Reactivity of Co-ordinated Ligands. Part XII.† Some Heptafulvene Complexes of Tricarbonyliron and their Electrophilic Reactions

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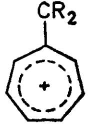
Tricarbonyliron complexes of some simple heptafulvenes, which are mono- or di-substituted at the 8-carbon atom are prepared in good yield from cycloheptatriene derivatives. Attempts to prepare the parent complex led to a dimer. The complexes of the unsymmetrical heptafulvenes were isolated as mixtures of *cis*- and *trans*-isomers. In contrast to the unco-ordinated systems the complexes undergo electrophilic attack on the ring. Thus protonation occurs to give stable dienyl salts; formylation of tricarbonyl-8-*p*-tolylheptafulveneiron gives tricarbonyl-1-formyl-8-*p*-tolylheptafulveneiron (1) which is not a mixture of isomers. A europium shift reagent was used to demonstrate that this was the *trans*-isomer. The aldehyde (1) may be reduced to the corresponding primary alcohol, which on treatment with hexafluorophosphoric acid gave a salt which contained two exocyclic double-bonds. Reaction of this salt with methoxide ion gave an ether which gave the expected adduct with tetracyanoethylene. Formylation of tricarbonyl-8-methyl-8-*p*-tolylheptafulveneiron afforded the uncomplexed aldehyde, 1-formyl-8-methyl-8-*p*-tolylheptafulvene in which the tolyl group is *trans* to the carbonyl function.

HEPTAFULVENE is a highly reactive system which has not been isolated.[2] The presence of electron-withdrawing substituents on the 8-carbon atom or annulation of the ring have been shown to stabilize the system.[3] The former may be important because of contributions from the resonance form (1) which connotes with the intrinsic stability of the tropylium ion.



(1)

In this study it will be shown that it is possible to prepare a wide variety of compounds of the type (5) and also to study their chemistry. In contrast to the unco-ordinated systems, where electrophilic reagents react to give the tropylium ion, in the co-ordinated species addition to the ring is observed. A tricarbonylheptafulveneiron complex in which the bonding is of the trimethylene methane type has been reported.[4] Recently the monomer of complex (11) has been synthesised.[5] Some aspects of this work have been reported in a preliminary communication.[6]

RESULTS AND DISCUSSION

Preparation of the Compounds.—Elimination of water from the alcohols (2), proton abstraction from the salts (3), or demethanolation of the ethers (4) produce the heptafulvene complexes (5) in good yield, Scheme 1. The dimethyl derivative (5b) may also be prepared by reaction of tricarbonyltroponeiron with isopropylmagnesium bromide at −30 °C, and dehydration of the alcohol produced on silica gel. This is in contrast to free tropone and tricarbonyltroponechromium, the former reacts with Grignard reagents by addition–substitution to the ring system,[7] while the latter under-

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† *Previous part:* R. J. H. Cowles, B. F. G. Johnson, J. Lewis, and A. W. Parkins, *J.C.S. Dalton*, 1972, 1768.

[1] B. F. G. Johnson, J. Lewis, P. McArdle, and G. L. P. Randall, *J.C.S. Dalton*, 1972, 456.

[2] W. von E. Doering and D. W. Wiley, *Tetrahedron*, 1960, **11**, 183.

[3] E. D. Bergmann, *Chem. Rev.*, 1968, **68**, 41.

[4] D. J. Ehntholt and R. C. Kerber, *Chem. Comm.*, 1970, 1451.

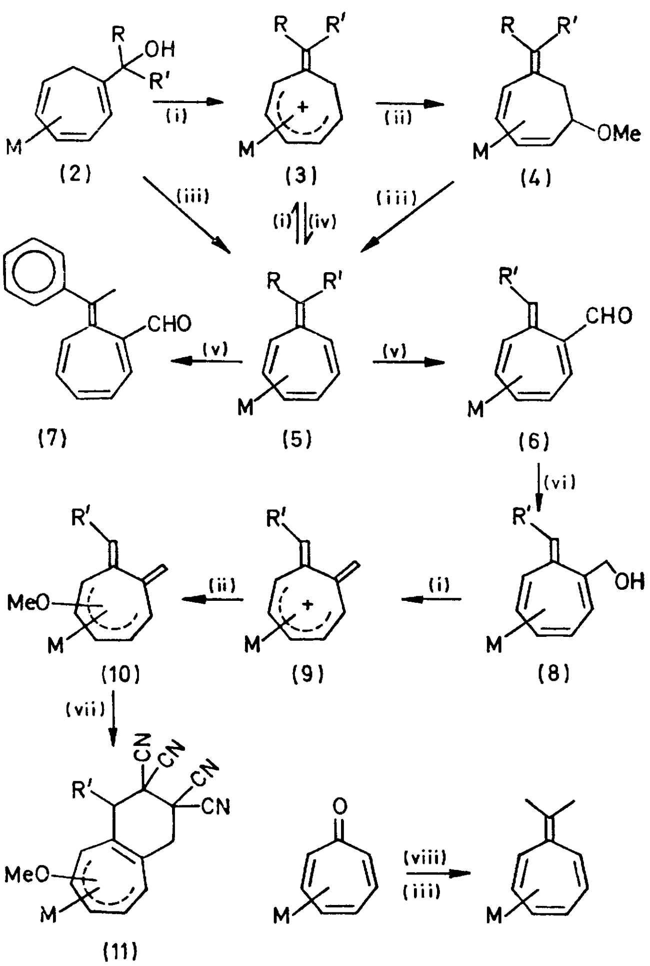
[5] G. T. Rodeheaver, G. C. Farrant, and D. F. Hunt, *J. Organometallic Chem.*, 1971, **30**, C22.

