohepta-1,3,5-trienyl)cyclohepta-1,3,5-triene]iron (**9c**) in a ratio of (**7c**)/(**9c**) = 1:5.6. Similarly, tricarbonyl(phenylcycloheptatrienide)iron with 2-chlorotropone also affords two products, tricarbonyl[1—4- η -6-phenyl-7-(2-oxocyclohepta-1,3,5-trienyl)cyclohepta-1,3,5-triene]iron (**7d**) and tricarbonyl[1—4- η -2-phenyl-7-(2-oxocyclohepta-1,3,5-trienyl)cyclohepta-1,3,5-triene]iron (**10d**), in a ratio of (**7d**)/(**10d**) = 3:1. The selective formation of (**7b**) and the product ratios of (**7c**):(**9c**) and (**7d**):(**10d**) are discussed on the basis of the electronic and steric factors of the substituent in the formally unco-ordinated allyl anion on the cycloheptatrienide ring. The stereochemistry of the tropone nucleus at C-7 is deduced to be *exo* to the $[Fe(CO)_3]$ entity on the basis of 1H n.m.r. spectral results. The products (**7a, b, d**) are easily decomplexed by trimethylamine oxide to give 7-(2-oxocyclohepta-1,3,5-trienyl)- and 1-substituted 7-(2-oxocyclohepta-1,3,5-trienyl)cyclohepta-1,3,5-triene derivatives in good yields.

Because of their instability and antiaromatic character, neither the free cycloheptatrienide ion¹ nor 1*H*-1,2-diazepine² are easily prepared; they have, therefore, been little used in organic synthesis. Previously, we have studied the reaction of tricarbonyl(4—7- η -1*H*-1,2-diazepine)iron (**1**)³ with activated acetylenes or with 2-halogenotropones to provide a convenient method for the preparation of novel 1-vinyl-1*H*-1,2-diazepine derivatives⁴ or three isomers of 1-(2-oxocyclohepta-1,3,5-trienyl)-1*H*-1,2-diazepine⁵ in good yields. Similarly, the tricarbonyl(cycloheptatrienide)iron (**2**), which is isoelectronic with (**1**), provides an example of the stability imparted upon a reactive ligand by the $[Fe(CO)_3]$ unit.⁶ The anion (**2**) can be prepared easily by the deprotonation of tricarbonyl(1—4- η -cyclohepta-1,3,5-triene)iron with several bases [$BuLi$ at $-78^\circ C$,^{6a} Bu^tOK ,⁷ $(Me_3Si)_2NNa$,⁸ and KH ⁹ at room temp.].

There are two bonding alternatives that can be written for the anion (**2**) (see Figure). In structure (A), the $[Fe(CO)_3]$ is

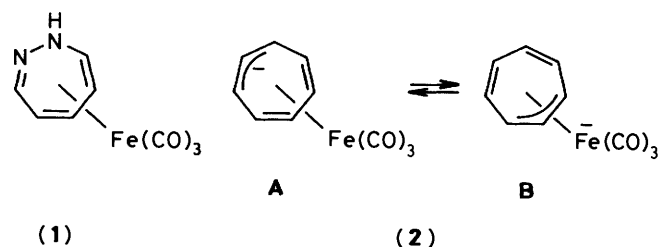


Figure.

bonded to a η^4 -diene unit, and the negative charge is formally located on the allyl part of the seven-membered ring. In structure (B), the $[Fe(CO)_3]$ is bonded to a η^3 -allyl unit carrying the negative charge, the diene unit remaining unco-

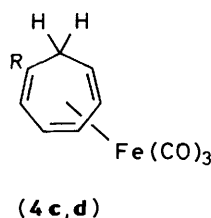
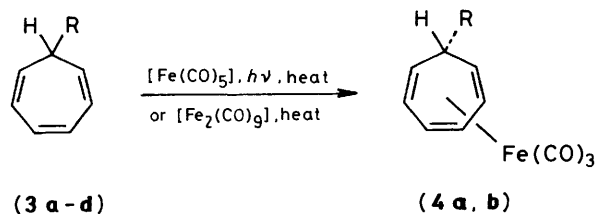
ordinated. A recent X-ray crystallographic study of $[C_7H_7Fe(CO)_3]^-$ stabilized with $[(C_6H_6)_4As]^+^{10}$ and the molecular orbital calculation have revealed that structure (B) is the preferred bonding mode of the anion.¹¹ The small energy difference (14 kJ mol^{-1}) between the two co-ordinated modes accounts for the observed high fluxionality of (**2**).⁹ Thus, the anion (**2**) can be seen as an ambident nucleophile reacting both at the iron centre and/or at the ring carbon atom. Indeed, the anion (**2**) reacts with transition-metal halides at the iron centre to give a complex of the type $[C_7H_7Fe(CO)_3M(CO)_y]$ (M = Mn, Re, $y = 3$; M = Rh, $y = 2$).¹² In contrast, the reaction of the anion (**2**) with Me_3SiCl , Me_3GeBr , Ph_3GeBr ,^{9,13} $[C_7H_7M(CO)_3]^+$ (M = Fe,^{14a} M = Cr, Mo, W^{7,14b}), chloroformates,^{7,15} and $PhCOCl$ ¹⁶ proceeds by ring carbon attack. No study of the behaviour of the anion (**2**) bearing a substituent on the cycloheptatrienide ring has, however, been reported.

In connection with our previous studies,^{4,5} we wished to introduce a cycloheptatriene ring into the tropone nucleus. To both achieve this and to gain insight into the substituent effect on the behaviour of the tricarbonyl(cycloheptatrienide)iron, we have investigated the preparation of tricarbonyl(1—4- η -cyclohepta-1,3,5-triene)iron derivatives and the reaction of their anions with 2-chlorotropone.

