Structure and Reactivity of Some Carbonium Ion Derivatives of [Alkyl(cyclo-octatetraenyl)methanol]tricarbonyliron

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Treatment of the title compounds, $[Fe(CO)_3\{C_8H_7C(OH)HR\}]$ (R = Et or Bu^n) with Ph_3CBF_4 or HPF_6 gives in almost quantitative yield the salts $[Fe(CO)_3\{C_8H_7CH(R)\}]X$ (X = BF_4 or PF_6). On the basis of ^{1}H n.m.r. spectroscopic evidence, the structure of these salts is thought to involve a pentadienyl fragment and an unco-ordinated double bond within the eight-membered ring system and an exocyclic double bond. Some reactions of these salts with nucleophilic reagents are also described.

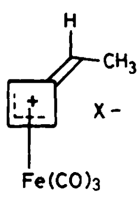
CARBONIUM ions in organic chemistry are generally encountered only as reactive transients and can rarely be isolated.[1] However, some carbonium ions, especially those involving conjugated systems, form stable isolable species when co-ordinated to metal carbonyl moieties as in tricarbonyl(cyclohexadienyl)iron tetrafluoroborate.[2] The higher stability of co-ordinated carbonium ions is thought to arise from the increased delocalisation of positive charge brought about by metal-to-ring back bonding.[3]

A special type of metal-stabilised carbonium ion are those formed by hydroxide abstraction from carbinols and were first observed as ferrocene derivatives.[4] Thus, protonation of α-ferrocenylbenzyl alcohol with fluoroboric acid gives a stable crystalline salt, α-ferrocenylbenzylium tetrafluoroborate.[5] The exact nature of the bonding in this and related compounds is still unclear, although it has been established that the bond from the ring to the carbonium carbon atom possesses a certain amount of double-bond character.[6]

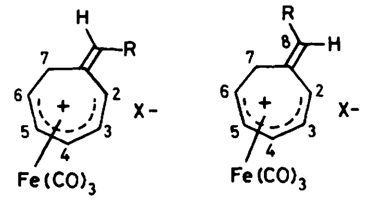
(Benzyl alcohol)tricarbonylchromium undergoes protonation to form a co-ordinated benzyl cation.[7] However, this co-ordinated carbonium ion has not been isolated and only its u.v. spectrum has been measured, from which little information could be deduced.[8]

Tricarbonyl(cyclobutadienylmethanol)iron, on treatment with strong acids, gives stable isolable salts which have been assigned structure (1) on the basis of their ^{1}H n.m.r. spectra.[9] Similarly, protonation of tricarbonyl(cyclohepta-1,3,5-trienylmethanol)iron gives the stable salt (2; R = H), which, on the basis of n.m.r. results, appears to have the structure shown.[10]

Tricarbonyl(cyclo-octatetraenylmethanol)iron produces yellow crystals of a salt when treated with hexafluorophosphoric acid in diethyl ether solution.[11] A number of possible structures including (3; R = H) were postulated for this salt, but none could be substantiated since the material decomposed in all solvents in which it was soluble, thereby precluding n.m.r. studies. However, we have now shown that the salts produced by hydroxide abstraction from [alkyl(cyclo-octatetraenyl)methanol]tricarbonyliron are sufficiently stable in organic solvents to permit n.m.r. studies and the results of these studies are reported here.



(1)



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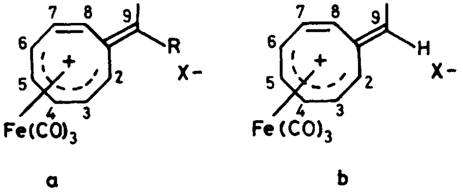


a b

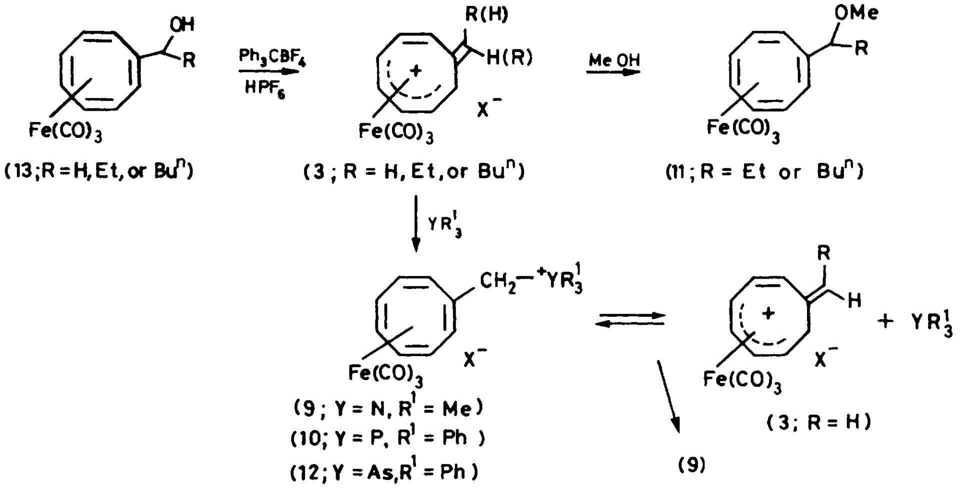
(3)

