206. *Spectroscopic Studies of Some Organoiron Complexes.*

By M. L. H. Green, L. Pratt, and G. Wilkinson.

Infrared and high-resolution nuclear magnetic resonance spectra of the following organoiron compounds have been measured: arenecyclopentadiene-iron compounds, norbornadieneiron tricarbonyl, the compounds of stoicheiometry $C_{11}H_6O_5Fe$, $C_8H_4O_4Fe$, and $C_7H_4O_3Fe$ first isolated by Reppe, and $C_{10}H_4O_6Fe_2$.

Infrared and high-resolution nuclear magnetic resonance spectra of several organoiron compounds have been measured and the structures of the compounds are discussed.

Arenecyclopentadieneiron Compounds.—In a previous note[1] it was shown that the di-π-cyclopentadienylmetal cations, $(\pi\text{-}C_5H_5)_2Co$(or Rh)$^+$, can be reduced by sodium borohydride or lithium aluminium hydride to the cyclopentadiene compounds, $\pi\text{-}C_5H_5(C_5H_6)Co$(or Rh). It was also shown that hydride-ion attack gave a C_5H_6 group in which the added hydrogen atom ($H_{(\alpha)}$) was in the 1-*endo*-position, *i.e.*, on the metal side of the ring, and that this hydrogen atom was readily removed chemically and was also responsible for an unusually low C–H stretching frequency at ~2750 cm.$^{-1}$.

Although in some other cases the hydride reduction of a di-π-cyclopentadienylmetal halide can lead to the formation of hydrides, *e.g.*, $(\pi\text{-}C_5H_5)_2WH_2$,[2] reduction of a $\pi\text{-}C_5H_5$ group to cyclopentadiene can be expected where the electronic structure of the metal atom is favourable, *i.e.*, four bonding electrons are required (from the C_5H_6 group) to give a formal inert-gas configuration for the metal atom. Thus the previous work can obviously be extended to the arene-π-cyclopentadienyliron cations which are isoelectronic with the di-π-cyclopentadienyl-cobalt and -rhodium cations.

The π-cyclopentadienyl(mesitylene)iron iodide is the only compound of this type reported,[3] but the simple benzene analogue, $[C_6H_6(\pi\text{-}C_5H_5)Fe]I$, can readily be prepared by the same method. From these two iodides, the neutral arenecyclopentadiene- and 1-*endo*deuterocyclopentadiene-iron compounds have been obtained by reduction with lithium aluminium hydride and lithium aluminium deuteride, respectively.

The physical and chemical properties of these compounds (I) show that the cyclopentadiene group is bound to the iron atom in the same way as in the cobalt and rhodium compounds and that it retains the unusual features attributed to the $>H_\alpha H_\beta$ methylene group.

The orange-red benzene compound (*A*) decomposes slowly in air and more quickly in

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[1] Green, Pratt, and Wilkinson, *J.*, 1959, 3753.
[2] Green, Street, and Wilkinson, *Z. Naturforsch.*, 1959, **14**b, 738.
[3] Coffield, Sandell, and Clossen, *J. Amer. Chem. Soc.*, 1957, **79**, 5826.

solution, giving, after a few hours, a precipitate which contains the benzene-π-cyclopentadienyliron cation together with some decomposition products and paramagnetic material. The dark red mesitylene derivative (*B*) is more readily oxidised by air than the benzene compound.

On treating the benzene compound (*A*) with 1 : 1-hydrochloric acid, the cation $[C_6H_6(\pi\text{-}C_5H_5)Fe]^+$, hydrogen, and olefin are obtained; the cation is also formed with chlorinated methanes and olefins in the reaction with carbon tetrachloride. These reactions are similar to those of the cobalt and rhodium compounds.[1]

