Reactivity of Co-ordinated Ligands. Part VII.[1] Electrophilic Substitution and Addition Reactions of Co-ordinated Cycloheptatriene

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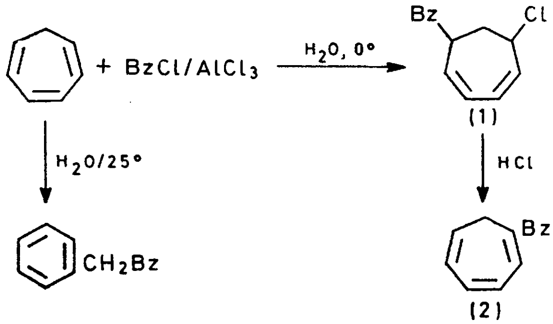
Under Friedel–Crafts conditions, with acetyl chloride and aluminium trichloride, tricarbonyl(cycloheptatriene)iron undergoes both electrophilic addition and substitution to give tricarbonyl(2—6-η-1-acetylcycloheptadienium)iron, isolated as the hexafluorophosphate salt, and tricarbonyl(1-acetylcyclohepta-1,3,5-triene)iron. Reaction of tricarbonyl(cycloheptatriene)iron with acyl tetrafluoroborates (RCO)BF_4 (R = Me or Ph) yields only addition salts of the tricarbonyl(2—6-η-1-acetylcycloheptadienium)iron type. These salts react with methoxide ion to give the ethers, tricarbonyl(1-acyl-6-methoxycyclohepta-2,4-diene)iron, which readily undergo 1,2-elimination of methanol on silica gel to yield substitution products. Formylation of tricarbonyl(cycloheptratriene)iron produces tricarbonyl(formylcycloheptatriene)iron. This aldehyde is readily reduced to the corresponding primary alcohol. This alcohol on treatment with hexafluorophosphoric acid gives tricarbonyl(2—6-η-1-methylenecycloheptadienium)iron hexafluorophosphate which contains an exocyclic double bond. The acetyl and formyl derivatives undergo protonation in acid media yielding ring and oxygen protonated species respectively. Reaction of tricarbonyl(cycloheptatriene)iron with the Simmons–Smith reagent produces hexacarbonyl[bi(cyclohepta-2,4,6-trienyl)]di-iron by hydrogen abstraction. The stereochemistry of the electrophilic addition to tricarbonyl(cycloheptatriene)iron is discussed.

In certain of its reactions with electrophilic reagents cycloheptatriene does not undergo simple substitution but rather hydride abstraction to give the tropylium cation. Thus attempted Friedel–Crafts alkylation with t-butyl chloride and aluminium trichloride [2] leads to this ion as does reaction with triphenylmethyl tetrafluoroborate.[3] Blair and Tate [4] have reported that benzoyl chloride and aluminium chloride react with cycloheptatriene to yield on hydrolysis either deoxybenzoin or the addition product (1). Treatment of compound (1) with HCl gas affords benzoylcycloheptatriene (2).



SCHEME 1

Previously it has been shown that the reactivity of cyclo-octatetraene towards electrophilic reagents is considerably modified on co-ordination to a tricarbonyliron unit and convenient synthetic routes to substituted cyclo-octatetraene derivatives were described.[1] It is now reported that, under suitable conditions, tricarbonyl(cycloheptatriene)iron undergoes substitution and addition reactions with some electrophilic reagents. In contrast to the reactions of cycloheptatriene, these reactions take place without concurrent polymerization or the formation of the tropylium ion. Some aspects of this work have been reported in a preliminary communication.[5] Recently Green and his co-workers [6] have described the 1,3-addition of tetracyanoethylene to tricarbonyl(cycloheptatriene)iron.

RESULTS AND DISCUSSION

Formylation.—Reaction of tricarbonyl(cycloheptatriene)iron with phosphoryl chloride in dimethylformamide at 0 °C gave, in 70% yield, tricarbonyl(formylcycloheptatriene)iron (11), identified on the basis of analytical and spectroscopic data. The ^1H n.m.r. is simple and readily interpreted (Table 1). In the i.r. spectrum, bands due to co-ordinated carbonyl groups and the aldehyde group are observed (Table 2). The mass spectrum is in complete accord with the proposed structure, exhibiting a molecular ion ($m/e = 260$) and daughter ions corresponding to $[P - CO]^+$, $[P - 2CO]^+$, $[P - 3CO]^+$, $[P - 3CO - HCO]^+$, and $(P - 3CO - CH_2O]^+$. In contrast to many other tricarbonyl(diene)iron systems attempts to remove the free organic molecule were unsuccessful. The mechanism of this formylation is probably similar to that discussed previously for tricarbonyl(cyclo-octatetraene)iron.[1] In this case however hydrolysis of the Vilsmeyer salt occurs slowly. Thus if extraction of the product is attempted immediately after hydrolysis a 5% yield of compound (11) is obtained; if however, the hydrolysing reaction mixture is set aside for 15 h prior to extraction a 70% yield is obtained.

Acylation.—Reaction of compound (3) with acetyl chloride and aluminium chloride in dichloromethane at 0 °C produced a yellow oil. Hydrolysis of the reaction mixture followed by separation of the organic layer gave the ketone (5a) in 25% yield. This ketone

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[1] Part VI, B. F. G. Johnson, J. Lewis, and G. L. P. Randall, *J. Chem. Soc.* (*A*), 1971, 422.

[2] D. Bryce-Smith and N. A. Perkins, *J. Chem. Soc.*, 1961, 2320.