RESULTS AND DISCUSSION

The reactions to be discussed are outlined in the Scheme.

Treatment of diethyl ether solutions of [alkyl(cyclo-octatetraenyl)methanol]tricarbonyliron (alkyl = ethyl or n-butyl) with aqueous hexafluorophosphoric acid gives, in almost quantitative yields, yellow crystals whose elemental analyses correspond to fluorophosphate salts (3) formed by abstraction of hydroxide ion from the carbinols. The analogous fluoroborate salts were formed by treatment of the carbinols in dichloromethane solution with trityl tetrafluoroborate. The i.r. spectra of these salts, both in solution and in the solid state, indicate considerable delocalisation of positive charge into the iron tricarbonyl moiety.

As previously reported,[11] the salt obtained by hydroxide ion abstraction from tricarbonyl(cyclo-octatetraenylmethanol)iron undergoes nucleophilic attack with methanol or morpholine solely at the exocyclic carbon atom to give tricarbonyl(cyclo-octatetraenylmethyl methyl ether)iron and tricarbonyl[(cyclo-octatetraenylmethyl)morpholine-*N*]iron respectively. In addition, we have now found that both trimethylamine and triphenylphosphine react instantaneously with suspensions of this salt to form tricarbonyl(cyclo-octatetraenylmethyltrimethylammonium)iron hexafluorophosphate (9) and tricarbonyl(cyclo-octatetraenylmethyltriphenylphosphonium)iron hexafluorophosphate (10) respectively, in very high yields. A similar reactivity was noted for the salts derived from protonation of [alkyl(cyclo-octatetraenyl)methanol]tricarbonyliron (alkyl = ethyl or n-butyl). Thus, treatment of these salts with excess of methanol at room temperature rapidly gave almost quantitative yields of the ethers, [alkyl(cyclo-octatetraenyl)methyl methyl ether]tricarbonyliron (alkyl = ethyl or n-butyl) (11) respectively. Thus, the chemical evidence suggests a certain amount of positive charge localised on the exocyclic carbon atom.



SCHEME Preparation and some reactions of the salts [Fe(CO)$_3${C$_8$H$_7$CH(R)}]X (R = H, Et, or Bu^n; X = BF$_4$ or PF$_6$)

In contrast to the stable onium salts formed by treatment of the salt (3), with NMe$_3$ or PPh$_3$ (see above), addition of triphenylarsine to a dichloromethane suspension of the salt gave a red solid. Elemental analysis indicated the formula to be tricarbonyl(cyclo-octatetraenylmethyltriphenylarsonium)iron hexafluorophosphate (12). However, the solution i.r. spectrum of this salt shows peaks at 2 114, 2 067, 2 056, and 1 989 cm^{-1}. When excess of AsPh$_3$ was added to the solution, the two peaks at 2 114 and 2 067 cm^{-1} disappeared leaving only those at 2 056 and 1 989 cm^{-1} [*cf.* 2 059, 2 000, and 1 989 cm^{-1} for (10)]. This suggests that in solution the arsonium salt is in equilibrium with free arsine and the original carbonium ion. Addition of NMe$_3$ to solutions of the arsonium salt leads to quantitative conversion into (9).

Unfortunately, the parent salt (3; R = H), *i.e.* the salt derived from hydroxide ion abstraction from tricarbonyl(cyclo-octatetraenylmethanol)iron, is insufficiently stable in solution to permit a detailed n.m.r. study.[11] However, the secondary alcohols (13; R = Et or Bu^n) gave both fluorophosphate and fluoroborate salts which were moderately stable in solution. Thus, a study of the ^{1}H and ^{13}C n.m.r. spectra of the n-butyl salt was undertaken.

The fluorophosphate and fluoroborate salts of the n-butyl cation gave identical ^{1}H n.m.r. spectra in both CD$_2$Cl$_2$ and CD$_3$CN, but because of its increased solubility, the fluoroborate salt was the more thoroughly studied. The ^{1}H n.m.r. spectrum of this salt is shown in Table 1. Spin-decoupling experiments were carried out in CD$_3$CN and the results are shown in Table 2. These observations are consistent with the structure (3; R = Bu^n), with the assignments and coupling constants as shown in Table 1.