[6] B. F. G. Johnson, J. Lewis, P. McArdle, and G. L. P. Randall, *Chem. Comm.*, 1971, 177.

[7] T. Nozoe, T. Mukai, and T. Tezuka, *Bull. Chem. Soc. Japan*, 1961, **34**, 619.

goes decarbonylation to yield tricarbonylbenzenechromium under similar conditions.[8] This emphasizes the effect of co-ordination on the chemical reactivity of an organic moiety and also that variation in electron configuration of the metal in the complex has important consequences on the course of reaction.

Attempts to prepare the parent complex led to the dimer $[C_8H_8Fe(CO)_3]_2$ (12) (although small amounts of the monomer were detected ($\simeq$1%). The alkyl derivatives, (5a), (5b), and (5c), are air-sensitive distillable yellow oils. The deep-yellow crystalline aromatic derivatives (5d), (5e), and (5f) are stable to air and sublime at 100°/760 mmHg without decomposition.



SCHEME 1
$M = Fe(CO)_3$

a; R = H, R' = Me
b; R = Me, R' = Me
c; R = Me, R' = Et
d; R = H, R' = *p*-tolyl
e; R = H, R' = Ph
f; R = Me, R' = *p*-tolyl

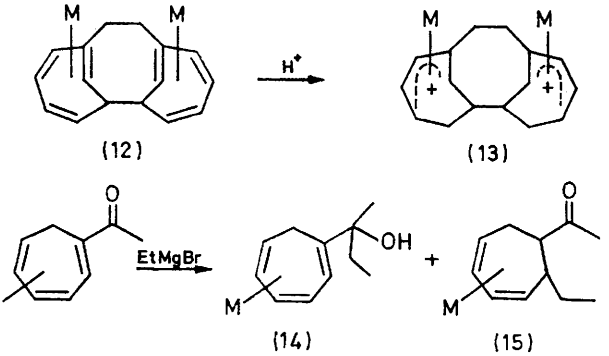
Reagents: i, H^+; ii, OMe^-; iii, silica gel; iv, Et_3N; v, $POCl_3$–Me_2NCHO; vi, BH_4^-; vii, tetracyanoethylene; viii, Pr^iMgBr

Tricarbonyl-1-formylcycloheptatrieneiron reacts with the appropriate Grignard reagents to give, by 1,2-addition, the secondary alcohols (2) in almost quantitative yield. The ketone, 1-acetyltricarbonylcycloheptatrieneiron, on the other hand reacts by both 1,2- and 1,4-addition leading to the alcohol (14) $\simeq$10%, which was not isolated, and the saturated ketone (15) $\simeq$60%. This follows the normal course observed for 1 : 4-, 1 : 2-addition reactions of crotonaldehyde and pent-3-en-2-one and is primarily attributed to steric factors. Complex (15) was purified by treating an ethereal solution of the mixture with hexafluorophosphoric acid; this precipitated the salt (3c), the ketone (15) remaining in solution.

Under Vilsmeyer conditions (5d) and (5e) are converted into the aldehyde complexes (6d) and (6e), which readily form dinitrophenylhydrazone derivatives. Reduction of (6d) with sodium borohydride in ethanol produces the primary alcohol (8). Hydroxide abstraction from (8) gives the salt (9) which contains two exocyclic double-bonds. This salt (9) is readily converted into the ether (10). The structure assigned to (10) is supported by its ready reaction with tetracyanoethylene to give (11). Formylation of (5f) in contrast to (5d) and (5e) produces 1-formyl 8-*p*-tolyl-8-methylheptafulvene.

Structure of the Complexes.—The mass spectrum of the dimer (12) exhibited a molecular ion (*m/e* 488), and daughter ions corresponding to the loss of six carbon monoxide groups and two iron atoms. The solid-state structure shows that an electrocyclic dimerization has taken place and that the tricarbonyliron moiety has changed its co-ordination position.[9] As this dimerization would be for the free ligand a formally non-allowed $(8 + 8)\pi$-cycloaddition the metal must play an important role. The n.m.r. spectrum is, with the aid of double-irradiation experiments, readily assigned in terms of the structure observed in the solid state and the complex is therefore dimeric in solution and formulated as (12) (Scheme 2).

The monomeric nature of complex (5d) was confirmed by a molecular-weight determination. Assignment of structure (5) to the substituted compounds follows from their n.m.r. spectra (Table). Taking complex (5b) as a specific example; double-irradiation studies show that the multiplicities of the resonances at τ 6·05 and 7·05 are due to coupling and that the doublet at τ 8·11, assigned to the methyl groups, is not coupled. The



SCHEME 2 Shifts in Hz at 100 MHz

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[8] P. L. Pauson and K. H. Todd, *J. Chem. Soc.* (*C*), 1970, 2315.