The infrared spectra of compounds *A* and *B* (Table 1) show the intense band at ~2750 cm.$^{-1}$ assigned to the C–H$_\alpha$ stretching mode. In the benzene-1-*endo*deuterocyclopentadiene compound, $C_6H_6(C_5H_5D)Fe$, this band disappears and the C–D stretching frequency occurs at ~2000 cm.$^{-1}$ ($\nu_H^{obs}/\nu_D^{obs} = 1{\cdot}34$). As with $\pi\text{-}C_5H_5(C_5H_5D)Co$ there is a marked splitting of the C–D band. Since this splitting occurs in both compounds it is unlikely to be due to Fermi resonance but must be due to other couplings in the metal–C_5H_5D system; no satisfactory explanation can be given. The assignments of the infrared spectra of compounds (*A*) and (*B*) (Table 1) and their bases are much the same as those for the cobalt and rhodium compounds.[1]

TABLE 1. *Infrared spectra of arenecyclopentadieneiron compounds (carbon disulphide solutions in 2700—3200 cm.$^{-1}$ region).*

$C_6H_6(C_5H_6)Fe$	$C_6H_3Me_3(C_5H_6)Fe$	$C_6H_6(C_5H_5D)Fe$ [a]	Assignment [b]
3095w	3075w	3097w	1
3047m [c]	3010m	3029m	2
3028m			2
—	2950m	—	3
2944m	2909m	2947m	4
2870w	—	—	5
—	2835m	—	3
2780s	2743s	2783w	6
		2124m	7
		2093s	7
		2088s(sh)	7
		2053s	7
		2033m	7

[a] *ca.* 95% isotopic purity. 1 C–H stretch of C_6H_6; 2 "olefinic" CH–CH stretch; 3 C–H stretch of Me; 4 C–H$_\beta$ stretch; 5 probably overtone or combination band; 6 C–H$_\alpha$ stretch; 7 C–D stretch. This splitting was resolved on a lithium fluoride prism instrument; all other spectra were measured with sodium chloride optics. The other compounds would be expected also to give two peaks under high resolution.

The nuclear magnetic resonance spectra of compound (*A*) and its deutero-derivative have three groups of lines showing that there are at least three types of hydrogen atom in the molecules. The single sharp line of relative intensity six is clearly assignable to the six protons of the benzene ring. The remaining lines, due to the C_5H_6 or C_5H_5D groups, are assignable as before.[1] The band of intensity two, which is on the low-field side at 5·89 p.p.m. (against tetramethylsilane) in both compounds, arises from the two equivalent protons on $C_{(3)}$ and $C_{(4)}$ of the C_5H_6 ring. It has a triplet structure which is actually an overlapping double doublet due to the spin coupling of each proton with those on $C_{(2)}$ and $C_{(5)}$. The band at ~2·0 p.p.m. arises from the remaining protons; the band structure is complicated since the chemical shifts between the protons in this group are of the same order of magnitude as the spin coupling between them. A rough assignment is as follows. The two peaks at ~2·02 and ~2·18 p.p.m., which are present in both the C_5H_6 and C_5H_5D compounds, represent part of the spectrum of the two equivalent protons on $C_{(2)}$ and $C_{(5)}$. The separation of about 6 cycles/sec. is probably the splitting due to the nearest proton of $C_{(3)}$ and $C_{(4)}$.

For the C_5H_6 compound, the bands at 1·50 and 1·81 p.p.m. and the group of lines at ~2·5 p.p.m. arise from the two protons on the methylene carbon atom $C_{(1)}$. When H$_\alpha$ is replaced by deuterium, the first two bands disappear and the group at ~2·5 p.p.m. becomes sharper. These changes show that the H_α and the H_β proton are not equivalent, the H_β resonance occurring on the low-field side of the $H_{(2)}H_{(5)}$ group and that of H_α on the high-field side, which might be expected from its proximity to the metal atom. In the deuterated derivative the H_β resonance is sharper since it is much less split by the deuterium nucleus than by the H_α proton in the parent compound. Similar spectra were observed for the cobalt and rhodium compounds.