[3] H. J. Dauben, F. A. Gradecki, K. M. Harman, and D. L. Pearson, *J. Amer. Chem. Soc.*, 1957, **79**, 4557.

[4] J. A. Blair and C. J. Tate, *J. Chem. Soc.* (*C*), 1971, 1592.

[5] B. F. G. Johnson, J. Lewis, and G. L. P. Randall, *Chem. Comm.*, 1969, 1273.

[6] M. Green, S. Tolson, J. Weaver, D. C. Wood, and P. Woodward, *Chem. Comm.*, 1971, 222.

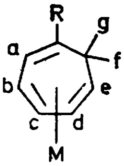
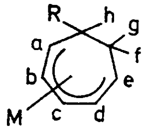
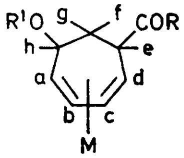
(5a) was characterized by its n.m.r. and i.r. spectra (see Tables 1 and 2), which are directly related to those of compound (11). Mass spectra were in complete accord with the proposed structure. Addition of ammonium hexafluorophosphate to the aqueous layer precipitated the hexafluorophosphate salt of tricarbonyl(2—6-η-1-acetylcycloheptadienium)iron. Treatment of this salt with strong base, triethylamine, did not produce the ketone (5a) but gave small amounts of a brown oil which could not be characterized.

Addition of (3) to acetyl and benzoyl tetrafluoroborates in dichloromethane at —78° afforded the salts (6a) and (6b) in almost quantitative yield. The n.m.r. spectrum of (6a) was identical to that of the salt isolated from the Friedel–Crafts reaction. No neutral ketones were detected in these reactions and neither of the salts gave the ketone complexes on treatment with strong base. However, as illustrated in Scheme 2, methoxide attack followed by elimination of methanol on silica produced the acyl derivatives in high yield.

Reactions of the Aldehyde (11) *and Ketone Complexes* (5).—It was of interest to investigate the general reactivity of these derivatives. In all cases the reactions shown by the functional groups RCHO and R_2CO appear normal. Reduction with sodium borohydride in ethanol or with the appropriate Grignard reagents gave the alcohols (8a—c) in good yields. These readily underwent hydroxide ion abstraction with hexafluorophosphoric acid or triphenylmethyl tetrafluoroborate to produce the yellow salts (9). These were characterized by analytical data and structure (9) assigned on the

TABLE 1

N.m.r. data *

Compound and solvent	Proton(s)	Chemical shift (τ)	Relative intensity	Multiplicity	*J*/Hz
					
(11)	H_a	3·20	1	d	8·5
R = CHO	H_b	6·82	1	t	8·5
CS_2	$H_c + H_d$	4·50	2	m	
	H_e	6·45	1	m	
	$H_f + H_g$	7·57	2	m	
	CHO	0·98	1	s	
(5a)	H_a	3·06	1	d	8·0
R = $COCH_3$	H_b	6·98	1	t	8·0
CS_2	$H_c + H_d$	4·65	2	m	
	H_e	6·54	1	m	
	$H_f + H_g$	7·55	2	m	
	CH_3CO	7·96	3	s	
(5b)	H_a	3·26	1	d	8·0
R = COPh	H_b	6·96	1	t	8·0
CS_2	$H_c + H_d$	4·66	2	m	
	H_e	6·53	1	m	
	$H_f + H_g$	7·52	2	m	
	PhCO	2·68	5	m	
					
(4)	H_c	2·80	1	t	6
R = $COCH_3$	$H_b + H_d$	3·94	2	m	
SO_2	H_a	5·30	1	2 × d	9·5, 6
	H_e	5·10	1	t	8
	H_f	7·05	1	m	
	H_g	8·05	1	d	16
	H_h	5·86	1	m	
	CH_3CO	7·86	3	s	
(6a)	H_c	2·77	1	t	6·0
R = $COCH_3$	$H_b + H_d$	3·90	2	m	
SO_2	H_a	5·29	1	2 × d	9·5, 6·0
	H_e	5·08	1	t	8
	H_f	7·06	1	m	
	H_g	8·07	1	d	16
	H_h	5·84	1	m	
	CH_3CO	7·88	3	s	
(6b)	H_c	2·75	1	t	8·0
R = COPh	$H_b + H_d$	3·92	2	m	
SO_2	$H_a + H_e + H_h$	5·13	3	m	
	H_f	6·83	1	m	
	H_g	8·23	1	d	17
	PhCO	2·25	5	m	
(3)	H_c	3·25	1	t	6
R = H	$H_b + H_d$	4·40	2	m	
CF_3CO_2H	$H_a + H_e$	5·40	2	m	
	$H_f + H_h$	7·65	2	m	
	H_g + R	8·50	2	m	
(12)	H_c	2·81	1	t	6·5
R = CH_3CO	$H_b + H_d$	3·93	2	m	
SO_2	$H_a + H_e$	4·98	2	m	
	$H_g + H_f + H_h$	7·23	3	m	
	CH_3CO	7·86	3	s	
(16)	H_c	2·83	1	t	6·5
R = D	$H_b + H_d$	3·98	2	m	
SO_2	$H_a + H_e$	5·02	2	m	
	$H_f + H_h$	7·30	2	m	
	H_g	8·10	1	m	
					
(7a)	$H_a + H_d$	7·10	2	m	
R^1 = H, R = CH_3	$H_b + H_c$	4·62	2	m	
$CDCl_3$	H_e	6·95	1	m	
	H_f	8·24	1	d	12
	H_g	8·98	1	q	12
	H_h	5·90	1	m	
	HO	7·42	1	s	
	CH_3CO	7·88	3	s	
(7b)	$H_a + H_d$	7·07	2	m	
R^1 = Me, R = Ph	$H_b + H_c$	4·62	2	m	
CS_2	H_h	6·30	1	m	
	H_g	8·31	1	d	13
	H_f	8·44	1	q	13
	CH_3O	6·80	3	s	
	PhCO	2·36	5	m	

* 100 MHz unless otherwise stated.