[9] R. Mason, personal communication.

most reasonable asymmetric structure containing non-coupled methyl groups is (5b). The complexes which do not have R = R′ are prepared as *ca.* 1 : 1 mixtures of *cis*/*trans* isomers. They exhibit a doubling of resonances for the protons which are most effected by the *cis*/*trans* isomer differences (Table). This does not however, rule out the possibility that the compounds are fluxional. Since the exocyclic double-bond in the salts (3) and the ethers (4) could also give rise to geometrical isomers their n.m.r. spectra were investigated. It was found that (3c), (3d), (3e), (4d), and (4e) show a non-coupled splitting of their methyl resonances indicating the presence of *cis*/*trans* isomers (ratio 1 : 1), but that (3a), (3f), (4a), and (4f) show no such splitting. Accidental degeneracy for this latter group was ruled out because addition of the europium shift reagent to solutions of (4a) and (4f) did not split the methyl resonances which move rapidly on varying

TABLE

N.m.r. data.* 100 MHz

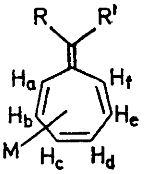
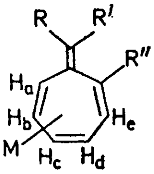
Compound and solvent	Protons	Chemical shift (τ)	Relative intensity	Multiplicity	*J*(Hz)
 (5a) R = H, R^1 = Me CS$_2$	H$_a$	6·36, 6·55	0·5, 0·5	2d	8
	R + H$_b$ + H$_c$ + H$_e$ + H$_f$	4·75	5	m	
	H$_d$	7·24	1	m	
	R′	8·53, 8·64	1·5, 1·5	2d	7
(5b) R = R′ = Me CS$_2$	H$_a$	6·05	1	d	8
	H$_b$ + H$_c$ + H$_f$ + H$_e$	4·58	4	m	
	H$_d$	7·05	1	t	7
	R + R′	8·26, 8·36	3, 3	2s	
(5d) R = H, R′ = *p*-tolyl CS$_2$	H$_a$	5·91, 6·36	0·45, 0·55	2d	6
	H$_b$ + H$_c$ + H$_e$ + H$_f$	4·55	4	m	
	H$_d$	7·12	1	t	8
	R	3·52, 3·76	0·55, 0·45	2s	
	Arene	3·08	4	m	
	Me	7·83, 7·88	1·35, 1·65	2s	
(5f) R = Me, R′ = *p*-tolyl	H$_a$	5·97, 6·11	0·5, 0·5	2d	7
	H$_b$ + H$_c$ + H$_e$ + H$_f$	4·6	4	m	
	H$_d$	7·13	1	t	7
	R	8·03, 8·16	1·5, 1·5	2s	
	R′(Me)	7·78, 7·82	1·5, 1·5	2s	
	R′(arene)	3·04	4	m	
 (6d) R = H, R′ = *p*-tolyl R″ = CHO	H$_a$	5·55	1	d	7
	H$_b$	4·62	1	t	6
	H$_c$	4·32	1	t	7
	H$_d$	6·86	1	t	6
	H$_e$	3·38	1	d	8
	R	1·80	1	s	
	R′(Me)	7·70	3	s	
	R′(arene)	2·77	4	m	
	R″	0·76	1	s	
(7) R′ = *p*-tolyl, R″ = CHO NO M CS$_2$	H$_a$ + H$_b$ + H$_c$ + H$_d$ + H$_e$	3·70	5	m	
	R	8·32	3	s	
	R′(Me)	7·72	3	s	
	R′(arene)	2·98	4	m	
	R″	0·54	1	s	
(8) R = H R′ = *p*-tolyl R″ = CH$_2$OH CS$_2$	H$_a$	5·80	1	d	8
	H$_b$	4·75	1	m	
	H$_c$	4·55	1	m	
	H$_d$	7·20	1	d	8
	H$_e$	4·24	1	d	8
	R	3·34	1	s	
	R′(arene)	2·94	4	m	
	R′(Me)	7·74	1	s	
	R″(CH$_2$)	6·05	1	m	
	R″(OH)	7·10	1	s	

TABLE (*Continued*)