The separation of the resonances of the protons on $C_{(2)}$ and $C_{(5)}$ from those on $C_{(3)}$ and $C_{(4)}$ does not necessarily mean that $C_{(2)}$ and $C_{(5)}$ have formed σ-bonds to the metal or that electron-density changes are involved; the separation could also be attributed to changes in the magnetic-shielding contribution of the π-electrons associated with their bonding to the metal atom as discussed previously.[1]

Norbornadieneiron Tricarbonyl.—This compound [4] has also been reported by Pettit.[5] The reaction of norbornadiene (bicyclo[2,2,1]hepta-2,5-diene) with iron pentacarbonyl is complex. There is no apparent reaction at temperatures below ~75—80° but thereat a rapid reaction sets in. Irradiation of the diene–carbonyl mixture with intense ultraviolet light at 25° for four hours did not cause reaction. The main products of the initial exothermic reaction at 80—90° are the tricarbonyl complex (in about 30% yield) and an organic ketone. However, if the reaction mixture is refluxed for two hours ferrocene, the binuclear π-*cyclo*pentadienyliron carbonyl, $[\pi\text{-}C_5H_5Fe(CO)_2]_2$, and at least two other organic ketones are also formed.* The formation of π-*cyclo*pentadienyl compounds in addition to carbonylation is not surprising in view of the possible reorganisations that the diene can be envisaged to undergo.

TABLE 2. *Infrared spectra of organoiron compounds (in cm.$^{-1}$).*

Compound	C–H stretching region	M–C≡O stretch	$>$C=O stretching region	Remainder of spectrum
$C_7H_8Fe(CO)_3$ (in CS_2 and CCl_4)	3060w (1) 3006w (1) 2964m (2) 2932m (3) 2846w (2)	2043vs 1964vs	—	3810vw, 3770vw, 2510vw, 1438w, 1398w, 1368vw, 1308s (C–H def.), 1220vw, 1179s, 1162w, 1104w, 1076m, 1032w, 995w, 948vw, 916w, 898w, 888w, 861w, 775m.
$C_5H_4OFe(CO)_3$ (in Nujol, hexachlorobutadiene, and CCl_4)	3105m (1) 3065m (1)	2084vs 2015vs	1634s	2340w, 1971w, 1792w, 1570m, 1463m, 1394m, 1235w, 1185m, 1162s, 1065w, 1045m, 897w, 874m, 723m, 664w.
$C_5H_4OFe(CO)_2$ (in (Nujol, hexachlorobutadiene, and CCl_4)	3073 (1)	2023vs 1975vs 1945s (4)	1567s	1632w, 1612w, 1502m, 1390w, 1323w, 1302w, 1207vw, 1185m, 1168m, 1066w, 1055w, 1018w, 856m, 818m, 800m, 794m, 720m, 707w, 689m.
$C_{11}H_6O_5Fe$ (in Nujol, hexachlorobutadiene, and CCl_4)	3080m 3030m 2910m 2820m 2745w? 2715w?	2083s 2028s 2009s	1668ms (5)	2600m, 2480w, 2340w, 1601s (4), 1580s (4), 1512w, 1498vw, 1462w, 1393w, 1471m, 1393w, 1364w, 1321w, 1250m, 1219m, 1184m, 1171m, 1098w, 1070w, 1058w, 1037w, 936m, 916w, 829m, 757m, 712m, 670m.
$C_4H_4Fe_2(CO)_6$ (in CS_2 and CCl_4)	3060w (1) 2990m (1)	2088s 2052vs 2014vs 1965m	—	1543w, 1399w, 1388w, 1247s, 1224m, 1096vw, 1079w, 1031vw, 954s, 874w, 844m.

(1) –CH=CH– stretch. (2) $>$CH stretch. (3) $\geqslant$CH stretch. (4) Not found in CCl_4 solution. (5) Found only in CCl_4 solution.

The infrared (Table 2) and nuclear magnetic resonance (Table 3) spectra of $C_7H_8Fe(CO)_3$ are consistent with structure (II) (cf. also ref. 5) where the diene is acting as a bifunctional olefin chelate as in the norbornadiene complexes of ruthenium and various other metals.[6]

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* These ketones and their method of formation are now being studied by Professor Cookson, University of Southampton.