Treatment of tricarbonyl(formylcyclo-octatetraene)iron[11] (with 80% deuterium incorporation on the aldehyde carbon) with an n-butyl Grignard reagent gave an alcohol, which on hydroxide abstraction with Ph$_3$CBF$_4$ gave a fluoroborate salt. The ^{1}H n.m.r. spectrum of this salt in CD$_3$CN was identical to that of the non-deuteriated salt, except that the triplet at τ 3.35 was much reduced in intensity and the lowest of the butyl resonances had simplified in multiplicity. This confirms the assignment of the resonance at τ 3.35 to the proton on the exocyclic carbon atom.

The alcohol, tricarbonyl[1-(5-methylcyclo-octatetraenyl)pentanol]iron was prepared by treating tricarbonyl(5-methylcyclo-octatetraenecarbaldehyde)iron[12] with n-butyl Grignard. Hydroxide-ion abstraction from this alcohol gave a yellow solid. Proton n.m.r. spectral data for this compound are shown in Table 1. Comparing this spectrum to that of (3; R = Bu^n), it can be seen that the resonance at τ 3.95 has disappeared, while the resonances at τ 3.12 and 5.51 have shifted slightly upfield and have become doublets. Thus, this spectrum indicates structure (4) for this compound and agrees with the assignments for (3; R = Bu^n).

Similarly, tricarbonyl[1-(4-methylcyclo-octatetraenyl)pentanol]iron, prepared from tricarbonyl(4-methylcyclo-octatetraenecarbaldehyde)iron,[12] gave a salt on treatment with Ph$_3$CBF$_4$. This salt did not crystallise but was isolated as a viscous oil. In theory, two structures (5) and (6) are possible for this salt but examination of the ^{1}H n.m.r. spectrum (Table 1) shows that only (5) is pro-