TABLE 1 (*Continued*)

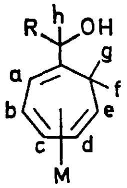
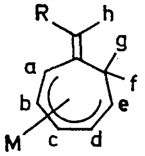
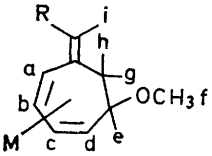
Compound and solvent	Proton(s)	Chemical shift (τ)	Relative intensity	Multiplicity	J/Hz
					
(8a)	H_a	4·3	1	d	8
$R = H$	H_b	7·0	1	t	8
CS_2/60 MHz	$H_c + H_d$	4·75	2	m	
	H_e	6·7	1	m	
	$H_f + H_g$	7·8	2	m	
	$H_h + R$	6·4	2	s	
	OH	7·8	1	s	
(8b)	H_a	4·3	1	d	8
$R = CH_3$	H_b	7·0	1	t	8
CS_2/60 MHz	$H_c + H_d$	4·8	2	m	
	H_e	6·7	1	m	
	$H_f + H_g$	7·8	2	m	
	H_h	6·2	1	q	6
	OH	7·5	1	s	
	CH_3	8·95	3	d	6
(8c)	H_a	4·30	1	d	8
$R = Ph$	$H_b + H_e + OH$	7·0	3	m	
CS_2	$H_c + H_d$	4·94	2	m	
	$H_g + H_f$	8·0	2	m	
	H_h	5·42	1	s	
	Ph	2·94	5	m	
					
(9a)	$H_a + H_b + H_h$	4·4	3	m	
$R = H, SO_2$	H_c	2·9	1	m	
	H_d	3·72	1	t	6
	H_e	5·02	1	m	
	H_f	7·92	1	2 × d	16, 8
	H_g	7·12	1	d	16
	R	4·9	1	s	
(9b)	$H_a + H_b + H_h$	4·4	3	m	
$R = CH_3, SO_2$ 60 MHz	H_c	3·0	1	m	
	H_d	3·8	1	m	
	H_e	5·1	1	m	
	H_f	6·9	1	2 × d	15, 7
	H_g	8·1	1	d	15
	CH_3	8·3	3	d	7
(9c)	$H_a + H_b$	4·3	2	m	
$R = Ph$	$H_c + Ph + H_h$	3·0	7	m	
SO_2	H_d	3·7	1	m	
	H_e	5·41	1	m	
	H_f	6·9	1	m	
	H_g	7·7	1	t	12
(13)	H_c	3·14	1	t	6
$R = OH$	$H_b + H_d$	3·72	2	m	
SO_2	$H_a + H_e$	5·12	2	m	
	H_f	6·88	1	m	
	H_g	8·07	1	m	
	H_h	2·86	1	s	
	OH	3·62	1	s	

TABLE 1 (*Continued*)

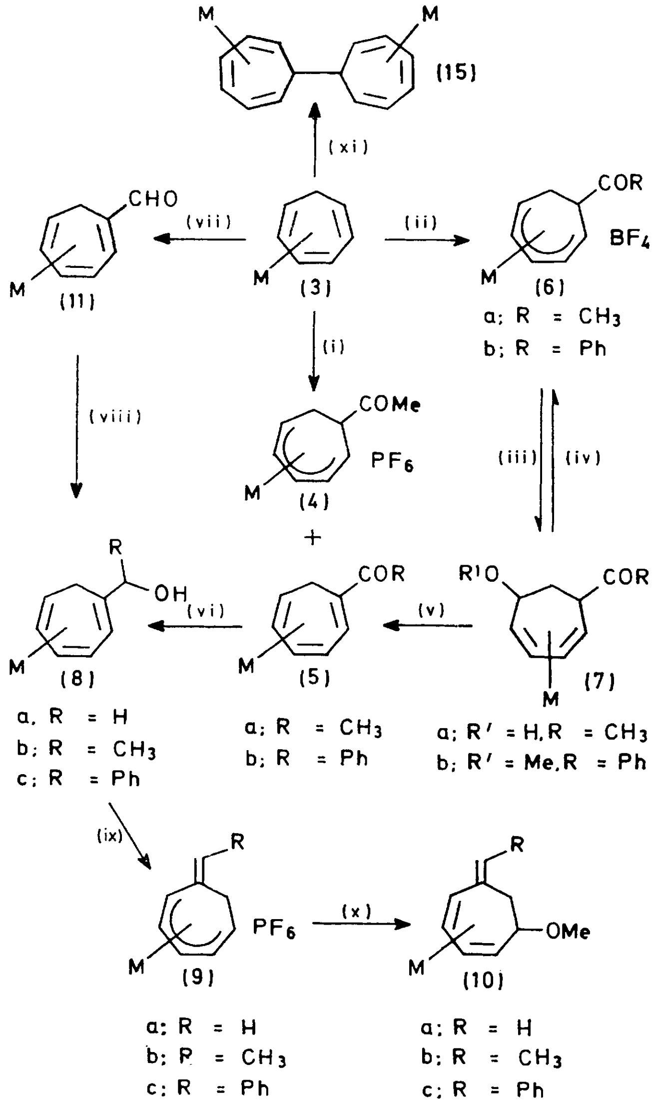
Compound and solvent	Proton(s)	Chemical shift (τ)	Relative intensity	Multiplicity	J/Hz
					