Results and Discussion

Initial experiments were conducted with cyclohepta-1,3,5-triene (**3a**) and 7-methoxycyclohepta-1,3,5-triene (**3b**). In these, compound (**3a**) was shown to react readily with $[Fe(CO)_5]$ at $115^\circ C$ under photoirradiation with a fluorescent lamp to give (**4a**) (46%) as described in the literature,¹⁷ whilst compound (**3b**) reacted with $[Fe_2(CO)_9]$ in ether under reflux to give tricarbonyl(1—4- η -7-methoxycyclohepta-1,3,5-triene)iron (**4b**) (30%).¹⁸ Interestingly, the reaction of the substituted cyclo-

heptatrienes (**3c**) and (**3d**) with $[\text{Fe}(\text{CO})_5]$ at 115°C under photoirradiation gave tricarbonyl[1—4- η -6-cyanocyclohepta-1,3,5-triene]iron (**4c**) and tricarbonyl[1—4- η -6-phenylcyclohepta-1,3,5-triene]iron (**4d**) in 28 and 20% yields, respectively, further demonstrating the easy hydrogen migration in these systems under the reaction conditions (Scheme 1). Although the



a, R = H ; **b**, R = OMe ; **c**, R = CN ; **d**, R = Ph

Scheme 1.

^1H and ^{13}C n.m.r. spectra of (**4a**) have been reported,¹⁹ this is not so for (**4b**).¹⁸ Thus, the structures of (**4b**—**d**) were unequivocally assigned on the basis of their ^1H n.m.r. and ^{13}C n.m.r. spectra, which are summarized in Table 1. Appearance of the 7-H signal at highfield (δ 3.25) suggests that the methoxy group of (**4b**) is *endo* to the $[\text{Fe}(\text{CO})_3]$ group.

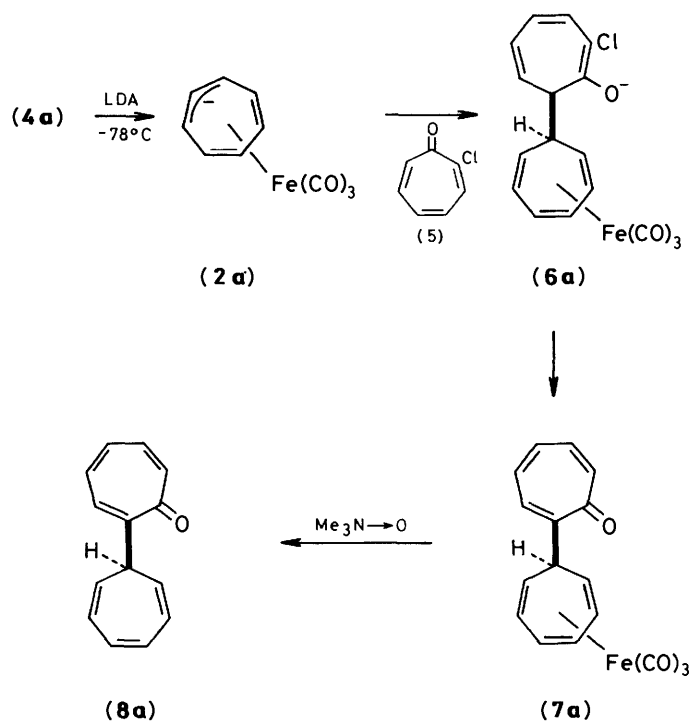
Complex (**2a**), generated by treatment of (**4a**) with LDA (lithium di-isopropylamide) at -78°C , was treated with 2-chlorotropone (**5**) at -78°C to give tricarbonyl[1—4- η -7-(2-oxocyclohepta-1,3,5-trienyl)cyclohepta-1,3,5-triene]iron (**7a**) (96%) which was identified on the basis of its analytical and spectroscopic data. The ^{13}C n.m.r. spectrum, summarized in Table 2, was assigned according to the selective decoupling technique and supported the η^4 -cycloheptatriene structure (Scheme 2). Although it has been suggested that unambiguous assignment of stereochemistry at C-7 on the basis of the ^1H n.m.r. spectrum of the complexed η^4 -cycloheptatriene is not feasible,^{9,16} X-ray crystallographic studies of the molecule seem not to support this view.^{9,16} Thus, the 7-H signal at δ 4.37 (td, J 4.5, 1.5 Hz) suggests that the tropone nucleus was introduced selectively on the *exo* face of the co-ordinated ring, possibly as a result of steric hindrance from the $[\text{Fe}(\text{CO})_3]$ group. Since nucleophilic substitution of 2-chlorotropone had been shown to take place at C-7 to give 2-substituted tropones, (**7a**) should be formed *via* (**6a**) in a similar way.²⁰ Treatment of (**7a**) with anhydrous trimethylamine oxide in dry acetone²¹ at 50°C then gave a good yield of 7-(2-oxocyclohepta-1,3,5-trienyl)cyclohepta-1,3,5-triene (**8a**), the structure of which was assigned on the basis of spectroscopic data.

Similarly, the reaction of (**4b**) with LDA and treatment of the resulting anion with (**5**) gave as the sole product tricarbonyl[1—4- η -6-methoxy-7-(2-oxocyclohepta-1,3,5-trienyl)cyclohepta-1,3,5-triene]iron (**7b**) (56%), the structure of which was established on the basis of the similarity of its ^{13}C n.m.r. (Table 2) and ^1H n.m.r. spectra with those of (**7a**).