[4] Burton, Green, Abel, and Wilkinson, *Chem. and Ind.*, 1958, 1592.

[5] Pettit, *J. Amer. Chem. Soc.*, 1959, **81**, 1266.

[6] Abel, Bennett, and Wilkinson, *J.*, 1959, 3178.

The nuclear magnetic resonance spectrum of norbornadiene shows three proton resonances centred at 6·65 (intensity = 4), 3·48 (intensity = 2), and 1·95 (intensity = 2) p.p.m., which are assigned to the olefinic, tertiary, and bridging methylene group protons, respectively, in agreement with the normal correlations between line position and bond type for organic molecules. The iron complex, however, shows only two bands, at ~3·1 and 1·25 p.p.m. with intensity ratio ~3 : 1. The high-field band at 1·25 p.p.m. can be assigned to the protons of the bridging methylene group as in the parent hydrocarbon; the triplet structure is produced by spin coupling of these protons with the two equivalent protons on the tertiary carbon atoms. The remaining six protons in the molecule give rise to the complex band at ~3·1 p.p.m. The position of this band is close to that of the protons on the tertiary carbon atoms in norbornadiene, but the resonances of the protons on $C_{(2)}C_{(3)}$ and $C_{(5)}C_{(6)}$ now appear in the same place, which is outside the region (3·5—6·4

TABLE 3. *Proton resonance spectra at* 40 *Mc./sec. at* 21° ± 1°.

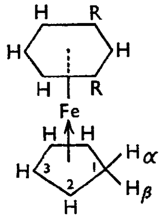
(Line positions are given in p.p.m. on the low-field side relative to tetramethylsilane.)

Compound	Line position (p.p.m.)	Rel. Int.	Structure	Splitting (in c./sec.)	Assignment
$(C_6H_6)(C_5H_6)Fe$	5·88	2	Triplet (double doublet)	5·2 ± 0·3	Protons on $C_{(3)}$ and $C_{(4)}$
	4·07	6	Singlet	—	C_6H_6 group
	2·50	4	(?) Triplet	~5	Part of H_β
	$2{\cdot}16_4$		Singlet	(width ~3)	Protons on $C_{(2)}$ and $C_{(5)}$
	2·02		Singlet	(width ~3)	
	1·81		(?) Triplet	~2·3	Part of H_α
	1·50		(?) Singlet		
$(C_6H_6)(C_5H_5D)Fe$	5·91	2	Triplet (double doublet)	5·2 ± 0·3	Protons on $C_{(3)}$ and $C_{(4)}$
	4·10	6	Singlet		C_6H_6 group
	2·65	≃1	(?) Triplet	~2	Part of H_β
	2·48				
	2·32				
	2·19	≃2	,,		Protons on $C_{(2)}$ and $C_{(5)}$
	2·04		,,		
	1·88		,,		
Norbornadiene $Fe(CO)_3$	3·2	6	Complex, width ~20 c./sec.	Two strong lines at 3·04 and 3·11 p.p.m.	Protons on " olefin " groups and on tertiary $>$C–H
	1·23	2	Triplet	1·4 ± 0·5	Protons on methylene
Norbornadiene	6·26	4	Triplet (double doublet)	1·9 ± 0·3	Olefin protons
	3·48	2	Septuplet	≃1·8	Protons on tertiary $>$C–H
	1·95	2	Triplet	1·7 ± 0·3	Protons on methylene
$(C_5H_4O)Fe(CO)_3$	5·89	2	Triplet (not well resolved)	Width ≃6, splitting ≃2·5	Protons on $C_{(3)}$ and $C_{(4)}$
	4·08	2	,, ,,	,, ,,	Protons on $C_{(2)}$ and $C_{(5)}$
$(C_5H_4O)Fe(CO)_2$	2·46 (centre of pattern)		Sym. double triplet (A_2B_2)	(Rel. to centre) ± 1·5; ±2·6 and ±4·8	Protons on $C_{(2)}$ and $C_{(5)} = H_A + H_A$ Protons on $C_{(3)}$ and $C_{(4)} = H_B + H_B$
$(C_4H_4)Fe_2(CO)_6$	(weak) 6·48 (centre of pattern)		Sym. double triplet (A_2B_2)	(Rel. to centre) ±8·0; ±11·6 and ±15·6)	Protons on $C_{(2)}$ and $C_{(5)} = H_A + H_A$ Protons on $C_{(3)}$ and $C_{(4)} = H_B + H_B$
$(C_{11}H_7O_5)Fe$	6·64	2	Singlet	width ≃2	Olefin protons
	5·84	2	Singlet	,, ~6	Protons on $C_{(3)}$ and $C_{(4)}$ of C_5-ring
	4·12	2	Singlet	,, ~7	Protons on $C_{(2)}$ and $C_{(5)}$ of C_5-ring