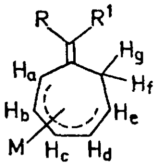
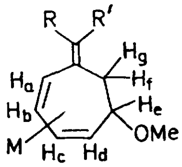
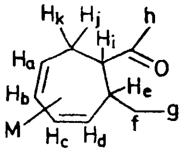
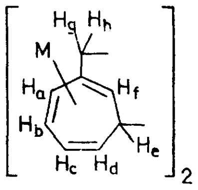
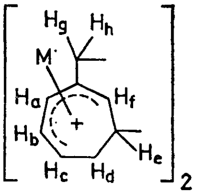
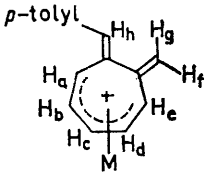
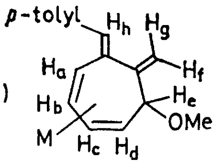
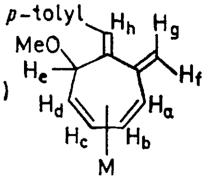
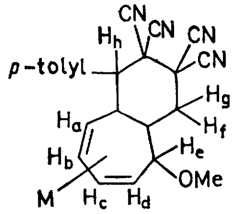
Compound and solvent	Protons	Chemical shift (τ)	Relative intensity	Multiplicity	*J* (Hz)
 (3c) R = Me R′ = Et SO_2	H_a	4·55	1	2d	7
	$H_b + H_d$	3·82	2	m	
	H_c	2·94	1	t	8
	H_e	5·16	1	m	
	$H_f + H_g + R'(CH_2)$	7·40	4	m	
	R	8·0, 8·24	1·5, 1·5	2s	
	$R'(CH_3)$	8·88, 9·00	1·5, 1·5	2t	8
(3d) R = H R′ = *p*-tolyl SO_2	H_a	3·68	1	m	
	$H_b + H_d$	4·24	2	m	
	H_e	5·10	1	m	
	$H_c + \frac{1}{2}R + R'$(arene)	2·8	5·5	m	
	$\frac{1}{2}R$	3·4	0·5	s	
	$R'(CH_3)$	7·65, 7·68	1·5, 1·5	2s	
(3f) R = Me R′ = *p*-tolyl SO_2	$H_a + H_d$	4·5	2	m	
	H_b	3·76	1	t	8
	$H_c + R'$(arene)	2·80	5	m	
	H_e	5·14	1	t	8
	H_f	6·62	1	2d	8
	H_g	7·70	1	m	
	$R'(CH_3)$	7·65	3	s	
	$R(CH_3)$	7·96	3	s	
 (4d) R = H R′ = *p*-tolyl CS_2	H_a	6·12	1	m	
	$H_b + H_c$	4·70	2	m	
	H_e	6·41	1	m	
	H_d*	≃6·85	1		
	H_f	7·22, 7·8 *	0·5, 0·5	d	12
	H_g	8·30, 8·70	0·5, 0·5	2t	12
	OMe	7·77, 7·81	1·5, 1·5	2s	
	R′(arene)	2·98	4	m	
	R′(Me)	7·78, 7·80	3	2s	
(4f) R = Me R′ = *p*-tolyl CS_2	H_a	6·22	1	d	8
	H_b	5·08	1	t	8
	H_c	4·71	1	t	7
	$H_d + H_e$	6·96	2	m	
	H_f	7·40	1	d	12
	H_g	8·62	1	t	10
	OMe	6·76	3	s	
	R	8·16	3	s	
	R′(arene)	2·98	4	m	
	R′(Me)	7·76	3	s	
 (15) CS_2	$H_b + H_c$	4·64	2	m	
	H_g	9·40	3	t	8
	H_h	8·10	3	s	
	$H_e + H_f + H_i + H_j + H_k$	7·00—8·00	6	m	
	H_a	4·80	1	d	8
	H_b	7·16	1	t	8
	H_c	4·28	1	t	8
	H_d	5·08	1	d	12
	$H_e + H_f + H_g + H_h$	7·04, 7·56	4	m, m	

Table (*Continued*)

Compound and solvent	Protons	Chemical shift (τ)	Relative intensity	Multiplicity	J(Hz)
 (12) in CF_3CO_2H	H_a	2·91	1	d	5
	H_b	3·82	1	t	5
	H_c	4·83	1	m	
	H_g	6·18	1	m	
	H_e	7·48	1	m	
	H_d	8·82	1	t	10
	$H_f + H_h$	6·45	2	m	
	H_i	7·20	1	d	7
 (8) SO_2	arene + H_c	2·7	5	m	
	$H_a + H_b + H_d + H_e + H_f + H_g + H_h$	4·30	7	m	
	H_e	7·65, 7·88	2·8, 0·02	2s	
(i) 	H_a	5·78	1	d	8
	$H_b + H_c + H_g + H_f + H_h$	4·53	5	m	
	H_d	7·07	1	t	7
(ii)  (10) CS_2	OMe	6·17, 6·89	3	2s	
	Me	7·71	3	s	
	Arene	3·03	4	m	
 and the isomer corresponding to (10) (ii) above (11) CS_2	$H_b + H_c$	3·38	2	m	
	Arene	2·90	4	m	
	$H_a + H_d + H_e + H_f + H_g + H_h$	5·6—7·2	6	m	
	OMe	6·60, 7·03	3	2s	
	Me	7·67	3	s	

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* Details of the n.m.r. spectra of compounds (5c), (5e), (6e), (12), 1-phenylcyclo-octatetraeneiron, and 1-phenyl(formyl)cyclo-octatetraeneiron are given in Supplementary Publication No. SUP 20483 (6 pp.) (for details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20).

the europium concentration. As these isomerically pure complexes are converted under mild conditions into neutral heptafulvene derivatives (5), which are 1 : 1 *cis*/*trans* mixtures, (5) are potentially fluxional but static on the p.m.r. time-scale. Attempts to detect any fluxional character were not successful up to 100°.