TABLE 1

Proton n.m.r. spectral data for new compounds

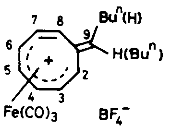
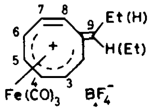
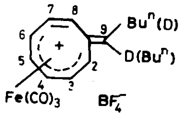
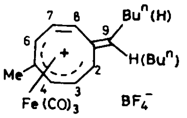
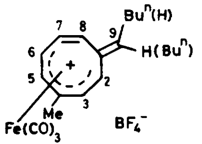
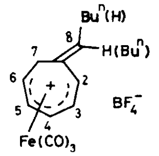
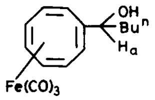
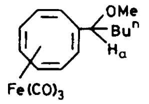
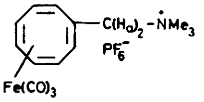
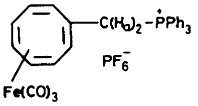
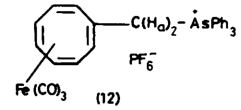
Compound and solvent	Peak position (τ)	Multiplicity	Relative intensity	Assignment	J/Hz
 (3; R = Bu^n) CD_3CN	3.12	t	1	H^4	$J(\mathrm{H}^3\mathrm{H}^4)$ 7.5 $J(\mathrm{H}^4\mathrm{H}^5)$ 7.5
	3.35	t	1	H^9	$J(\mathrm{H}^9\mathrm{Bu}^n)$ 8.5
	3.53	d	1	H^8	$J(\mathrm{H}^7\mathrm{H}^8)$ 11.0
	3.95	dd	1	H^5	$J(\mathrm{H}^4\mathrm{H}^5)$ 7.5, $J(\mathrm{H}^5\mathrm{H}^6)$ 9.5
	4.21	dd	1	H^7	$J(\mathrm{H}^6\mathrm{H}^7)$ 7.2, $J(\mathrm{H}^7\mathrm{H}^8)$ 11.0
	4.36	dd	1	H^3	$J(\mathrm{H}^2\mathrm{H}^3)$ 11.1, $J(\mathrm{H}^3\mathrm{H}^4)$ 7.5
	4.75	d	1	H^2	$J(\mathrm{H}^2\mathrm{H}^3)$ 11.1
	5.51	dd	1	H^6	$J(\mathrm{H}^5\mathrm{H}^6)$ 9.5, $J(\mathrm{H}^6\mathrm{H}^7)$ 7.2
	7.66	m	2	Bu^n	
	8.58	m	4	Bu^n	
	9.10	t	3	Bu^n	7.0
 (3; R = Et) CD_2Cl_2	2.92	t	1	H^4	$J(\mathrm{H}^3\mathrm{H}^4) = J(\mathrm{H}^4\mathrm{H}^5)$ 7.0
	3.31	t	1	H^9	$J(\mathrm{H}^9\mathrm{Et})$ 6.8
	3.57	d	1	H^8	$J(\mathrm{H}^7\mathrm{H}^8)$ 10.5
	3.90	dd	1	H^5	$J(\mathrm{H}^4\mathrm{H}^5)$ 7.0, $J(\mathrm{H}^5\mathrm{H}^6)$ 8.5
	4.25	m	2	H^3 and H^7	
	4.68	d	1	H^2	Partly obscured by solvent
	5.56	dd	1	H^6	$J(\mathrm{H}^5\mathrm{H}^6)$ 8.5, $J(\mathrm{H}^6\mathrm{H}^7)$ 8.0
	7.64	m	2	Et	
	8.92	t	3	Et	9.0
 (3; R = Bu^n)* CD_3CN	3.12	t	1	H^4	$J(\mathrm{H}^3\mathrm{H}^4) = J(\mathrm{H}^4\mathrm{H}^5)$ 7.5
	3.53	d	1	H^8	$J(\mathrm{H}^7\mathrm{H}^8)$ 11.0
	3.93	dd	1	H^5	$J(\mathrm{H}^4\mathrm{H}^5)$ 7.5, $J(\mathrm{H}^5\mathrm{H}^6)$ 9.5
	4.22	d	1	H^7	$J(\mathrm{H}^6\mathrm{H}^7)$ 7.2, $J(\mathrm{H}^7\mathrm{H}^8)$ 11.0
	4.36	dd	1	H^3	$J(\mathrm{H}^2\mathrm{H}^3)$ 11.1, $J(\mathrm{H}^3\mathrm{H}^4)$ 7.5
	4.75	d	1	H^2	$J(\mathrm{H}^2\mathrm{H}^3)$ 11.1
	5.51	dd	1	H^6	$J(\mathrm{H}^5\mathrm{H}^6)$ 9.5, $J(\mathrm{H}^6\mathrm{H}^7)$ 7.2
	7.67	m	2	Bu^n	
	8.58	m	4	Bu^n	
	9.11	t	3	Bu^n	7.0
 (4) CD_2Cl_2	3.24	d	1	H^4	$J(\mathrm{H}^3\mathrm{H}^4)$ 8.0
	3.36	t	1	H^9	$J(\mathrm{H}^9\mathrm{Bu}^n)$ 8.0
	3.57	d	1	H^8	$J(\mathrm{H}^7\mathrm{H}^8)$ 11.0
	4.23	dd	1	H^7	$J(\mathrm{H}^6\mathrm{H}^7)$ 7.5, $J(\mathrm{H}^7\mathrm{H}^8)$ 11.0
	4.52	dd	1	H^3	$J(\mathrm{H}^2\mathrm{H}^3)$ 10.5, $J(\mathrm{H}^3\mathrm{H}^4)$ 8.0
	4.73	d	1	H^2	$J(\mathrm{H}^2\mathrm{H}^3)$ 10.5
	5.74	d	1	H^6	$J(\mathrm{H}^6\mathrm{H}^7)$ 7.5
	7.50	s	3	Me	
	7.67	m	2	Bu^n	
	8.56	m	4	Bu^n	
	9.08	t	3	Bu^n	7.5

TABLE 1 (*continued*)