(10a)	H_a	6·37	1	d	7
$R = H_1CS_2$	$H_b + H_c$	4·69	2	m	
	H_d	6·98	1	2 × d	7, 2
	H_e	6·50	1	3 × d	11, 4, 5, 2
	H_f	6·78	3	s	
	H_g	7·84	1	3 × d	11, 4, 5, 2
	H_h	8·44	1	t	11
	$R + H_i$	5·28	2	d	Not coupled
(10b)	H_a	6·34	1	2 × d	6
$R = CH_3$	$H_b + H_c + H_i$	4·75	3	m	
CS_2	H_d	7·04	1	d	4
	H_e	6·65	1	m	
	H_f	6·78	3	2 × s	
	$H_g + H_h$	7·3—9·0	2	m	
	CH_3	8·48	3	2 × d	6·5
(10c)	H_a	6·06, 6·16	0·4, 0·6	2 × d	7, 7
$R = Ph, CS_2$	$H_b + H_c$	4·68	2	m	
	H_d	6·88	1	m	
	H_e	6·42	1	2d × 2	11, 2
	H_f	6·74, 6·78	1·2, 1·8	2s	
	H_g	7·26, 7·88	0·6, 0·4	2d	11
	H_h	8·26, 8·68	0·4, 0·6	2t	11
	H_i	3·65, 3·95	0·6, 0·4	2s	
	Ph	2·85	5·0	m	

basis of ^1H n.m.r. spectra for solutions in liquid sulphur dioxide (Table 1). The proposed structure which contains a π-pentadienyl fragment and an exocyclic double-bond, is fully consistent with the results of double-irradiation experiments and supported by the chemical behaviour shown by the salts, see Scheme 2.

Treatment of (9) with methoxide ion in methanol gave ethers (10) in which addition has occurred to the ring system rather than to the exocyclic methylene group. Such behaviour is in marked contrast to that shown by the system $[C_9H_9Fe(CO)_3]PF_6$ and $[C_{10}H_{11}Fe(CO)_3]PF_6$ derived from tricarbonyl(cyclo-octatetraene)iron[1] and reflects possible different structural types for the two complexes. The generation of stable π-pentadienyl groupings is a common feature of the chemistry of tricarbonyl(cyclo-diene)iron complexes and is presumably the driving force in the formation of the exocyclic double-bond.

In this work it has not been possible to liberate the free organic molecule from the tricarbonyliron unit. Attempted oxidation with cerium(IV) led to mixtures of compounds. As cycloheptatriene is itself readily oxidized by this reagent[7] other methods are being investigated.

The Stereochemistry of Electrophilic Attack.—Complex (3) is readily protonated in acid to give the tricarbonyl-(cycloheptadienium)iron cation.[8,9] The n.m.r. spectrum in the τ 7—9 region consists of two absorptions due to the methylene protons (see Figure). On irradiation at H_a, H_e (τ 5·0) a typical AA'BB' pattern is observed.*



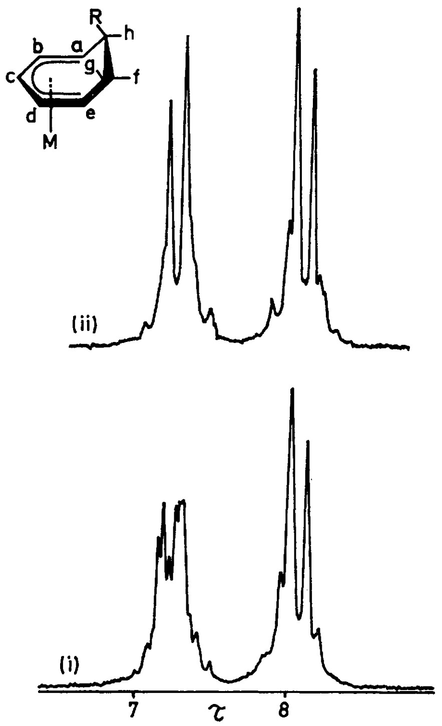
SCHEME 2 M = Fe(CO)$_3$. Reagents: (i) acetyl chloride–aluminium chloride, (ii) RCOBF$_4$, (iii) OR^{1-}, (iv) HBF$_4$, (v) silica-gel, (vi) NaBH$_4$, (vii) POCl$_3$–HCONMe$_2$, (viii) RMgX, (ix) HPF$_6$, (x) OMe$^-$, and (xi) CH$_2$I$_2$–ZnCu

TABLE 2

I.r. spectra (ν in cm^{-1})

Compound	Metal carbonyl absorption	Other functional groups	
(4)	2100, 2050	C=O	1720
		P–F	840[a]
(5a)	2060, 1995, 1983	C=O	1663[b]
(5b)	2060, 1993, 1980	C=O	1630[c]
(6a)	2120, 2060	C=O	1720
		B–F	1100[a]
(6b)	2120, 2070	C=O	1680
		B–F	1100[d]
(7a)	2058, 1993	C=O	1708
		O–H	3593
			3403[e]
(7b)	2050, 1978[b]	C=O	1686[f]
(8a)	2048, 1983, 1973[b]	O–H	3300[f]
(8b)	2053, 1985, 1982[b]	O–H	3350[f]
(8c)	2055, 1990, 1980[e]	O–H	3390[f]
(9a)	2110, 2060	C=C	1625
		P–F	840[a]
(9b)	2110, 2060	C=C	1635
		P–F	840[a]
(9c)	2118, 2075, 2060	C=C	1610
		P–F	840[a]
(10a)	2053, 1983, 1978[b]	C=C	1610[a]
		C–O	1079[a]
(10b)	2053, 1993, 1983[b]	C=C	1632[a]
		C–O	1085[a]
(10c)	2049, 1988, 1980[e]	C=C	1600[f]
		C–O	1080[f]
(11)	2044, 2004, 1999	C=O	1684
		C=C	1644[b]
(12)	2100, 2050	C=O	1720
		P–F	840[a]
(13)	2100, 2060	O–H	3520
		C=C	1650
		P–F	840[a]
(15)	2050, 1993, 1980[c]		
(16)	2120, 2080	B–F	1100[a]