Electrophilic Reactions.—Protonation of (5d—f), leads to a reversal of the triethylamine reaction to give the salts (3). The n.m.r. spectra of these salts in liquid sulphur dioxide are identical to those of the salts prepared from the alcohols (2), particularly with respect to the isomer distribution noted above.

In phosphorus oxychloride–dimethylformamide at 0° (5d) and (5e) are formylated in 70% yield (after 72 h) to give the ring-substituted aldehydes (6c) and (6d). The n.m.r. spectra of these aldehydes are simple (all except the aromatic resonances are well separated) and are readily assigned in terms of structure (6) (Table). That these were not cyclo-octatetraene derivatives was proved by preparation of the phenylcyclo-octatetraene analogue, the n.m.r. of which is quite different (Table). Addition of the shift reagent Eu(dpm)$_3$ to solutions of (6c) demonstrates that the *p*-tolyl group is *cis* to the iron. The fact that pure *cis* (w.r.t. Fe) non-fluxional aldehyde (6c) is prepared in 70% yield from 1 : 1 *cis*/*trans* (5d) and that the recovered (5d), 10% is also 1 : 1 *cis*/*trans* supports an implicit fluxional nature for (5d). Formylation of (5e) under identical conditions to the above gives 1-formyl-8,8-methyl-*p*-tolylheptafulvene (7) in 50% yield. The n.m.r. spectrum of (7) is analogous to (6c) except that the olefinic hydrogens resonate together at the lower τ value of 3·70. Use of Eu(dpm)$_3$ demonstrated that the *p*-tolyl group was *trans* to the aldehyde. The increased steric requirements of the disubstituted complex may be responsible for the loss of the tricarbonyliron unit, but its apparently ready expulsion is surprising.

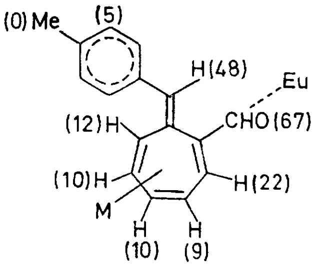
In all cases electrophilic attack occurs on the ring, and this emphasizes the very great tendency to form dieniumiron tricarbonyl species either as intermediates or as final products in these reactions.

N.m.r. spectra of the dimeric complex (12) in trifluoroacetic acid indicate that it is protonated; on the basis of deuteriation studies and double-irradiation experiments the dication is assigned structure (13).

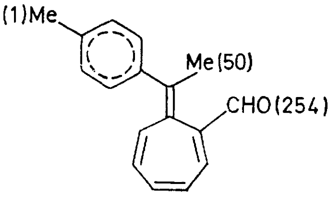
Reactions of the Aldehyde Complex (6d).—The presence of the aldehyde group in (6d) offers the possibility of further reactivity. Thus (6d) is readily reduced by borohydride in ethanol to give the alcohol (8). This compound is not fluxional at room temperature and retains the geometry of (6d). On treatment with hexafluorophosphoric acid a salt is obtained which is formulated as (9). The n.m.r. spectra of (9) in sulphur dioxide and hexadeuterioacetone are similar and difficult to assign as, firstly the dienium and olefinic protons give rise to one large multiplet and secondly there are two CH$_3$ resonances one of which is relatively weak. Since the salt (9) reacts with methoxide to give an ether (10) in good yield, the minor component of (9) is either unreactive to methoxide, which seems impossible, or a conformer of (9). Mass spectra support the formulation of (10) and the n.m.r. spectrum which contains two methoxy resonances suggests that methoxide attack has taken place at both ends of the dienium system in (9). The presence of two exocyclic double-bonds in (10) with the *p*-tolyl group *trans* to the second methylene group is substantiated by ready reaction of the complex with tetracyanoethylene to afford the adduct (11). The spectroscopic, mass, n.m.r., and i.r. data support the assignment of structure (11) to this adduct.

Complex (6d) was heated in toluene at 100° for 20 h in an attempt to prepare its shift isomer. The aldehyde was recovered unchanged (90%) together with a small amount, (2%), of (5d), indicating that some decarbonylation had taken place. This stereochemical rigidity of the aldehyde (6d) is in agreement with work on substituted cyclo-octatetraene complexes, where it has been shown that the presence of electronegative substituents freezes the iron tricarbonyl group into one of the co-ordination positions furthest from the point of substitution.[10] As has been pointed out previously this contrasts with the behaviour shown by the corresponding acyclic systems where the favoured co-ordination site is adjacent to the electronegative grouping.[11]

Experiments with Tris(2,2,6,6-*tetramethylheptane*-3,5-*dionato*)-*europium*(III).—It was clear from the n.m.r. spectrum of (6d) (Table), that M and CHO are disposed as in structure (6) but that the geometry of the methylene group cannot be deduced from this spectrum. Addition of a solution of the shift reagent dropwise to a solution of (6d) produced the shifts shown below. The europium position was estimated making the following assumptions. (1) That C=O · · · Eu was linear even if the aldehyde group was rotating with respect to the rest of the molecule, [d(C–Eu) $\simeq$ 3·1 Å].[12] (2) That the angular contribution to the shift was constant. (3) That the molecule (neglecting M) was planar. The calculated Eu position is given above. It is therefore possible to rule out the alternative configuration for the *p*-tolyl group as this would make co-ordination of europium unlikely and impose a large upfield shift on the methyl group. Parallel results were obtained for the phenyl derivative (6e). The data for compound (7) again place the *p*-tolyl group *trans* to the aldehyde, but here much larger shifts were observed. This is probably due to the steric effect of the tricarbonyliron group.