Compound and solvent	Peak position (τ)	Multiplicity	Relative intensity	Assignment	J/Hz
 (5) CD_3CN	3.39	t	1	$\mathrm{H^9}$	$J(\mathrm{H^9Bu^n})$ 7.5
	3.57	d	1	$\mathrm{H^8}$	$J(\mathrm{H^7H^8})$ 11.5
	4.00	d	1	$\mathrm{H^5}$	$J(\mathrm{H^5H^6})$ 9.0
	4.23	dd	1	$\mathrm{H^7}$	$J(\mathrm{H^6H^7})$ 7.0, $J(\mathrm{H^7H^8})$ 11.5
	4.42	dd	1	$\mathrm{H^3}$	$J(\mathrm{H^2H^3})$ 10.7
	4.89	d	1	$\mathrm{H^2}$	$J(\mathrm{H^2H^3})$ 10.7
	5.67	dd	1	$\mathrm{H^6}$	$J(\mathrm{H^5H^6})$ 9.0, $J(\mathrm{H^6H^7})$ 7.0
	7.45	s	3	Me	
	7.70	m	2	$\mathrm{Bu^n}$	
	8.60	m	4	$\mathrm{Bu^n}$	
	9.12	t	3	$\mathrm{Bu^n}$	6.0
 (2; R = $\mathrm{Bu^n}$) CD_2Cl_2	3.06	t	1	$\mathrm{H^4}$-	$J(\mathrm{H^3H^4}) = J(\mathrm{H^4H^5})$ 6.5
	3.76	dd	1	$\mathrm{H^5}$	$J(\mathrm{H^4H^5})$ 6.5, $J(\mathrm{H^5H^6})$ 9.0
	4.05	t	1	$\mathrm{H^8}$	$J(\mathrm{H^8Bu^n})$ 7.5
	4.24—4.67	m	2	$\mathrm{H^2}$, $\mathrm{H^3}$	
	5.17	dt	1	$\mathrm{H^6}$	$J(\mathrm{H^5H^6}) =$ $J(\mathrm{H^6H^7})$(*exo*) 9.0 $J(\mathrm{H^6H^7})$(*endo*) 2.5
	7.01	m	1	$\mathrm{H^7}$(*exo*)	
	7.80—8.35	m	3	$\mathrm{Bu^n}$ and $\mathrm{H^7}$(*endo*)	
	8.66	m	4	$\mathrm{Bu^n}$	
	9.12	t	3	$\mathrm{Bu^n}$	6.5
 (13; R = $\mathrm{Bu^n}$) $CDCl_3$	4.10—5.50	m	7	Ring protons	
	6.17	t	1	$\mathrm{H_a}$	$J(\mathrm{H_aBu^n})$ 5.0
	7.94	s	1	OH	
	8.43	m	2	$\mathrm{Bu^n}$	
	8.73	m	4	$\mathrm{Bu^n}$	
	9.13	t	3	$\mathrm{Bu^n}$	6.5
 (11; R = $\mathrm{Bu^n}$) $CDCl_3$	4.35—5.40	m	7	Ring protons	
	6.49	t	1	$\mathrm{H_a}$	$J(\mathrm{H_aBu^n})$ 6.5
	6.80	s	3	OMe	
	8.40	m	2	$\mathrm{Bu^n}$	
	8.69	m	4	$\mathrm{Bu^n}$	
	9.11	t	3	$\mathrm{Bu^n}$	7.0
 (9) CD_3COCD_3	4.18	d	2	Ring protons	11.2
	4.63	t	2	Ring protons	9.5
	4.94	m	3	Ring protons	
	5.88	s	2		
	6.88	s	9		
 (10) $CDCl_3$	2.05—2.60	m	15	Ph	
	4.70—5.10	m	7	Cyclo-octatetraene ring protons	
	5.97	d	2	$\mathrm{H_a}$	J(HP) 13.5
 (12) + free $AsPh_3$ (4:1 excess) CD_3COCD_3	2.30	m	15	Ph	
	2.76	m		Free as Ph_3	
	4.56	m	3	Cyclo-octatetraene ring protons	
	4.97	m	4	Cyclo-octatetraene ring protons	
	5.38	s	2	$\mathrm{H_a}$	

* With 80% deuterium incorporation. Peaks which have almost disappeared are omitted for clarity.

duced. Again this confirms the assignments made for the structure (**3**; R = $\mathrm{Bu^n}$).

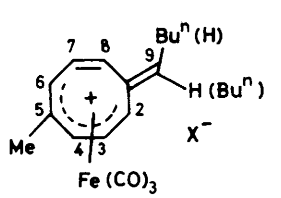
Two isomers of structure (**3**), a and b, can be drawn; however, only one resonance arising from the proton on the exocyclic carbon atom is observed suggesting the presence of only one isomer. It was not possible to deduce which isomer was formed. The seven-membered ring carbonium ion (**7**) has been shown to exist in solution

TABLE 2

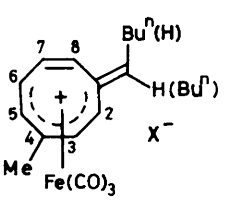
Results of spin-decoupling experiments on (3; R = Bu^n)