Table 1. ^{13}C Chemical shifts (p.p.m.) of the tricarbonyl(cycloheptatriene)iron derivatives (**4a**—**d**) in CDCl_3 ^a

Compd.	C-1	C-2	C-3	C-4	C-5	C-6	C-7	Remaining absorption
(4a) ^b	55.9	88.3	93.4	60.2	128.4	125.4	30.7	
(4b)	63.4	83.2	94.0	54.0	129.5	125.4	71.7	OMe: 56.5
(4c)	57.7	88.5	94.6	52.3	146.8	107.1	31.5	CN: 119.6
(4d)	59.3	87.9	92.5	56.3			32.4	C-5, C-6, Ph: 124.9, 126.6, 128.1, 135.5, 141.5

^a Tetramethylsilane as internal standard. ^b The spectrum has been recorded in $[\text{C}_2\text{H}_5]_2\text{S}$ (ref. 18).



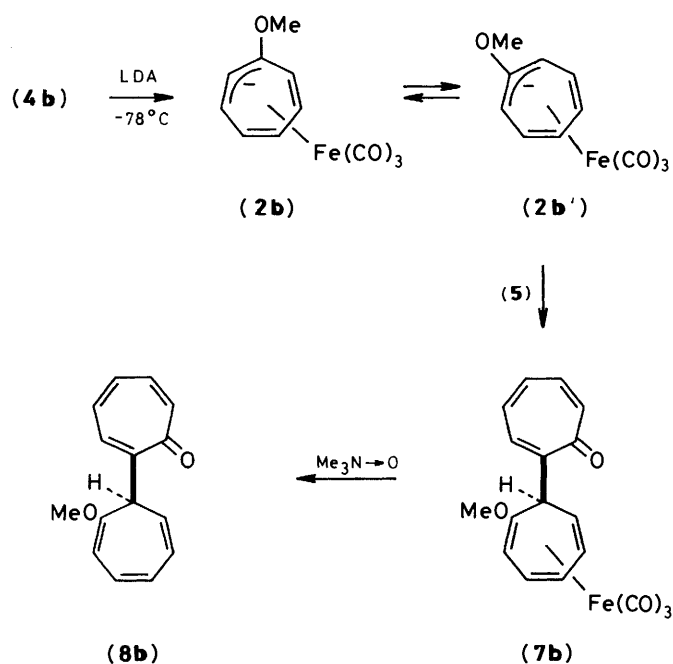
Scheme 2.

Appearance of the 7-H signal at δ 4.40 as a doublet (J 5.1 Hz) suggests that the methoxy group is located at the 6-position, and that the tropone nucleus was introduced from the *exo* face as depicted (Scheme 3).¹⁶ In this reaction, the initially formed anion (**2b**), which has an electron releasing methoxy group at the terminal carbon atom of the allyl anion, is presumably less stable than (**2b'**) both electronically and sterically. In (**2b'**), the methoxy group is located at the cross-conjugating position and remote from the $[\text{Fe}(\text{CO})_3]$ entity. Thus, since the equilibrium between (**2b**) and (**2b'**) is probably shifted in favour of the latter, the tropone nucleus could be introduced exclusively into (**2b'**) to give (**7b**). Decomplexation of the latter by trimethylamine oxide then afforded, in good yield (**8b**),²¹ the structure of which was unequivocally assigned on the basis of spectroscopic results. Appearance of the 7-H signal at lower field (δ 4.44) indicates that a conformer with an axial 7-(2-oxocycloheptatrienyl) group is more stable than the corresponding equatorial compound, in which the methoxy group and 2-oxocycloheptatrienyl group are subject to nonbonded interaction.²²

Table 2. ^{13}C Chemical shifts (p.p.m.) of the tricarbonyl[(2-oxocyclohepta-1,3,5-trienyl)cycloheptatriene]iron derivatives (**7a—d**) and (**9c, d**) in CDCl_3 ^a

Compd.	Tropone	C-1	C-2	C-3	C-4	C-5	C-6	C-7	Remaining absorption
(7a)	132.8, 133.2, 134.0, 135.1, 140.0, 158.6, 185.7	63.2	86.9	94.2	55.1	130.2	127.9	45.1	
(7b)	131.7, 133.3, 134.2, 135.2, 140.1, 156.8 or 158.3, 185.1	60.6	85.3	91.8	54.9	100.2	156.8 or 158.3	46.9	OMe: 54.4
(7c)	132.5, 133.7, 134.3, 135.6, 140.4, 155.1, 185.2	61.9	87.4	95.7	52.2	149.6	110.2	47.1	CN: 119.0
(9c)	133.5, 133.6, 134.2, 135.6, 140.3, 155.4, 185.0	60.7	88.6	93.2	51.2	117.1	141.4	45.3	CN: 118.9
(7d)	132.0, 133.4, 134.3, 135.4, 140.3, 155.4, 185.0	63.3	86.4	93.8	56.6	130.4	138.2 or 140.7	46.2	Ph: 125.0, 126.7, 128.1, 138.2, or 140.7
(10d)	132.0, 133.4, 134.3, 135.4, 140.0, 159.4, 185.6	61.1	104.9	94.0	50.9	130.6	128.0 or 128.1	44.9	Ph: 127.0, 128.0 or 128.1, ^b 128.1, 140.2

^a Tetramethylsilane as internal standard. ^b Overlapping two carbon signal.