[a] Nujol mull. [b] In CCl$_4$. [c] In cyclohexane. [d] In CH$_2$Cl$_2$. In CHCl$_3$. [f] Liquid film.



N.m.r. spectrum of compound (3) in trifluoroacetic acid, (i); and (ii), with H_a, H_e resonance irradiated

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* Spectra synthesized using $J_{AA'} = J_{BB'} = 8$ Hz, $J_{AB} = J_{A'B} = -12$ Hz, $J_{AB'} = J_{A'B} = 1$ Hz and $\Delta = 84$ Hz are superposable on the double-resonance spectrum Figure.

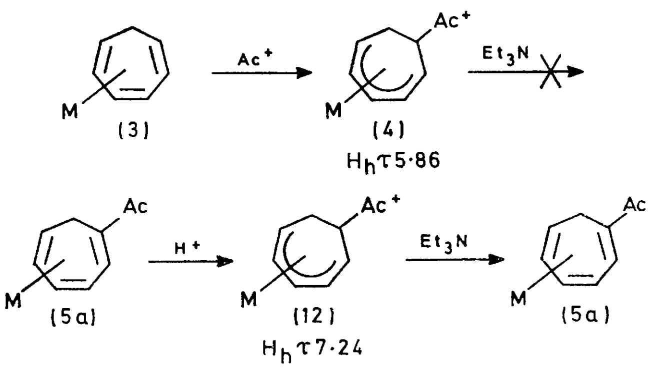
[7] W. S. Trahanovsky, L. B. Young, and M. D. Robbins, *J. Amer. Chem. Soc.*, 1969, **91**, 7084.

[8] H. J. Dauben and D. J. Bertelli, *J. Amer. Chem. Soc.*, 1961, **83**, 497.

[9] A. Davison, W. McFarlane, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 1962, 4821.

The molecule must therefore possess a plane of symmetry and have a structure similar to that illustrated. Wilkinson *et al.* have shown that, in [$^2H_2$]sulphuric acid, the resonance at highest field is of unit intensity. It was concluded on a chemical shift basis that the added proton was *endo* with respect to the metal atom.[9] The cation $[(\pi\text{-}C_7H_8D)Fe(CO)_3]^+$ may be prepared by treatment of (3) with D^+;[9] treatment of this cation with triethylamine in acetone yields a 1 : 1 mixture of $(\pi\text{-}C_7H_8)Fe(CO)_3$ and $(\pi\text{-}C_7H_7D)Fe(CO)_3$ indicating equal loss of H^+ and D^+. Protonation and deprotonation are therefore stereospecific and proceed in a similar manner.

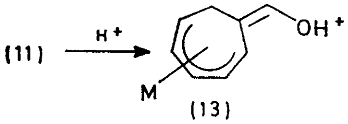
Pauson and his co-workers have clearly demonstrated that for certain ring systems *exo*- and *endo*-isomers may be differentiated, using their n.m.r. spectra, provided both derivatives are available.[10] By an *X*-ray study[11] they have shown that *exo*-protons lie at higher field due to shielding by the ring system. On this basis, and in contrast to previous work,[9] the proton which adds to compound (3) in acid solution must be *exo*.



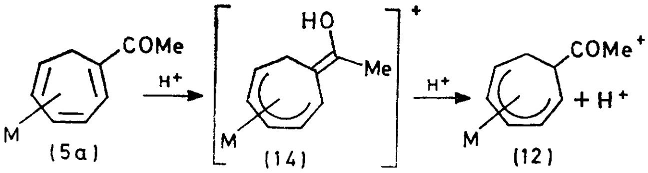
SCHEME 3

The alternative isomer of (4) is obtained on protonation of (5a) (Scheme 3). The i.r. spectrum of this salt is identical to that of (4). In the n.m.r. spectrum however, H_1 lies at τ 7·24 and this is therefore the *endo*-acyl isomer. It is unlikely that the salt (4) is an intermediate in the Friedel–Crafts reaction, for the production of the ketone (5a) because elimination of the *endo* proton from (4) does not occur even in the presence of triethylamine. As the *endo*-acyl salt (12) readily eliminates its *exo*-proton, it is possible that the substitution product arises from *endo* attack by acyl groups which may occur *via* the metal atom. The difference in structure distribution between these two reagents, aluminium chloride and boron trifluoride, is probably associated with the high degree of covalent character for the aluminium chloride adduct. This aspect of the reaction process is being further investigated.

Protonation of Complexes (11) *and* (5a).—Addition of HPF_6 (60%) to ether solutions of (11) yields a bright orange salt (13). The i.r. spectrum of this salt exhibits a sharp band due to the alcoholic group (3520 cm^{-1}) bands due to M at 2120 and 2060 and a band at 1640 cm^{-1} which may be assigned to the exocyclic double-bond. The n.m.r. spectrum in sulphur dioxide exhibits the characteristic dienyl pattern, Table 1. The alcoholic proton which is absent in spectra in trifluoroacetic acid solution, lies at τ 3·62. Addition of methanol or diazomethane to (13) regenerates the aldehyde complex (11).