Group irradiated	H^2	H^3	H^4	H^5	H^6	H^7	H^8	H^9	Bu^n
	Peak position (τ), multiplicity, and coupling constants (J/Hz, in parentheses)								
H^2		4.36, d (7.5)	3.12, t (7.5, 7.5)	3.95, dd (7.5, 9.5)	5.51, dd (9.5, 7.2)	4.21, dd (7.2, 11.0)	3.53, d (11.0)	3.35, t (8.5)	7.66, m (—)
H^3	4.75, s		3.12, d (7.5)	3.95, dd (7.5, 9.5)	5.51, dd (9.5, 7.2)	4.21, dd (7.2, 11.0)	3.53, d (11.0)	3.35, t (8.5)	7.66, m (—)
H^4	4.75, d (11.1)	4.36, d (11.1)		3.95, d (9.5)	5.51, dd (9.5, 7.2)	4.21, dd (7.2, 11.0)	3.53, d (11.0)	3.35, t (8.5)	7.66, m (—)
H^5	4.75, d (11.1)	4.36, dd (11.1, 7.5)	3.12, d (7.5)		5.51, d (7.21)	4.21, dd (7.2, 11.0)	3.53, d (11.0)	3.35, t (8.5)	7.66, m (—)
H^6	4.75, d (11.1)	4.36, dd (11.1, 7.5)	3.12, t (7.5, 7.5)	3.95, d (7.5)		4.21, d (11.0)	3.53, d (11.0)	3.35, t (8.5)	7.66, m (—)
H^7	4.75, d (11.1)	4.36, dd (11.1, 7.5)	3.12, t (7.5, 7.5)	3.95, dd (7.5, 9.5)	5.51, d (9.5)		3.53, s	3.35, t (8.5)	7.66, m (—)
H^8	4.75, d (11.1)	4.36, dd (11.1, 7.5)	3.12, t (7.5, 7.5)	3.95, dd (7.5, 9.5)	5.51, dd (9.5, 7.2)	4.21, d (7.2)		3.35, t (8.5)	7.66, m (—)
H^9	4.75, d (11.1)	4.36, dd (11.1, 7.5)	3.12, t (7.5, 7.5)	3.95, dd (7.5, 9.5)	5.51, dd (9.5, 7.2)	4.21, dd (7.2, 11.0)	3.53, d (11.0)		7.66, m (—)
Bu^n	4.75, d (11.1)	4.36, dd (11.1, 7.5)	3.12, t (7.5, 7.5)	3.95, dd (7.5, 9.5)	5.51, dd (9.5, 7.2)	4.21, dd (7.2, 11.0)	3.53, d (11.0)	3.35, s	

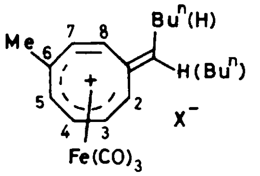
as a 1 : 1 mixture of two isomers (7a) and (7b).[13] For comparison the salt (2; R = Bu^n) was prepared. Only one resonance due to the proton on the exocyclic carbon atom was found in the ^{1}H n.m.r. spectrum (Table 1),



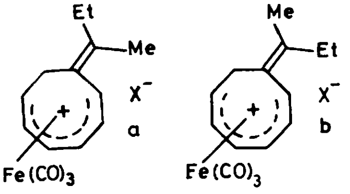
(4)



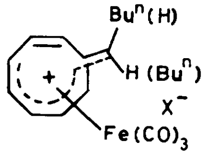
(5)



(6)



(7)



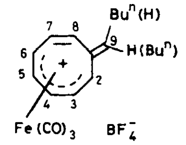
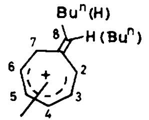
(8)

suggesting that in contrast to the methyl ethyl compound (7), (2; R = Bu^n) like (3; R = Bu^n) exists as one isomer. The ^{1}H n.m.r. spectrum of (2; R = Bu^n) closely resembles that of (3; R = Bu^n) and further justifies the proposed structure for the latter.

A puzzling aspect of structure (3) is the site of nucleophilic attack (see above). In general, co-ordinated pentadienyl systems are highly susceptible to nucleophilic attack.[14] The salt (2; R = H), which contains an exocyclic double bond and a pentadienyl system, undergoes nucleophilic attack by methoxide ion solely on the pentadienyl system leaving the exocyclic double bond intact.[10] The couplings observed in the ^{1}H n.m.r. spectra of (3; R = Et or Bu^n) are all large and the implications of the Karplus equation [15] suggest that the structure must be very nearly planar. Such a planar or nearly planar structure will be a highly strained system and this strain may be relieved by the reversion to a cyclo-octatetraene structure by nucleophilic attack on the exocyclic carbon atom.