**Scheme 3.**

Reaction of (**4c**) with LDA and treatment of the resulting anion with 2-chlorotropone (**5**) at -78°C gave tricarbonyl[1—4- η -6-cyano-7-(2-oxocyclohepta-1,3,5-trienyl)cyclohepta-1,3,5-triene]iron (**7c**) and tricarbonyl[1—4- η -5-cyano-7-(2-oxocyclohepta-1,3,5-trienyl)cyclohepta-1,3,5-triene]iron (**9c**) in 10 and 56% yields, respectively. The structures of these were established on the basis of ^{13}C n.m.r. (Table 2) and ^1H n.m.r. spectral evidence. In particular, the signals of 7-H of (**7c**) and (**9c**) appearing at δ 4.43 (dd, J 4.8, 1.3 Hz) and 4.47 (dd, J 4.6, 4.4 Hz), respectively, are suggestive of the position of the cyano group and the stereochemistry at C-7 as depicted in Scheme 4. Similarly, the reaction of (**4d**) with LDA and treatment of the resulting anion with 2-chlorotropone (**5**) gave tricarbonyl[1—4- η -6-phenyl-7-(2-oxocyclohepta-1,3,5-trienyl)cyclohepta-1,3,5-triene]iron (**7d**) (74%) and tricarbonyl[1—4- η -2-phenyl-7-(2-oxocyclohepta-1,3,5-trienyl)cyclohepta-1,3,5-triene]iron (**10d**) (23%). Although compound (**7d**) was isolated pure after recrystallization, neither t.l.c. nor repeated recrystallizations gave a pure sample of (**10d**). However, ^{13}C n.m.r. and ^1H n.m.r. spectral results for the latter were obtained by recording the

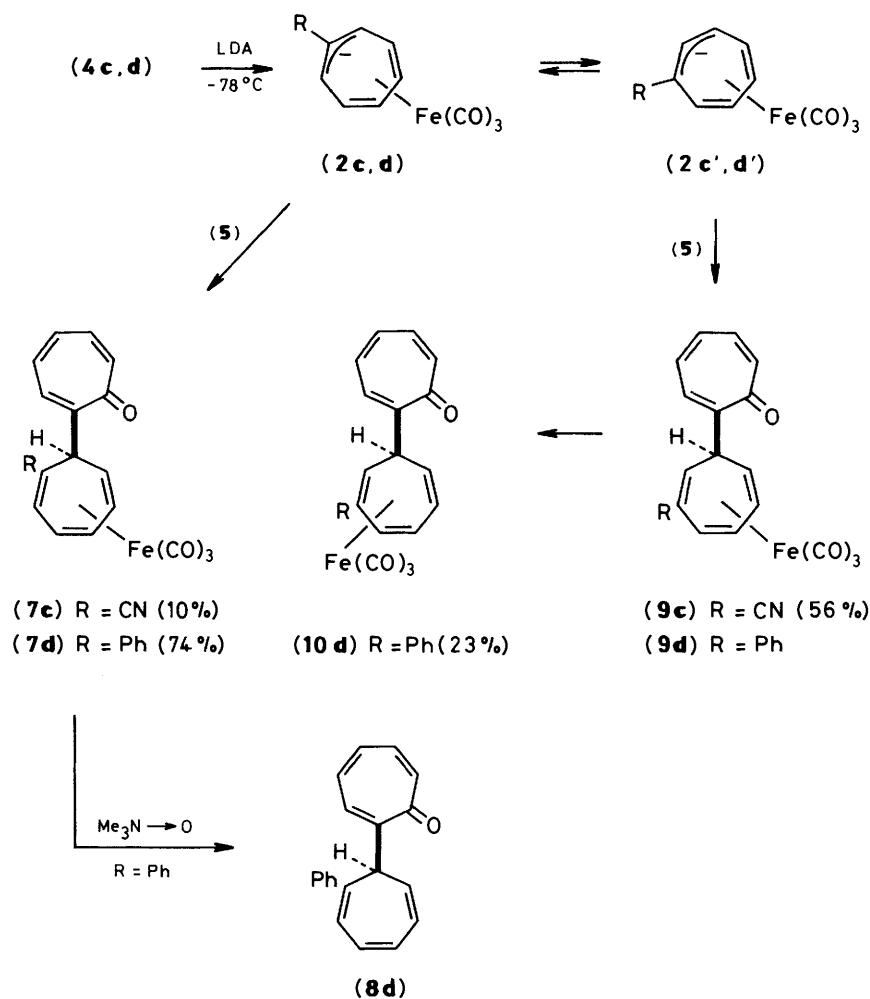
spectra for the mixture of (**7d**) and (**10d**). The signals at δ 5.06 (d, J 5.0 Hz) and δ 4.54 (ddd, J 4.8, 4.6, and 1.5 Hz) were assigned to the 7-H for each of (**7d**) and (**10d**). The chemical shifts and the coupling constants are suggestive of the position of the phenyl groups and the stereochemistry at C-7 as depicted in Scheme 4. The ^{13}C n.m.r. spectrum, which is summarized in Table 2, indicates that the phenyl group of (**10d**) was attached to the η^4 -diene unit. On decomplexation, the cyano compound (**9c**) afforded only tarry materials, while compound (**7d**) afforded (**8d**) in good yield. For the latter, appearance of the 7-H signal at lowfield (δ 5.27) indicates that a conformer with an axial 7-(2-oxocyclohepta-1,3,5-trienyl) group is more stable, as in the case of (**8b**).

With respect to the substituent effect of the electron-withdrawing group on the intermediate, the anion (**2c'**) is probably more stable electronically than (**2c**) since its cyano group is fully conjugated with the allylic anion moiety. Thus, the equilibrium between (**2c**) and (**2c'**) would be shifted in favour of the latter, with (**9c**) being formed preferentially over (**7c**). Although, the phenyl substituted anion (**2d'**) seems similarly to be more stable than (**2d**), formation of (**7d**) predominated over (**10d**) in the reaction of (**4d**), probably as a result of steric hindrance between the phenyl and $[\text{Fe}(\text{CO})_3]$ groups. Thus, since the bulky phenyl group in (**2d'**) is in the vicinity of the $[\text{Fe}(\text{CO})_3]$ steric hindrance is greater than that of (**2d**). This would result in a shift in the equilibrium between (**2d**) and (**2d'**) in favour of the former and thus (**7d**) would be formed preferentially over (**10d**). The product (**10d**) probably derives from (**9d**), the ligand migration of which is not reasonably explained.