(6d)



(7)

EXPERIMENTAL

Microanalyses were by the microanalytical department of this laboratory. ^{1}H N.m.r. spectra were measured on a Varian Associates HA 100 machine. I.r. spectra were recorded using a Perkin-Elmer 257 spectrometer. M.p.s were measured in open capillary tubes on a Gallenkamp melting point apparatus. All reactions were carried out

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under pure dry nitrogen. Compounds (3a), (3e), (4a), and (4e) were prepared as described previously.[1]

Tricarbonyl[6-*ethyl*(*methyl*)*methylenecyclohepta*-1-5η-*dienium*]*iron Hexafluorophosphate* (3c).—Tricarbonylacetylcycloheptatrieneiron [1] (16) (2·0 g) was treated with a five-fold excess of ethylmagnesium bromide at −50° in ether. The mixture was stirred at −30° for 20 min and was then hydrolysed with ammonium chloride solution. The ether layer was separated, washed with water (2 × 100 ml), dried ($MgSO_4$), and evaporated *in vacuo* to a yellow oil. This oil in ether was treated dropwise with hexafluorophosphoric acid until no further precipitation was observed. The bright orange solid was washed with dry ether to give the product (0·31 g, 10%) (Found: C, 38·45; H, 3·5. $C_{14}H_{15}F_6FeO_3P$ requires C, 38·8; H, 3·5%). I.r. (Nujol mull) νMC–O 2100 and 2060 cm^{-1}, νPF_6^- 840 cm^{-1}.

Tricarbonyl(6-*acetyl*-5-*ethylcyclohepta*-1,3-*diene*)*iron* (15).—The acid solution from the preparation of (3c) was neutralized with sodium hydrogencarbonate and washed with water (3 × 100 ml). After drying ($MgSO_4$) and evaporation *in vacuo* a yellow oil was obtained. Chromatography on silica-gel using 5% ethyl acetate in toluene as eluant, evaporation of the yellow band which developed gave an oil which was distilled to give the product (1·33 g, 60%) (Found: C, 54·75; H, 4·85. $C_{14}H_{14}FeO_4$ requires C, 55·2; H, 5·25%). I.r. (liq. film) νMC–O 2050 and 1920, νMeCO 1720 cm^{-1}.

Tricarbonyl(6-p-*tolylmethylenecyclohepta*-1-5η-*dienium*)-*iron Hexafluorophosphate* (3d).—Tricarbonylformylcycloheptatrieneiron (1·5 g) in ether (70 ml) at −50° was treated with a five-fold excess of *p*-tolylmagnesium bromide. After being stirred for 20 min the mixture was hydrolysed with ammonium chloride, dried ($MgSO_4$), and treated with hexafluorophosphoric acid until no further precipitate formed. The precipitate was washed with dry ether to give the product as a bright yellow solid 2·7 g (98%) (Found: C, 44·8; H, 3·1. $C_{18}H_{15}F_6FeO_3P$ requires C, 45·0; H, 3·1%). I.r. (Nujol mull) νMC–O 2116, 2073, and 2060, νPF_6^- 840 cm^{-1}.

Tricarbonyl(6-*methyl*-p-*tolylmethylenecyclohepta*-1—5η-*dieniumiron Hexafluorophosphate* (3f).—This complex was prepared from compound (16) using *p*-tolylmagnesium bromide, by the method used for (3d), to give the product as a yellow solid (20%) (Found: C, 47·0; H, 3·3. $C_{19}H_{17}FeF_6O_3P$ requires C, 47·2; H, 3·35%). I.r. (Nujol mull) νMC–O 2114 and 2060, νPF_6^- 840 cm^{-1}.

Tricarbonyl(5-*methoxy*-7-p-*tolylmethylenecyclohepta*-1,3-*diene*)*iron* (4d).—The salt (3d) (500 mg) was suspended in methanol (30 ml) and treated with sodium methoxide in methanol until a clear solution was obtained. Extraction with ether–water, washing with water (3 × 100 ml), drying ($MgSO_4$), and evaporation *in vacuo* gave the product as a yellow oil (344 mg, 90%) (Found: C, 62·35; H, 4·8. $C_{19}H_{24}FeO_4$ requires C, 62·2; H, 4·9%). I.r. (liq. film) νMC–O 2049 and 1980 cm^{-1}.

Tricarbonyl(5-*methoxy*-7-*methyl*-p-*tolylmethylenecyclohepta*-1,3-*diene*)*iron* (4f).—This ether was prepared under the same conditions as (4d) to give the product as a yellow oil (90%) (Found: C, 62·75; H, 5·2. $C_{20}FeH_{26}O_4$ requires C, 63·2; H, 5·25%). I.r. (liq. film) νMC–O 2048 and 1980 cm^{-1}.