p.p.m.) found to be associated with protons of olefinic groups in organic molecules. However, this does not mean that $C_{(2)}$, $C_{(3)}$, $C_{(5)}$, and $C_{(6)}$ have changed their basic sp^2 hybridization in the complex, as application of the simple correlation rules would suggest, since the shift of the proton resonances to higher fields in the metal compound is probably due to magnetic effects associated with the metal atom as noted for high-field shifts in other olefin-metal complexes.[1]

Compounds $C_8H_4O_4Fe$, $C_7H_4O_3Fe$, *and* $C_{11}H_6O_5Fe$.—These were prepared and isolated according to Reppe and Vetter's procedure.[7] Analytical and other results agree with the molecular formulæ and general properties which Reppe has reported for the C_7 and C_8 compounds, but the C_{11} compound originally reported as $C_{11}H_7O_5Fe$ must be reformulated $C_{11}H_6O_5Fe$.

(*a*) $C_8H_4O_4Fe$. From reactions of substituted acetylenes with iron carbonyls a variety of compounds have been isolated, some of which have been clearly demonstrated [8-10] to have a substituted cyclopentadienone ring bound to the metal atom. $C_8H_4O_4Fe$ has spectroscopic properties which are consistent with its formulation as (III), as suggested by Weiss and Hübel.[8c] It is appreciably soluble in water, undoubtedly owing to the polar nature of the keto-group; water solubility has not been noticed for the substituted derivatives [8-10] but has been noted for π-cyclopentadienylcyclopentadienonecobalt.[11] The infrared spectrum and some assignments are given in Table 2. In the nuclear magnetic resonance spectrum (Table 3) there are two proton resonance lines of equal intensity, each a poorly resolved triplet with a splitting of about 2-cycles/sec. This spectrum is consistent with structure (III) if one line is assigned to the two equivalent protons $H_{(2)}$ and $H_{(5)}$ and the other to $H_{(3)}$ and $H_{(4)}$. The triplet structure would arise from double-doublet splittings of the protons in one group by first one and then the other proton in the other group. As in other compounds containing a four-carbon conjugated diolefin system bound to the metal atom, *e.g.*, the cyclopentadiene complexes discussed above and previously,[1] butadieneiron tricarbonyl,[1] and thiopheniron tricarbonyl,[4] there is a characteristic separation of the resonances of the protons on $C_{(2)}C_{(5)}$, and $C_{(3)}C_{(4)}$. The low-field line, which occurs at almost the same position here as that due to protons $C_{(3)}C_{(4)}$ in the cyclopentadiene compounds, may be assigned to protons in the same relative position, *i.e.*, on $C_{(3)}C_{(4)}$. The proton resonances for hydrogen atoms on $C_{(2)}$ and $C_{(5)}$ in cyclopentadienoneiron tricarbonyl are not shifted to as high a field as in the cyclopentadiene complexes, however; this is attributable to the presence of the >C=O rather than the $>CH_{\alpha}H_{\beta}$



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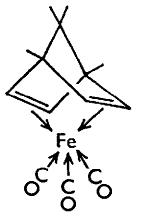

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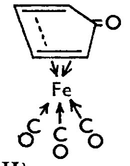

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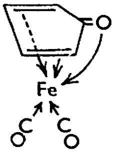

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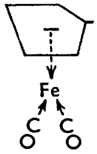

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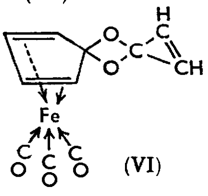

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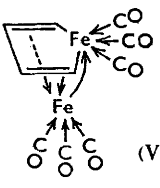

(VII)

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[7] Reppe and Vetter, *Annalen*, 1953, **582**, 156.