In conclusion, the reaction of tricarbonyl(1—4- η -cyclohepta-1,3,5-triene)iron (**4a—d**) with 2-chlorotropone represents a convenient method for the synthesis of cycloheptatrienes bearing a tropone nucleus at C-7 and other substituents at C-1 or C-2. The original substituent on the cycloheptatriene ring is directed to C-6 and/or C-5; for compounds (**4b**) and (**4d**) C-6 is the favoured position whilst for (**4c**) it is C-5. The directing effect is explained in terms of the electronic and steric factors of the formally unco-ordinated allylic entities of (**2b—d**) and (**2b'—d'**). The available functionalization of the cycloheptatriene invariably produces mixtures of isomers that are difficult to separate. The present results may also be of interest for specific functionalization of the cycloheptatriene ring at C-7, C-1, and/or C-2 positions.

Experimental

I.r. spectra were recorded on a Shimadzu IR-400 spectrometer. ^1H N.m.r., and ^{13}C n.m.r., spectra were recorded on Hitachi



Scheme 4.

R-24 and Hitachi R-90H spectrometers and chemical shifts are given in p.p.m. (δ) relative to the internal SiMe_4 standard. The mass spectral studies and the high resolution mass spectral (h.r.m.s.) studies were conducted using Shimadzu GCMS-QP 1000 and JEOL DX-300 spectrometers. All experimental procedures were performed under a dry nitrogen atmosphere. Tetrahydrofuran (THF) was dried with Na under reflux, and was distilled under nitrogen prior to use. M.p.s were recorded on a Büchi apparatus and are uncorrected.

Preparation of Tricarbonyl(1-(4- η -cyclohepta-1,3,5-triene)iron (4a).—A mixture of cycloheptatriene (**3a**) (8.88 g, 96.4 mmol) and $[\text{Fe}(\text{CO})_5]$ (14.98 g, 76.1 mmol) was irradiated externally with a 60 W fluorescent lamp through Pyrex at 115 °C for 24 h. After this it was filtered through Celite to remove insoluble materials, and (**3a**) was removed under reduced pressure. The resulting residue was then distilled to give (**4a**) (8.21 g, 46%).

Preparation of Tricarbonyl(1-(4- η -7-methoxycyclohepta-1,3,5-triene)iron (4b).—A solution of 7-methoxycycloheptatriene (**3b**) (1.34 g, 11 mmol) and $[\text{Fe}_2(\text{CO})_9]$ (4.77 g, 13.1 mmol) in dry ether (22 ml) was heated under reflux for 24 h. The reaction mixture was then filtered through Celite and the filtrate was concentrated and purified by column chromatography on silica gel. The fractions eluted with hexane–benzene (1:2) afforded (**4b**) (858 mg, 30%), m.p. 43–44 °C (from hexane); $\delta_{\text{H}}(\text{CDCl}_3)$ 3.00 (1 H, br t, J 8.1 Hz), 3.25 (1 H, td, J 2.9, 2.3 Hz),

3.42 (3 H, s), 3.46–3.61 (1 H, m), 5.22–5.48 (3 H, m), and 5.94 (1 H, ddd, J 10.9, 8.1, 2.3 Hz); $\nu_{\text{max.}}(\text{film})$ 3 033, 2 986, 2 933, 2 829, 2 062, 1 977, 1 306, 1 185, 1 108, 1 086, 1 031, 956, and 788 cm^{-1} ; $\lambda_{\text{max.}}(\text{EtOH})$ 236sh and 321sh (log ϵ 4.14 and 3.53); m/z 234 ($M^+ - \text{CO}$, 4.9%) and 91 (100) (Found: C, 50.45; H, 3.75. $\text{C}_{11}\text{H}_{10}\text{FeO}_4$ requires C, 50.42; H, 3.85%).

Preparation of Tricarbonyl(1-(4- η -6-cyanocyclohepta-1,3,5-triene)iron (4c).—A mixture of 7-cyanocycloheptatriene (**3c**) (8.2 g, 70 mmol) and $[\text{Fe}(\text{CO})_5]$ (16.4 g, 83.8 mmol) was irradiated externally with a 60 W fluorescent lamp through Pyrex at 115 °C for 23 h. After this it was filtered through Celite and the filtrate was concentrated and chromatographed on silica gel. The fractions eluted with hexane–ethyl acetate (15:1) afforded (**3c**) (2.16 g, 26%). The fractions eluted with hexane–ethyl acetate (5:1) afforded (**4c**) (5.03 g, 28%), m.p. 89–90 °C (from EtOH); $\delta_{\text{H}}(\text{CDCl}_3)$ 2.36–2.57 (2 H, m), 3.00 (1 H, ddd J 8.1, 7.9, 2.2 Hz), 3.37 (1 H, dddd, J 8.1, 4.8, 4.0, 2.2 Hz), 5.29–5.52 (2 H, m), and 6.75 (1 H, ddd, J 8.1, 2.4, 1.8 Hz); $\nu_{\text{max.}}(\text{CHCl}_3)$ 3 010, 2 235, 2 214, 2 061, 1 991, 1 634, 1 450, 1 418, 1 136, 1 004, 901, 888, and 873 cm^{-1} ; $\lambda_{\text{max.}}(\text{EtOH})$ 241sh and 320 (log ϵ 4.03 and 3.76); m/z 229 ($M^+ - \text{CO}$, 43%) and 173 (100) (Found: C, 51.3; H, 2.75; N, 5.5. $\text{C}_{11}\text{H}_7\text{FeNO}_3$ requires C, 51.40; H, 2.75; N, 5.45%).