Tricarbonyl(8-*methylheptafulvene*)*iron* (5a).—The salt (3a) (500 mg) was dissolved in acetone (30 ml) and treated with an excess of triethylamine. Extraction with ether–water, washing with water, drying ($MgSO_4$), evaporation *in vacuo*, and distillation onto a cold-finger gave the product as a yellow oil (220 mg, 70%) (Found: C, 55·35; H, 4·3. $C_{12}H_{10}FeO_3$ requires C, 55·8; H, 3·85%). I.r. (n-heptane solution) νMC–O 2050, 1988, and 1979 cm^{-1}.

Tricarbonyl(8,8-*dimethylheptafulvene*)*iron* (5b).—Tricarbonyltroponeiron (500 mg) in ether (20 ml) at −50° was treated dropwise with a five-fold molar excess of isopropylmagnesium bromide. The reaction mixture was stirred at −60° for 30 min, hydrolysed with ammonium chloride, washed with water (3 × 100 ml), dried ($MgSO_4$), and evaporated *in vacuo*. The oil obtained was placed on top of a silica-gel column (made up with toluene) and left for 15 h. Toluene eluted a golden-yellow band which was evaporated *in vacuo* to give the product as a yellow oil (332 mg, 60%) (Found: C, 57·4; H, 4·55. $C_{13}H_{12}FeO_3$ requires C, 57·4; H, 4·40%). I.r. (n-heptane solution) 2052, 1989, and 1978 cm^{-1}.

Tricarbonyl(8-*ethyl*-8-*methylheptafulvene*)*iron* (5c).—The salt (3c) (300 mg) was used to prepare (5c) in a manner analogous to that used for the preparation of (5a) to yield the product (178 mg, 90%) (Found: C, 58·7; H, 5·15. $C_{14}H_{14}FeFeO_4$ requires C, 58·7; H, 4·9%. I.r. (n-heptane solution) 2050, 1987, and 1978 cm^{-1}.

Tricarbonyl(8-p-*tolylheptafulvene*)*iron* (5d).—The salt (3d) (1 g) in acetone (30 ml) was treated with an excess of triethylamine. All volatiles were evaporated *in vacuo*. The semi-solid obtained was extracted with the minimum quantity of toluene and chromatographed on alumina using toluene as eluant. The deep golden band which developed was evaporated to give the product as an oil which crystallized (660 mg, 95%), m.p. 95° (Found: C, 65·15; H, 4·3. $C_{18}H_{14}FeO_3$ requires C, 64·65; H, 4·2%). I.r. (n-heptane solution) 2051, 1992, and 1976 cm^{-1}.

Tricarbonyl(8-*phenylheptafulvene*)*iron* (5e).—This compound was prepared from the salt (3e) by the method used for the preparation of complex (5d) to give the product as a yellow solid (96%), m.p. 101° (Found: C, 63·35; H, 4·05. $C_{17}H_{12}FeO_3$ requires C, 63·75; H, 3·75%). I.r. (n-heptane solution) 2052, 1993, and 1976 cm^{-1}.

Tricarbonyl(8-*methyl*-8-p-*tolylheptafulvene*)*iron* (5f).—By the same method as that used for complex (5e), complex (5f) was prepared from compound (3f) as a yellow solid (90%), m.p. 105° (Found: C, 65·75; H, 4·55. $C_{19}H_{16}FeO_3$ requires C, 65·5; H, 4·6%). I.r. (n-heptane solution) 2050, 1992, and 1974 cm^{-1}.

Tricarbonyl(1-*formyl*-8-p-*tolylheptafulvene*)*iron* (6d).—Phosphorus oxychloride (20 ml), was added dropwise to dimethylformamide (80 ml) at −20°. This solution was treated with (5d) (1·0 g) in the minimum quantity of dimethylformamide. The reaction mixture was stirred at 0° for 72 h, poured into ice–water (1500 ml), purged with nitrogen and was then set aside for 15 h at room temperature. Extraction with ether (2 × 150 ml), washing with water, drying ($MgSO_4$), and evaporation *in vacuo* gave an oil. This oil was chromatographed on silica-gel. Toluene eluted a yellow band which was determined on evaporation to be starting material (10%). Ethyl acetate–toluene (1 : 10) eluted an orange band which was evaporated to give the product as an orange solid (760 mg, 70%), m.p. 97°. I.r. (CS_2 solution) νMC–O 2059, 1999, and 1987 cm^{-1}, νCHO 1684 cm^{-1}. The aldehyde readily formed a DNP derivative (Found: C, 56·2; H, 3·3; H, 10·15. $C_{25}FeH_{20}N_4O_7$ requires C, 55·15; H, 3·8; N, 10·3%).

Tricarbonyl(1-*formyl*-8-*phenylheptafulvene*)*iron* (6e).—The method used to prepare (6e) was the same as that for (6d).

The product was obtained as an orange crystalline solid, (70%), m.p. 105°. I.r. (CS_2 solution) νMC–O 2060, 2000, and 1989, νCHO 1686 cm^{-1}. This complex readily formed a DNP derivative (Found: C, 54·75; H, 3·15; N, 9·85. $C_{24}H_{18}FeN_4O_7$ requires C, 54·3; H, 3·4; N, 10·6%).