Treatment of (5a) with hexafluorophosphoric acid in ether gave an immediate precipitate of a yellow salt, on continued stirring (0·5 h) the colour changed to off-white. Rapid filtration isolated the yellow salt ' (14) ', which had an i.r. spectrum similar to that of (13). It was, however, too unstable to characterise further, but this is possibly the protonated oxygen intermediate formed prior to the formation of salt (12). The stable salt (12) had an identical i.r. spectrum to that of the addition salt (4). However, the n.m.r. spectra of (4) and (12) show important differences which have been discussed above. The *endo*-acyl complex probably arises from *exo*-proton attack on the unstable *O*-protonated species ' (14) '.



The Reaction of Tricarbonyl(cycloheptatriene)iron with Carbene.—The electrophilic reactions described above involve cationic electrophiles and it was of interest to investigate the reaction of carbene, a neutral electrophile, with the system.

Carbene, generated from di-iodomethane and a zinc–copper couple, was allowed to react with (3) in refluxing ether. The product of this reaction crystallized from pentane as yellow needles, m.p. 115°. Elemental analysis indicated the stoicheiometry $C_{10}H_7FeO_3$. The mass spectrum did not contain a molecular ion at *m/e* 462, but ions corresponding to the successive loss of six carbon monoxide groups were observed. I.r. spectra in cyclohexane exhibited three sharp bands in the terminal carbonyl region. The n.m.r. spectrum in carbon disulphide is very similar to that of (3) except that the methylene resonance is of unit intensity. The compound is therefore formulated as a bi(cyclohepta-2,4,6-trienyl) complex (15).

EXPERIMENTAL

Tricarbonyl(cycloheptatriene)iron (3).—Irradiation (125 W mercury discharge lamp) of a solution of pentacarbonyliron (100 g) and cycloheptatriene (100 ml) in benzene (100 ml) at

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[10] P. L. Pauson, G. H. Smith, and J. H. Valentine, *J. Chem. Soc.* (*C*), 1967, 1061.

[11] P. E. Baikie, O. S. Mills, P. L. Pauson, G. H. Smith, and J. Valentine, *Chem. Comm.*, 1965, 425.

reflux temperature for 48 h followed by evaporation *in vacuo* gave a yellow-brown oil. Distillation gave *the product*, 148 g, as an orange oil (b.p. 55—65°, 0·05 mmHg).

Tricarbonyl(1-*formylcyclohepta*-1,3,5-*triene*)*iron*(11).—Tricarbonyl(cycloheptatriene)iron (2·8 g) in dimethylformamide (15 ml) was added to a solution of phosphorus oxychloride (8·0 ml) in dimethylformamide (20 ml) at 0°. The mixture was stirred for 1 h and was then poured into water (400 ml); this was set aside for 15 h at 20 °C and was then extracted with ether (5 × 30 ml). The combined extracts were washed with water (5 × 50 ml) and dried ($MgSO_4$). Evaporation *in vacuo* gave a yellow-brown solid which was chromatographed on silica gel. Elution with toluene gave unchanged starting material (0·1 g); 5% ethyl acetate eluted a deep orange band. Evaporation of this eluant *in vacuo* gave the product as an orange-yellow solid (2·2 g, 70%), m.p. 88—89°. The *product* sublimes *in vacuo* (70°, 0·01 mmHg) (Found: C, 51·1; H, 3·5. $C_{11}H_8FeO_4$ requires C, 50·8; H, 3·1%).

The product readily forms a 2,4-dinitrophenylhydrazone, m.p. 180° (dec.) (Found: C, 46·0; H, 2·9; N, 12·6. $C_{17}H_{12}FeN_4O_7$ requires C, 46·4; H, 2·7; N, 12·7%).

Tricarbonyl(2—6-η-1-*acetylcycloheptadienium*)*iron Hexafluorophosphate* (4).—Tricarbonyl(cycloheptatriene)iron (2·8 g) in dichloromethane (10 ml) was added dropwise to a solution of aluminium trichloride (3·0 g), acetyl chloride (2·0 ml) and dichloromethane (40 ml) at 0°. The mixture was stirred at 0° for 10 min and was then hydrolysed with ice–water (150 ml). The organic layer was removed and the aqueous layer was extracted with ether (3 × 20 ml). The organic extracts were dried ($MgSO_4$) and evaporated *in vacuo* to give an orange-yellow oil.

The aqueous layer was stirred with 15% aqueous ammonium hexafluorophosphate until no more precipitate formed. The precipitate was washed with water (2 × 10 ml) and anhydrous ether (5 × 5 ml), and then dried *in vacuo* to give the *product* as a pale yellow solid (3·0 g, 60%), m.p. 120° (dec.) (Found: C, 34·45; H, 2·75. $C_{12}H_{11}F_6FeO_4P$ requires C, 34·4; H, 2·6%).

Tricarbonyl(1-*acetyl*-6-*hydroxycyclohepta*-2,4-*diene*)*iron* (7a).—The aqueous layer from the preparation of (4) was stirred with saturated sodium hydrogen carbonate until pH 4 was obtained. The mixture was extracted with ether (5 × 20 ml) and the extract was dried; evaporation *in vacuo* gave a pale yellow solid. Recrystallization from light petroleum gave the *product* as pale yellow crystals (1·4 g, 40%), m.p. 108—110° (Found: C, 49·65; H, 4·2. $C_{12}H_{12}FeO_5$ requires C, 49·35; H, 4·1%).