Preparation of Tricarbonyl(1-(4- η -6-phenylcyclohepta-1,3,5-triene)iron (4d).—A mixture of 7-phenylcycloheptatriene (**3d**) (5.89 g, 35 mmol) and $[\text{Fe}(\text{CO})_5]$ (8.23 g, 42 mmol) was

irradiated externally with a 60 W fluorescent lamp through Pyrex at 115 °C for 72 h. It was then filtered through Celite and the filtrate was concentrated and chromatographed on silica gel. The first fractions eluted with hexane afforded (**3d**) (1.93 g, 33%). The second fractions afforded (**4d**) (2.19 g, 20%), m.p. 98–99 °C (from EtOH); $\delta_{\text{H}}(\text{CDCl}_3)$ 2.62–2.82 (2 H, m), 3.25 (1 H, br dd, J 8.8, 8.1 Hz), 3.46 (1 H, m), 5.29–5.47 (2 H, m), 6.21 (1 H, ddd, J 8.1, 1.5, 1.3 Hz), and 7.22 (5 H, s); $\nu_{\text{max}}(\text{CHCl}_3)$, 3 009, 2 045, 1 982, 1 559, 1 494, 1 446, 1 076, 1 002, and 861 cm^{-1} ; $\lambda_{\text{max}}(\text{EtOH})$ 241sh, 289sh, and 325 nm (log ϵ 4.07, 3.84, and 3.81); m/z 280 ($M^+ - \text{CO}$, 27%) and 224 (100) (Found: C, 62.85; H, 3.85. $\text{C}_{16}\text{H}_{12}\text{FeO}_3$ requires C, 62.37; H, 3.93%).

Reaction of Tricarbonyl(cycloheptatrienide)iron with 2-Chlorotropone (5).—A solution of LDA (lithium di-isopropylamide) was prepared by the reaction of di-isopropylamine (354 mg, 3.5 mmol) in THF (5 ml) with BuLi (3 mmol, 1.8 ml of 1.67M hexane solution) at 0 °C. To a stirred solution of tricarbonyl(cyclohepta-1,3,5-triene)iron (**4a**) (580 mg, 2.5 mmol) in THF (5 ml) was added a solution of LDA at –70 °C, and the mixture was stirred for a further 30 min. 2-Chlorotropone (**5**) (351 mg, 2.5 mmol) in THF (5 ml) was then added to it over 30 min and stirring continued for a further 1 h at –70 °C. After the reaction had been quenched with aqueous NH_4Cl , the mixture was extracted with benzene, and the benzene extract was dried (Na_2SO_4) and evaporated. The resulting residue was chromatographed on silica gel using hexane–ethyl acetate (5:1) as eluant. The first fraction contained (**4a**) (79 mg, 14%). The second fraction gave (**7a**) (642 mg, 76%). The third fraction contained (**5**) (35 mg, 10%). For (**7a**): yellow crystals, m.p. 118–119 °C (from hexane–benzene); $\delta_{\text{H}}(\text{CDCl}_3)$ 3.10 (1 H, br t, J 7.6 Hz), 3.53 (1 H, m), 4.37 (1 H, td, J 4.5, 1.5 Hz), 4.97–5.27 (2 H, m), 5.39 (1 H, ddd, J 7.3, 4.7, 1.5 Hz), 6.03 (1 H, ddd, J 10.6, 7.9, 1.5 Hz), and 6.85–7.38 (5 H, m); $\nu_{\text{max}}(\text{CHCl}_3)$ 3 000, 2 050, 1 969, 1 627, 1 564, 1 510, 1 468, 1 405, 1 281, 1 241, 1 110, 1 099, 895, and 867 cm^{-1} ; $\lambda_{\text{max}}(\text{EtOH})$ 288, 306, and 386sh nm (log ϵ 4.49, 4.05, and 3.67); m/z 308 ($M^+ - \text{CO}$, 40%) and 252 (100) (Found: C, 60.65; H, 3.6. $\text{C}_{17}\text{H}_{12}\text{FeO}_4$ requires C, 60.75; H, 3.60%).

Reaction of Tricarbonyl(methoxycycloheptatrienide)iron with 2-Chlorotropone (5).—A solution of tricarbonyl(1–4- η -7-methoxycyclohepta-1,3,5-triene)iron (**4b**) (524 mg, 2.0 mmol) in THF (4 ml) was treated with LDA [prepared by using di-isopropylamine (293 mg, 2.9 mmol) and BuLi (1.5M hexane solution; 1.6 ml) as described above], at –78 °C for 5 min and at room temperature for a further 50 min. The reaction mixture was then cooled to –78 °C and 2-chlorotropone (281 mg, 2.0 mmol) in THF (4 ml) was added to it over a period of 5 min; it was then stirred for a further 35 min. After work-up as described above, the product was purified by column chromatography on silica gel. The fractions eluted with hexane–ethyl acetate (5:1) afforded (**4b**) (27 mg, 5%). The fractions eluted with hexane–ethyl acetate (3:2) afforded (**7b**) (409 mg, 56%) as yellow crystals, m.p. 129–130 °C (from EtOH); $\delta_{\text{H}}(\text{CDCl}_3)$ 3.16–3.48 (1 H, m), 3.32 (3 H, s), 3.54 (1 H, ddd, J 7.3, 5.1, 1.8 Hz), 4.40 (1 H, d, J 5.1 Hz), 5.05–5.39 (3 H, m), and 6.78–7.20 (5 H, m); $\nu_{\text{max}}(\text{CHCl}_3)$ 3 005, 2 058, 1 963, 1 660, 1 629, 1 598, 1 511, 1 471, 1 173, 1 112, and 1 018 cm^{-1} ; $\lambda_{\text{max}}(\text{EtOH})$ 226, 263sh, and 314 nm (log ϵ 4.49, 4.12, and 4.10); m/z 338 ($M^+ - \text{CO}$, 24%) and 282 (100) (Found: C, 58.95; H, 3.75. $\text{C}_{18}\text{H}_{14}\text{FeO}_5$ requires C, 59.05; H, 3.85%).