TABLE 3

Proton-decoupled ^{13}C n.m.r. spectra of (3; R = Bu^n) and (2; R = Bu^n)

Compound and solvent	Peak position (p.p.m. downfield from SiMe$_4$)	Assignment
 Fe(CO)$_3$ BF$_4^-$ (3; R = Bu^n) CD$_2$Cl$_2$	154.4	C^9
	122.8	C^7 or C^8
	105.1	C^4
	94.9	C^2, C^3, C^5, C^6
	94.1	
	83.7	
	70.6	
	31.0	Bu^n carbons
	29.7	
	22.6	
	13.9	
 Fe(CO)$_3$ BF$_4^-$ (2; R=Bu^n) CD$_2$Cl$_2$	138.9	C^1 or C^8
	137.3	C^1 or C^8
	103.3	C^4
	98.1	C^2, C^3, C^5, C^6
	96.2	
	85.0	
	26.4	C^7
	31.0	Bu^n carbons
	29.0	
	22.6	
	13.9	

In order to gain further insight into the possible reasons for the difference in reactivity of (2) and (3), the ^{13}C n.m.r. spectra of (2; R = Bu^n) and (3; R = Bu^n) were examined. The proton-decoupled spectral data of (2; R = Bu^n) and (3; R = Bu^n) in CD$_2$Cl$_2$ are shown in Table 3. The latter salt exhibited almost exactly the same spectrum in both CD_2Cl_2 and CD_3CN. The proton-decoupled ^{13}C n.m.r. spectrum of the analogue of (3; R = Bu^n) with 80% deuterium on the exocyclic carbon was measured and showed exactly the same spectrum as (3; R = Bu^n) except that the resonance at 154.4 p.p.m. was very much reduced in intensity due to lack of Overhauser enhancement because of deuterium coupling. Thus, this resonance may be assigned to the exocyclic carbon atom. Of the other peaks in the spectrum of (3; R = Bu^n), those at 31.0, 29.7, 22.6, and 13.9 p.p.m. are readily assigned to the n-butyl resonances. This leaves six peaks for the eight remaining carbonyl atoms. The carbon carrying the exocyclic double bond would be least likely to show an intense peak and may be neglected in the assignments. The five peaks between 105.1 and 70.6 p.p.m. are in a region where typically tricarbonyliron co-ordinated pentadienyl resonances occur,[16,*] while that at 122.8 p.p.m. is in the olefinic carbon regions.[17] Thus, it would appear that one of the olefinic carbons in structure (3; R = Bu^n) does not give a peak in the ^{13}C n.m.r. spectrum.

The spectrum of (2; R = Bu^n) shows, in addition to the four n-butyl resonances, a peak at 26.4 p.p.m. due to the ring methylene carbon, four peaks between 103.3 and 85.0 p.p.m. assignable to the pentadienyl carbons,[16] and two peaks at 138.9 and 137.3 p.p.m. The latter two peaks must be due to the carbons comprising the exocyclic double bond. Thus, the proton-decoupled ^{13}C n.m.r. spectra of (2; R = Bu^n) and (3; R = Bu^n) are very similar apart from the difference in the resonance positions of the exocyclic carbon atoms in the two structures. This may be explained by assuming that the exocyclic double bond in (3; R = Bu^n) is more polarised than that in (2; R = Bu^n), with the positive end of the dipole on the exocyclic carbon. This polarisation is also indicated by the rather low ^1H n.m.r. resonance of the proton on the exocyclic carbon atom in (3; R = Bu^n). This slight but significant polarisation of the exocyclic double bond may implicate small contributions from tautomers such as (8). This, together with the relief of strain accompanying reversion to a cyclo-octatetraene structure, could explain the difference in reactivity of (2) and (3) towards nucleophiles.

Conclusion.—The salts obtained by hydroxide-ion abstraction from [alkyl(cyclo-octatetraenyl)methanol]-tricarbonyliron (alkyl = ethyl or n-butyl) exist in solution as shown (3), with possibly a slight polarisation of the exocyclic double bond with the exocyclic carbon atom carrying the positive end of the dipole. The similarity of the i.r. spectra in solution and in the solid state indicate an analogous structure in the crystal, although confirmation of this must await an *X*-ray diffraction study. Furthermore, there is no reason to believe that the parent salt (3; R = H), which could not be studied by n.m.r. spectroscopy, has any different structural features.

EXPERIMENTAL

Tricarbonyl(formylcyclo-octatetraene)iron,[11] tricarbonyl-(formylcyclohepta-1,3,5-triene)iron,[10] and trityl tetrafluoroborate were prepared as previously described.[18] Other chemicals were commercial samples. Proton n.m.r. spectra were measured at 100 MHz on a Varian Associates HA-100 machine and ^{13}C n.m.r. spectra were obtained at 25.2 MHz using a Varian Associates XL-100-15 (FT) instrument. Infrared spectra were measured on a Perkin-Elmer PE 257 instrument. Microanalyses were carried out by the Microanalytical Department of Cambridge University.