[8] (*a*) Hübel, Braye, Clauss, Weiss, Krüerke, Brown, King, and Hoogzand, *J. Inorg. Nuclear Chem.*, 1959, **9**, 204; (*b*) Hübel and Braye, *J. Inorg. Nuclear Chem.*, in the press; (*c*) Weiss and Hübel, *ibid.*, in the press.

[9] Schrauzer, *Chem. and Ind.*, 1958, 1403, 1404.

[10] Leto and Cotton, *Chem. and Ind.*, 1958, 1592; *J. Amer. Chem. Soc.*, 1959, **81**, 2970.

[11] Markby, Sternberg, and Wender, *Chem. and Ind.*, 1959, 1381.

grouping. The presence of an electron-withdrawing group, trichloromethyl, in the 1-*endo*-position also lowers the high-field shift.[1]

(*b*) $C_7H_4O_3Fe$. A warm aqueous solution of $C_8H_4O_4Fe$ is readily oxidised by molecular oxygen to give carbon dioxide and the orange-brown compound, $C_7H_4O_3Fe$.[7] The compound is monomeric in benzene; physical and chemical properties indicate that it must by formulated as cyclopentadienoneiron dicarbonyl (IV, V). A formulation such as (V) with delocalisation of electrons from the keto-group has been proposed for a dicyclopentadienonecobalt anion by Weiss and Hübel.[8c] The nuclear magnetic resonance spectrum consists of a double triplet centred at 4·55 p.p.m. The symmetry of the spectrum about its centre suggests that the four protons form a group of the type A_2B_2 in which the chemical shift between protons A and B (~6 cycles/sec.) is small enough to be of the same order of magnitude as the spin coupling between them [$J(A_2B_2)$ ~4 cycles/sec.]. The small shift between the two main bands is more in accord with structure (V), since the protons here would be expected to approximate to the complete equivalence observed in the π-cyclopentadienyl compounds, where only a single sharp resonance line occurs. For structure (IV), a larger separation of the resonances, as in the above cyclopentadiene and cyclopentadienone compounds, would have been expected.

The infrared spectrum of $C_7H_4O_3Fe$ in carbon tetrachloride shows two very strong bands at 1973 and 2030 cm.$^{-1}$ (in mulls, solid-state splitting leads to three bands at 2021, 1973, and 1945 cm.$^{-1}$, suggesting that the molecule can occupy different sites in the lattice) as expected for the dicarbonyl. These frequencies are more than 50 cm.$^{-1}$ lower than those in the cyclopentadienoneiron tricarbonyl, such a shift being consistent with an increase in the negative charge flowing to the metal atom[12] as would be expected on the present formulation. The strong band at 1567 cm.$^{-1}$ may be assigned to a C–O stretching frequency; again this band is lower (by 57 cm.$^{-1}$) than that of the keto-group in cyclopentadienoneiron tricarbonyl, the shift being consistent with loss of π-electron density from this group to the ring and metal as in structure (V). The appearance of only a single sharp band at 3073 cm.$^{-1}$ in the olefinic C–H stretching region, whereas $(C_5H_4O)Fe(CO)_3$ has two, may be explained by the more extensive delocalisation in the unsaturated ring system.

The compound is sparingly soluble in non-polar solvents, has a high melting point, and is not volatile in a vacuum, perhaps owing to intermolecular interaction in the lattice. Like the cyclopentadienone tricarbonyl compound, it is soluble in polar solvents but not in water. The loss of water solubility can be attributed to a shift in polarity of the keto-group compared with the cyclopentadienoneiron tricarbonyl.