Reaction of Tricarbonyl(cyanocycloheptatrienide)iron with 2-Chlorotropone (5).—A solution of tricarbonyl(1–4- η -6-cyanocyclohepta-1,3,5-triene)iron (**4c**) (206 mg, 0.8 mmol) in THF (2 ml) was treated with LDA [prepared by using di-isopropylamine (116 mg, 1.15 mmol) and BuLi (1.5M hexane solution; 0.64 ml)] at –78 °C for 50 min. 2-Chlorotropone (**5**)

(113 mg, 0.8 mmol) in THF (2 ml) was then added over 5 min at –78 °C and the mixture stirred for a further 3 h at –50 °C. After work-up as described above, the product was separated by t.l.c. on silica gel using CH_2Cl_2 as developer. The first band from the t.l.c. plates gave (**7c**) (29 mg, 10%), and the second band gave (**9c**) (163 mg, 56%). For (**7c**): m.p. 138–139 °C (from EtOH); $\delta_{\text{H}}(\text{CDCl}_3)$ 3.07 (1 H, ddd, J 8.6, 7.3, 1.3 Hz), 3.68 (1 H, ddd, J 7.7, 4.8, 1.8 Hz), 4.43 (1 H, dd, J 4.8, 1.3 Hz), 5.24 (1 H, ddd, J 7.7, 4.8, 1.3 Hz), 5.55 (1 H, ddd, J 7.3, 4.8, 1.8 Hz), and 6.87–7.39 (6 H, m); $\nu_{\text{max}}(\text{CHCl}_3)$ 3 009, 2 222, 2 070, 1 995, 1 630, 1 579, 1 514, 1 469, 1 446, 1 407, 1 141, 1 102, and 907 cm^{-1} ; $\lambda_{\text{max}}(\text{EtOH})$ 227, 312, and 378sh nm (log ϵ 4.45, 4.10, and 3.79); m/z 333 ($M^+ - \text{CO}$, 46%) and 227 (100) (Found: C, 59.8; H, 3.25; N, 3.85. $\text{C}_{18}\text{H}_{11}\text{FeNO}_4$ requires C, 59.87; H, 3.07; N, 3.88%). For (**9c**): m.p. 129–130 °C (from EtOH); $\delta_{\text{H}}(\text{CDCl}_3)$ 3.02 (1 H, dt, J 7.5, 1.3 Hz), 3.45 (1 H, dddd, J 7.7, 4.6, 1.8, 1.5 Hz), 4.47 (1 H, dd, J 4.6, 4.4 Hz), 5.26 (1 H, ddd, J 7.7, 4.8, 1.3 Hz), 5.49 (1 H, ddd, J 7.5, 4.8, 1.8 Hz), 5.97 (1 H, ddd, J 4.4, 1.5, 1.3 Hz), and 6.88–7.26 (5 H, m); $\nu_{\text{max}}(\text{CHCl}_3)$ 3 008, 2 233, 2 069, 2 001, 1 630, 1 576, 1 515, 1 470, 1 404, 1 279, 1 102, 1 009, and 896 cm^{-1} ; $\lambda_{\text{max}}(\text{EtOH})$ 309 and 366sh nm (log ϵ 3.98 and 3.68); m/z 333 ($M^+ - \text{CO}$, 18%) and 221 (100) (Found: C, 59.3; H, 3.1; N, 3.8. $\text{C}_{18}\text{H}_{11}\text{FeNO}_4$ requires C, 59.87; H, 3.07; N, 3.88%).

Reaction of Tricarbonyl(phenylcycloheptatrienide)iron with 2-Chlorotropone (5).—A solution of tricarbonyl(1–4- η -6-phenylcyclohepta-1,3,5-triene)iron (**4d**) (924 mg, 3 mmol) in THF (3 ml) was treated with LDA [prepared by using di-isopropylamine (364 mg, 3.6 mmol) and BuLi (1.5M hexane solution; 2.4 ml) and THF (6 ml)] at –78 °C for 17 min. 2-Chlorotropone (**5**) (422 mg, 3 mmol) in THF (6 ml) was added dropwise over 10 min and the mixture stirred for 15 min. After work-up, the product was separated by column chromatography on silica gel. The fractions eluted with hexane–ethyl acetate (3:1) afforded a mixture of (**7d**) and (**10d**) (1.155 g). The first band from the t.l.c. plates gave (**7d**) (33 mg, 4%) and a mixture of (**7d**) and (**10d**) (1.155 g). The mixture was then recrystallized from ethanol to give pure (**7d**) (507 mg, 41%). The filtrate contained 645 mg of (**7d**) (359 mg, 29%) and (**10d**) (284 mg, 23%). For (**7d**): m.p. 138–139 °C (from EtOH); $\delta_{\text{H}}(\text{CDCl}_3)$ 3.38 (1 H, ddd, J 8.4, 8.1, 1.5 Hz), 3.74 (1 H, ddd, J 7.0, 5.0, 2.0 Hz), 5.06 (1 H, d, J 5.0 Hz), 5.09–5.46 (2 H, m), 6.49 (1 H, d, J 8.4 Hz), and 6.70–7.32 (5 H, m); $\nu_{\text{max}}(\text{CHCl}_3)$ 3 010, 2 061, 1 991, 1 628, 1 598, 1 565, 1 511, 1 472, 1 450, 1 407, 1 279, 1 097, 1 077, 993, 918, 889, and 864 cm^{-1} ; $\lambda_{\text{max}}(\text{EtOH})$ 227, 272, and 316 nm (log ϵ 4.46, 4.14, and 4.15); m/z 384 ($M^+ - \text{CO}$, 11%) and 328 (100) (Found: C, 66.05; H, 3.8. $\text{C}_{23}\text{H}_{16}\text{FeO}_4$ requires C, 67.02; H, 3.91%). Although the product (**10d**) was not obtained pure even after repeated recrystallization, the ^1H n.m.r. and ^{13}C n.m.r. (Table 2) spectra of (**10d**) could be assigned by recording the mixture of (**7d**) and (**10d**). For (**10d**): $\delta_{\text{H}}(\text{CDCl}_3)$ 3.09 (1 H, t, J 7.9 Hz), 4.00 (1 H, ddd, J 4.8, 2.2, 2.0 Hz), 4.54 (1 H, ddd, J 4.8, 4.6, 1.5 Hz), 5.04–5.34 (1 H, m), 5.77 (1 H, dd, J 7.9, 2.2 Hz), 6.11 (1 H, ddd, J 10.3, 7.9, 1.5 Hz), and 6.79–7.56 (5 H, m).