Tricarbonyl(1-*hydroxymethyl*-8-p-*tolylheptafulvene*)*iron* (8).—The aldehyde (6d) (500 mg) was dissolved in ethanol (100 ml). Sodium borohydride (1 g) was added to the mixture which was then stirred for 1 h at room temperature. Extraction with ether–water, washing with water (3 × 100 ml), drying ($MgSO_4$), and evaporation *in vacuo* gave an oil. This oil was chromatographed on alumina (activity V) using toluene. The light yellow band which developed was evaporated to give the product as a yellow gum. I.r. (liq. film) νO–H 3350 cm^{-1}, νMC–O 2045 and 1960 cm^{-1} (Found: C, 65·75; H, 4·55. $C_{19}H_{16}FeO_4$ requires C, 65·5; H, 4·6%).

Tricarbonyl(6-*methylene*-7-*tolylmethylene*-1—5η-*dienium*)-*iron Hexafluorophosphate* (9).—Complex (8) (300 mg) in dry ether, was treated with hexafluorophosphoric acid dropwise until no further precipitate was formed. The yellow solid was washed with dry ether to give the product (350 mg, 80%). I.r. (Nujol mull) νMC–O 2020 and 1972 cm^{-1}, νPF_6^- 840 cm^{-1} (Found: C, 48·5; H, 3·2. $C_{19}H_{15}F_6FeO_3P$ requires C, 48·4; H, 3·05%).

Tricarbonyl(6-*methylene*-7-*p*-*tolylmethylenemethoxycyclohepta*-1,3-*diene*)*iron* (10).—The method used to prepare complex (4d) was employed for the preparation of complex (10); it gave the product as a yellow oil (90%). I.r. (liq. film) νMC–O 2070 and 1955 cm^{-1} (Found: C, 63·6; H, 5·0. $C_{20}H_{18}FeO_4$ requires C, 63·5; H, 4·8%).

Tricarbonyl(9,9,10,10-*tetracyano*-8-p-*tolylmethoxybicyclo*-[5,4,0]*undecadiene*)*iron* (11).—Complex (10) (300 mg) and a molar quantity of tetracyanoethylene were heated in benzene (30 ml) at 80° for 3 h. All volatiles were removed *in vacuo* at room temperature and the solid was extracted and chromatographed on silica-gel. Toluene eluted some unchanged tetracyanoethylene and ethyl acetate–toluene (1 : 5) eluted a red band which was evaporated to give the product as a red-brown oil (100 mg; 25%). I.r. (liq. film) νC≡N 2140 cm^{-1}, νMC–O 2070 and 1960 cm^{-1}. The mass spectrum contained peaks due to $[P^+ (506)]$, $[P - (CO)]^+$, $[P - (CO)_2]^+$, $[P - (CO)_3]^+$. Analyses were high in carbon and hydrogen and low in nitrogen due to the presence of some toluene; its presence was also observed in the n.m.r. spectrum.

1-*Formyl*-8-*methyl*-8-p-*tolyheptafulvene* (7).—This compound was prepared from compound (5f) in an analogous manner to that used in the preparation of (6d); it gave the product (60%) as an orange oil. I.r. νCHO 1670 cm^{-1}. This aldehyde readily formed a DNP derivative (Found: C, 55·2; H, 3·3; N, 10·15. $C_{22}H_{21}N_4O_4$ requires C, 55·2; H, 3·6; N, 10·3%).

Tricarbonylphenylcyclo-octatetraeneiron.— Phenylcyclo-octatetraene (3·4 g) and $Fe_3(CO)_{12}$ (6·0 g) were refluxed in benzene for 5 h. All volatiles were removed *in vacuo* to give a red oil. This oil was chromatographed on alumina using toluene as eluant, the red band which developed was evaporated to give a red solid. Recrystallization from pentane afforded the product as red needles (3·6 g, 60%). I.r. (n-heptane solution) νMC–O 2060, 2000, and 1985 cm^{-1} (Found: C, 63·8; H, 3·95. $C_{17}H_{12}FeO_3$ requires C, 63·75; H, 3·75%).

Tricarbonyl(*formylphenylcyclo-octatetraene*)*iron*.— Tricarbonylphenylcyclo-octatetraeneiron was formylated as described previously.[13] The aldehyde was obtained as an orange oil (60%). I.r. (liq. film) νMC–O 2063 and 1960 cm^{-1}, νCHO 1680 cm^{-1}. The complex readily formed a DNP derivative (Found: C, 54·55; H, 3·35; N, 10·8. $C_{24}H_{18}FeN_4O_4$ requires C, 54·3; H, 3·4; N, 10·6%).

The Dimer $[C_8H_8Fe(CO)_3]_2$ (12).—Tricarbonylhydroxymethylcycloheptatrieneiron [1] (1 g) in toluene was placed on top of a silica-gel column. After 15 h toluene eluted a golden band which was evaporated to a yellow oil which crystallized. This was recrystallized from pentane to give the product (600 mg, 60%), as pale yellow crystals. I.r. (n-heptane solution) νMC–O 2046, 1991, and 1979 cm^{-1} (Found: C, 54·1; H, 3·25. $C_{22}H_{16}Fe_2O_6$ requires C, 54·1; H, 3·3%).

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