Thus it seems clear that the cyclopentadienone ring can donate π-electron density to a metal atom in two distinct ways owing to the ability of electron transfer in the C–O link behaving, formally, as either a four- or a six-electron donor system.

(*c*) $C_{11}H_6O_5Fe$. This compound is formed in good yield in the Reppe reaction. It was originally formulated as $C_{11}H_7O_5Fe$; it is now formulated with six hydrogen atoms on the basis of its nuclear magnetic resonance spectrum. It was also shown that the compound is hydrolysed very readily under mild conditions (water at 70°) to give cyclopentadienoneiron tricarbonyl and quinol, essentially quantitatively.[7] This reaction suggests that in $C_{11}H_6O_5Fe$ there is a five-membered carbon ring bound to an iron tricarbonyl unit, together with a C_3 grouping. In view of the very mild hydrolytic conditions, it seems unlikely that C–C bonds are being broken. A structure such as (VI) is reasonably consistent with the formation of quinol *via* benzoquinone as an intermediate in the hydrolysis and with the spectroscopic evidence available; but the precise nature of the substance cannot yet be stated, and further work on the mechanism of hydrolysis of the compound and *X*-ray structural investigations (by R. Mason, University College) are in progress.

The properties are those reported by Reppe and Vetter and we have shown that the

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[12] Cf. Stammreich, Sala, Tavares, Krumholtz, and Behmoiras, *J. Chem. Phys.*, in the press; Abel, Bennett, and Wilkinson, *J.*, 1959, 2323.

compound is not hydrogenated catalytically in presence of Adams's catalyst at room temperature. The nuclear magnetic resonance spectrum shows three main bands of equal intensity at 4·12, 5·84, and 6·64 p.p.m. The first two bands lie at the same position as the two bands in cyclopentadienoneiron tricarbonyl and show similar widths; they are hence assigned analogously to the protons on $C_{(2)}C_{(5)}$ and $C_{(3)}C_{(4)}$ respectively of the five-membered carbon ring. The third band (relative intensity 2) occurs at a lower field in the region normally associated with olefinic protons, and since no fine structure is observed, this peak is assigned to two equivalent olefinic protons, although this observation does not confirm the proposed structure, and we have no data to show whether the line positions of the olefin protons in cyclopropene rings occur in the normal olefin region or not. There is no band in the nuclear magnetic resonance spectrum in the characteristic low-field region for the proton resonance of aldehyde groups.

The infrared spectrum shows three strong bands at 2083, 2028, and 2009 cm.$^{-1}$ which are undoubtedly associated with the $Fe(CO)_3$ grouping. There is a strong band at 1668 cm.$^{-1}$ (CCl_4 solution) which is in the region of $>C=O$ and $C=C$ stretching modes; the intensity is weaker than that of normal keto-bands, and may be due to a $C=C$ stretch with enhanced intensity, as in cyclopropene itself.[13] Bands of medium intensity are found in the 1150—1250 cm.$^{-1}$ region, but no strong characteristic ether or ester C–O–C frequencies are observed. The C–H stretch region could be examined only with hexachlorobutadiene mulls, and although there are a number of bands, good resolution could not be obtained.

The Compound $C_4H_4Fe_2(CO)_6$.—If the products from the acetylene reaction are separated chromatographically on alumina elution with ether allows the isolation of an orange-yellow compound, $C_{10}H_4O_6Fe_2$, not reported by Reppe and Vetter. The phenyl-substituted derivatives, however, have been prepared and characterised by Hübel and Braye [8b] from the reactions of mono- and di-phenylacetylene with iron carbonyls. These workers have suggested structures for these compounds which have the same basic configurations as the but-2-yne compound, $C_6H_8O_2Fe_2(CO)_6$, whose structure has been determined unequivocally by *X*-ray methods.[14] The present compound appears to be the corresponding unsubstituted derivative (VII).