General Procedure for the Decomplexation of Tricarbonyl[1–4- η -7-(2-oxocyclohepta-1,3,5-trienyl)cyclohepta-1,3,5-triene]iron Derivatives (7a, b, d).—A solution of compound (**7**) (0.5 mmol) and trimethylamine oxide (300 mg, 4 mmol) in dry acetone (5 ml) was stirred at 50 °C for 10–30 min after which hexane (5 ml) was added to it. The reaction mixture was then filtered through Celite to remove insoluble material. The filtrate was concentrated and the residue was purified by t.l.c. on silica gel using hexane–ethyl acetate (5:1) as developer to give (**8a**) (73%), (**8b**) (63%), and (**8d**) (98%). For (**8a**): oil; $\delta_{\text{H}}(\text{CDCl}_3)$ 3.47 (1 H, br t, J 6.0 Hz), 5.37 (2 H, dddd, J 8.9, 6.0, 0.9, 0.7 Hz),

6.25 (2 H, dddd, J 8.9, 3.9, 2.7, 0.9 Hz), 6.60 (2 H, dddd, J 3.9, 2.7, 0.9, 0.7 Hz), 6.89–7.21 (4 H, m), and 7.25–7.42 (1 H, m); $\delta_{\text{C}}(\text{CDCl}_3)$ 43.7 (d), 124.7 (2C, d), 124.8 (2C, d), 130.0 (2C, d), 132.8 (d), 133.1 (d), 134.1 (d), 134.8 (d), 140.3 (d), 153.7 (s), and 185.9 (s); $\nu_{\text{max}}(\text{CHCl}_3)$ 2 990, 1 627, 1 577, 1 514, 1 466, 1 406, 1 391, 1 250, 1 226, 1 128, 1 001, 946, 915, 861, and 837 cm^{-1} ; $\lambda_{\text{max}}(\text{EtOH})$ 229 and 307 nm ($\log \epsilon$ 4.29 and 3.86); m/z 196 (M^+ , 100%) [h.r.m.s. M^+ , 196.0882. $\text{C}_{14}\text{H}_{12}\text{O}$ requires M , 196.0889]. For (**8b**): m.p. 77–78 °C (from hexane); $\delta_{\text{H}}(\text{CDCl}_3)$ 3.62 (3 H, s), 4.44 (1 H, ddd, J 8.1, 1.1, 0.9 Hz), 5.68 (1 H, br d, J 8.8 Hz), 5.84 (1 H, td, J 8.1, 2.8 Hz), 5.98–6.46 (3 H, m), and 6.76–7.20 (5 H, m); $\delta_{\text{C}}(\text{CDCl}_3)$ 47.3 (d), 56.2 (q), 98.7 (d), 122.7 (d), 123.7 (d), 126.5 (d), 126.8 (d), 132.4 (d), 132.8 (d), 132.9 (d), 134.7 (d), 140.3 (d), 149.2 (s), 152.6 (s), and 186.1 (s); $\nu_{\text{max}}(\text{CHCl}_3)$ 3 004, 1 619, 1 597, 1 569, 1 518, 1 470, 1 342, 1 281, 1 155, 1 033, 1 012, and 837 cm^{-1} ; m/z 226 (M^+ , 93%) and 120 (100) [h.r.m.s. M^+ , 226.1003. $\text{C}_{15}\text{H}_{14}\text{O}_2$ requires M , 226.0994]. For (**8d**): m.p. 98–99 °C (from hexane–benzene); $\delta_{\text{H}}(\text{CDCl}_3)$ 5.27 (1 H, br dd, J 5.5, 3.7 Hz), 5.85–6.56 (4 H, m), 6.60–7.13 (6 H, m), and 7.15–7.50 (5 H, m); $\delta_{\text{C}}(\text{CDCl}_3)$ 46.7 (d), 125.6 (d), 126.0 (d), 126.7 (d), 127.3 (2C, d), 127.4 (d), 128.1 (2C, d), 128.3 (d), 129.2 (d), 131.9 (d), 132.3 (d), 132.5 (d), 134.6 (d), 134.8 (d), 139.9 (d), 142.2 (s), 149.9 (s), and 186.2 (s); $\nu_{\text{max}}(\text{CHCl}_3)$ 3 005, 1 631, 1 598, 1 569, 1 517, 1 496, 1 471, 1 453, 1 441, 1 404, 1 385, 1 276, 1 101, 1 075, and 877 cm^{-1} ; m/z 272 (M^+ , 100%) [h.r.m.s. M^+ , 272.1197. $\text{C}_{20}\text{H}_{16}\text{O}$ requires M , 272.1201].

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