Tricarbonyl(1-*acetylcyclohepta*-1,3,5-*triene*)*iron* (5a).—The product from the organic fraction in the preparation of (4) was chromatographed on silica gel. Toluene eluted a weak yellow band and 5% ethyl acetate in toluene eluted a deep yellow band which was evaporated *in vacuo* to give a yellow oil. The oil was distilled on to a cold finger (80°, 0·05 mmHg) and this crystallized to give the *product* as a yellow solid (800 mg, 24%), m.p. 88—89° (Found: C, 52·4; H, 3·8. $C_{12}H_{10}FeO_4$ requires C, 52·5; H, 3·65%).

Tricarbonyl(2—6-η-1-*acetylcycloheptadienium*)*iron Tetrafluoroborate* (6a).—Boron trifluoride was bubbled through a solution of acetyl fluoride (0·54 g) in dichloromethane (30 ml) at −80 °C until no further precipitate formed. Compound (3) (2·0 g) in dichloromethane (10 ml) was added dropwise and the mixture was stirred for 10 min. The solvent was removed under reduced pressure at −20 °C. A pale yellow solid was washed with anhydrous ether and dried *in vacuo* to give the *product* (2·8 g, 90%) (Found: C, 39·6; H, 3·2. $C_{12}H_{11}BF_4FeO_4$ requires C, 39·8; H, 3·04%).

Tricarbonyl(2—6-η-1-*benzoylcycloheptadienium*)*iron Tetrafluoroborate* (6b).—This compound was prepared in a similar manner to (6a) using benzoyl fluoride, to give the complex (90%) as an off-white solid (Found: C, 47·95; H, 3·2. $C_{17}H_{13}BF_4FeO_4$ requires C, 48·2; H, 3·05%).

Tricarbonyl(1-*benzoyl*-6-*methoxycyclohepta*-2,4-*diene*)*iron* (7b).—Complex (6b) (1 g) was stirred in methanol (50 ml) until it was dissolved. The solution was treated with brine (300 ml) and extracted with ether (4 × 100 ml). The ether extracts were combined, dried ($MgSO_4$), and evaporated *in vacuo* to give a pale yellow oil. Chromatography on silica gel using 10% ethyl acetate in toluene as eluant gave, on evaporation of the only band which developed, the *product* as an almost colourless oil (0·78 g, 90%) (Found: C, 58·05; H, 4·35. $C_{18}H_{16}FeO_5$ requires C, 58·6; H, 4·4%).

Tricarbonyl(1-*hydroxymethylcyclohepta*-1,3,5-*triene*)*iron* (8a).—The aldehyde (11) (840 mg) in absolute ethanol (75 ml) was stirred with sodium borohydride (1·5 g) for 45 min at 20°. The mixture was poured into water and extracted with ether (4 × 25 ml) and the extracts were dried ($MgSO_4$). The extracts were evaporated *in vacuo* to give a yellow solid. Chromatography on silica gel and elution with 5% ethyl acetate in toluene gave two bands. The first band was very pale yellow, the second band which was deep yellow was evaporated *in vacuo* to give the *product* as a yellow volatile solid (760 mg, 91%), which sublimes 80°, 0·05 mmHg (Found: C, 50·9; H, 4·12. $C_{11}H_{10}FeO_4$ requires C, 50·4; H, 3·8%).

Tricarbonyl(1-α-*hydroxyethylcyclohepta*-1,3,5-*triene*)*iron* (8b).—This alcohol was prepared from the ketone, (5a), by reduction with sodium borohydride. The experimental conditions were the same as used in the preparation of the alcohol (8a). The *product* was obtained as a yellow oil by distillation onto a cold finger at 100°, 0·05 mmHg (80%) (Found: C, 52·0; H, 4·65. $C_{12}H_{12}FeO_4$ requires C, 52·5; H, 4·35%).

Tricarbonyl(1-*hydroxyphenylmethylcyclohepta*-1,3,5-*triene*)-*iron* (8c).—The aldehyde (10) (800 mg, 1 mol equiv.) in anhydrous ether (50 ml) at −30° was treated with 1M-phenyl Grignard reagent (4 mol equiv.). The reaction mixture was stirred at −30° for 15 min, and a saturated aqueous solution of ammonium chloride (25 ml) was added to it. The hydrolysis mixture was warmed to 20°. The ether layer was separated, washed with sodium hydrogen carbonate solution (3 × 20 ml) and dried ($MgSO_4$). Evaporation *in vacuo* gave a pale yellow involatile oil, 930 mg (90%) (Found: C, 60·7; H, 4·5. $C_{17}H_{14}FeO_4$ requires C, 60·3; H, 4·15%).

Tricarbonyl(2—6-η-1-*methylenecycloheptadienium*)*iron Hexafluorophosphate* (9a).—The alcohol (8a) 50 mg, in ether (5 ml) was treated with hexafluorophosphoric acid (65% aq.) until no more precipitate formed. The precipitate was washed with ether (3 × 10 ml), anhydrous ether (5 × 10 ml) and was dried *in vacuo* to give the *product* as a yellow solid 90% (Found: C, 34·2; H, 2·6. $C_{11}H_9F_6FeO_3P$ requires C, 33·9; H, 2·8%). N.m.r. double-irradiation experiments: H_b is coupled to H_c and H_c is coupled to H_d. H_e is coupled to H_d and H_g. The resonances due to H_h and R = H are not coupled.