Tricarbonyl(1-*cyclo-octatetraenylpentanol*)*iron*.—A solution of $MgBrBu^n$ was prepared in dry diethyl ether (30 cm^3) under nitrogen from n-butyl bromide (10 mmol) and magnesium metal (10 mmol). This solution was then cooled to −78 °C and an ethereal solution (10 cm^3) of tricarbonyl-(formylcyclo-octatetraene)iron (1 mmol) added. After stirring at −78 °C for 1 h, the solution was allowed to warm to room temperature and hydrolysed with water. The ether layer was separated, dried ($MgSO_4$), and evaporated. The residue was then chromatographed on silica gel, eluting with benzene. A broad orange band gave the *product* as a red-orange oil. Yield 80% [Found: *M* (mass spectrometry), 330. Calc. for $C_{16}H_{18}FeO_4$: *M*, 330]. I.r. (pentane): 2 054, 1 994, and 1 978 cm^{-1}.

Preparation of (2)—(5) (R = Bu^n).—Tricarbonyl(1-cyclo-octatetraenylpentanol)iron (1 mmol) was dissolved in dry dichloromethane (5 cm^3). A solution of Ph_3CBF_4 (1 mmol) in CH_2Cl_2 (5 cm^3) was added slowly with stirring. After 10 min, diethyl ether (50 cm^3) was slowly added to the solution with stirring. The precipitated solid was filtered off, washed with diethyl ether, and dried *in vacuo* to give a 95% yield of (3; R = Bu^n), m.p. 138—140 °C (Found: C, 47.7; H, 4.1. Calc. for $C_{17}H_{17}BF_4FeO_3$: C, 48.0; H, 4.3%). I.r. (CH_2Cl_2): 2 109, 2 065, and 2 056 cm^{-1}. Similarly prepared in high yields were: (4), m.p. 122—124 °C (Found: C, 49.0; H, 4.7. Calc. for $C_{17}H_{19}BF_4FeO_3$; C, 49.3; H, 4.6%), i.r. (CH_2Cl_2), 2 108 and 2 064 cm^{-1}; (5) as a yellow viscous oil (Found: C, 49.1; H, 4.6. Calc. for $C_{17}H_{19}BF_4FeO_3$; C, 49.3; H, 4.6%), i.r. (CH_2Cl_2) 2 106, 2 064, and 2 056 cm^{-1}; and (2), i.r. (CH_2Cl_2) 2 109, 2 065, and 2 055 cm^{-1}.

Tricarbonyl(*cyclo-octatetraenylmethyltrimethylammonium*)-*iron Hexafluorophosphate*.—Compound (3; R = H) (1 mmol) was suspended in CH_2Cl_2 (10 cm^3) and the suspension cooled to 0 °C. An excess of NMe_3 was added with stirring. The mixture momentarily became a homogeneous red solution, but almost immediately red crystals of the *product* were deposited. Yield 97%. Decomposes <165 °C (Found: C, 39.0; H, 3.9; N, 2.9. Calc. for $C_{25}H_{18}F_6FeNO_3P$: C, 39.0; H, 3.9; N, 3.0%). I.r. (acetone): 2 053 and 1 984 (br) cm^{-1}.

Tricarbonyl(*cyclo-octatetraenylmethyltriphenyl-phosphonium*)*iron and -arsonium*)*iron Hexafluorophosphate*.—Compound (3; R = H) (1 mmol) was suspended in CH_2Cl_2 (10 cm^3). The compound PPh_3 or $AsPh_3$ (1 mmol) was added and the mixture stirred for 10 min. The red solution was then filtered and on addition of pentane a red oil separated. This oil was washed well with pentane and dried under vacuum whereupon it solidified. Yield *ca.* 95%. The phosphonium salt gave a red solid, m.p. 80—82 °C (Found: C, 55.1; H, 4.0; P, 8.9. Calc. for $C_{30}H_{24}F_6FeO_3P_2$: C, 54.3; H, 3.6; P, 9.3%). I.r. ($CHCl_3$): 2 059, 2 000, and 1 989 cm^{-1}. The arsonium salt gave a red solid (decomposes *ca.*

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[*] For example 101.4, 88.9, 64.3, and 23.0 p.p.m. for tricarbonyl-(cyclohexadienyl)iron tetrafluoroborate (ref. 6).

155 °C) (Found: C, 50.5; H, 3.6. Calc. for $C_{30}H_{24}AsF_6FeO_3P$: C, 50.8; H, 3.4%). I.r. (CH_2Cl_2 with excess of $AsPh_3$): 2 056 and 1 989 (br) cm^{-1}.

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