Tricarbonyl(2—6-η-1-*methylmethylenecycloheptadienium*)-*iron Hexafluorophosphate* (9b).—This complex was prepared from the alcohol (8b) under the same experimental conditions as used for the preparation of (9a). The product was obtained as a yellow solid (90%) (Found: C, 35·2; H, 2·8. $C_{12}H_{11}F_6FeO_3P$ requires C, 35·7; H, 2·75%).

Tricarbonyl(2—6-η-1-*phenylmethylenecycloheptadienium*)-*iron Hexafluorophosphate* (9c).—The experimental conditions for the preparation of this complex from the alcohol (8c) were the same as used in the preparation of (9a). The product was obtained as a yellow solid (95%) (Found: C, 44·0; H, 3·05. $C_{17}H_{13}F_6FeO_3P$ requires C, 43·8; H, 2·8%).

Tricarbonyl(1-*benzoylcyclohepta*-1,3,5-*triene*)*iron* (5b).—The methoxide derivative (7b) (1·0 g) was placed on top of a column of silica-gel made up in toluene. After 6 h at 20°, a deep yellow band was eluted with 10% ethyl acetate in toluene. Evaporation *in vacuo* gave a golden oil which crystallized on addition of pentane. Recrystallization from pentane afforded golden crystals of the *product* 0·93 g (80%), m.p. 95° (Found: C, 60·65; H, 3·9. $C_{17}H_{13}BF_4FeO_4$ requires C, 60·7; H, 3·55%).

Tricarbonyl(1-*methoxy*-6-*methylenecyclohepta*-2,4-*diene*)-*iron* (10a).—The hexafluorophosphate salt (9a) (560 mg) was stirred in methanol (25 ml) for 20 min. The salt dissolved to give a yellow solution which was poured into water (200 ml) and extracted with ether (4 × 50 ml); the extract was dried ($MgSO_4$) and evaporated *in vacuo* to give a yellow solid which was sublimed at 90°, 0·05 mmHg to give the *product* as a yellow solid (370 mg, 95%) (Found: C, 52·4; H, 4·55. $C_{12}H_{12}FeO_4$ requires C, 52·2; H, 4·35%).

Tricarbonyl(1-*methoxy*-6-*methylmethylenecyclohepta*-2,4-*diene*)*iron* (10b).—This methoxy-derivative was prepared from the salt (9b) under the same conditions used for the preparation of (10a) from (9a). The product was obtained as a yellow oil by distillation onto a cold finger (80°, 0·05 mmHg) (Found: C, 54·3; H, 5·0. $C_{13}H_{14}FeO_4$ requires C, 53·75; H, 4·85%).

Tricarbonyl(1-*methoxy*-6-*phenylmethylenecyclohepta*-2,4-*diene*)*iron* (10c).—This complex was prepared from the salt (9c) by reaction with methanol under exactly the same conditions as used for the preparation of (10a) from (9a). The product was obtained as a yellow oil by distillation onto a cold finger (120°, 0·05 mmHg) (Found: C, 61·9; H, 4·5. $C_{18}H_{16}FeO_4$ requires C, 61·4; H, 4·6%).

Tricarbonyl(2—6-η-[1-²H]*cycloheptadienium*)*iron Tetrafluoroborate* (16).—Tetrafluoroboric acid (40%, 2·0 g) in propionic anhydride (5 ml) at 0° was treated dropwise with (3) (3·3 g) in deuteriotrifluoroacetic acid (the minimum quantity). The precipitate which formed was filtered and washed with light petroleum to give the *product* as an off-white solid, 2·7 g (60%) (Found: C, 37·2; H, 3·15. $C_{10}H_8{}^2HBF_4FeO_3$ requires C, 37·5; H, 3·1%).

Reaction of Compound (16) *with Triethylamine*.—The salt (16) (1·0 g) in acetone (25 ml) was treated with an excess of triethylamine. Dilute HCl was added until pH 2 was attained. Extraction with ether–brine and drying of the ether extract ($MgSO_4$) followed by evaporation *in vacuo* and chromatography on alumina with light petroleum (30—40°), gave a yellow oil. This oil was determined to be a *ca.* 1 : 1 mixture of (π-C_7H_8)Fe(CO)$_3$ and (π-C_7H_7D)Fe(CO)$_3$ from its n.m.r. and mass spectra.

Tricarbonyl(2—6-η-1-*hydroxymethylenecycloheptadienium*)-*iron Hexafluorophosphate* (13).—The aldehyde (11) (1 g) in ether (50 ml) was treated, dropwise, with hexafluorophosphoric acid (60%). The bright orange solid which separated was washed with absolute ether to give the *product* (1·4 g, 90%) (Found: C, 32·4; H, 2·15. $C_{11}H_9F_6FeO_4P$ requires C, 32·5; H, 2·2%).

Tricarbonyl(2—6-η-1-*acetylcycloheptadienium*)*iron Hexafluorophosphate* (12).—This salt was prepared by the method used for the preparation of (13) to give the product as an off-white solid (80%) (Found: C, 33·4; H, 2·6. $C_{12}H_{11}F_6FeO_4P$ requires C, 33·4; H, 2·6%).

Microanalyses were by the microanalytical department of this Laboratory. ^1H N.m.r. spectra were measured at 60 MHz with a Perkin-Elmer R10 instrument and at 100 MHz on a Varian Associates HA 100 machine. I.r. spectra were obtained using a Perkin-Elmer 257 spectrometer.

M.p.s were measured in open capillary tubes on a Gallenkamp apparatus. All reactions were carried out under pure dry nitrogen.

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