The nuclear magnetic resonance spectrum shows a symmetrical triplet similar to that observed for cyclopentadienoneiron dicarbonyl, but centred at a lower field (6·5 p.p.m.). The structure can again be interpreted in terms of an A_2B_2 group of protons with a small chemical shift (*ca.* 24 cycles/sec.) between the groups. This separation is considerably smaller than those observed in the C_4H_4 groups of the cyclopentadienoneiron tricarbonyl and the cyclopentadiene metal compounds.

The infrared spectrum and assignments are given in Table 2. The band in the C–H stretching region at 3060 cm.$^{-1}$ lies in the region associated with co-ordinated olefinic groups in other compounds (see ref. 1 for references). The lower band at 2990 cm.$^{-1}$ occurs at a frequency rather low for such a grouping. On the basis of formula (VII), the band at 3060 cm.$^{-1}$ is best assigned as the C–H stretch of the hydrogen atom on $C_{(2)}C_{(3)}$ and the 2990 cm.$^{-1}$ band to the C–H stretches for $C_{(1)}C_{(4)}$. The rather low frequency may thus be due to the influence of the bonding of $C_{(1)}C_{(4)}$ to one of the iron atoms by σ-bonds.[14]

EXPERIMENTAL

Microanalyses and molecular-weight determinations (ebullioscopic in benzene) are by the Microanalytical Laboratory, Imperial College. All preparations, reactions, and chromatographic separations were carried out in nitrogen or in a vacuum. Solvents were thoroughly degassed before use; light petroleum was " AnalaR," b. p. <40°.

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[13] Erskine and Jackman, personal communication.

[14] Hock and Mills, *Proc. Chem. Soc.*, 1958, 233.

Preparation of Benzene-π-cyclopentadienyliron(I) *Tribromide.*—Dicarbonyl-π-cyclopentadienyliron chloride [15] (10 g.) and finely ground anhydrous aluminium trichloride (10 g.) were refluxed in benzene (60 ml.) for 3 hr. The mixture was carefully hydrolysed by water (200 ml.), the aqueous layer was filtered, and the cation precipitated therefrom by addition of bromine water. The yellow flocculent precipitate was washed with water and dried (yield ~60%). A small portion of the precipitate was dissolved in warm concentrated hydrochloric acid, the solution filtered, and the *tribromide* reprecipitated, washed with water and acetone, and dried in a vacuum (Found: C, 30·7; H, 2·7; Br, 52·7; Fe, 13·1. $C_{11}H_{11}FeBr_3$ requires C, 30·9; H, 2·6; Br, 53·5; Fe, 13·1%). The tribromide is soluble in tetrahydrofuran and acetone but is insoluble in water; with concentrated hydrochloric or nitric acid, bromine is lost and the cation, $[C_6H_6(\pi\text{-}C_5H_5)Fe]^+$, is obtained in solution; these solutions give the usual precipitates with large anions such as silicotungstate and Reineckate.

The *mesitylene* derivative was similarly prepared as the tribromide (Found: C, 34·6; H, 3·5; Fe, 11·8. $C_{14}H_{17}FeBr_3$ requires C, 34·9; H, 3·5; Fe, 11·6%).

Preparation of Benzenecyclopentadieneiron(0).—Benzene-π-cyclopentadienyliron tribromide (5 g.) in ethylene glycol dimethyl ether (25 ml.) was treated with small portions of lithium aluminium hydride (2 g.). After ½ hr., an excess of water (100 ml.) was carefully added, and the mixture extracted with light petroleum (100 ml.). The petroleum layer was washed with water, dried ($CaCl_2$), and concentrated to a small volume which was transferred to a column of alumina. The light-petroleum eluate was evaporated and the residue sublimed in a high vacuum on to an ice-cold probe. The *product* formed orange-red crystals (50% based on the tribromide), m. p. 135—136° (Found: C, 65·6; H, 6·2%; *M*, 198·7. $C_{11}H_{12}Fe$ requires C, 66·1; H, 6·1%; *M*, 200·2). The compound is fairly stable in air. With 5 ml. of 1 : 1 hydrochloric acid, 39·06 mg. of the compound gave 2·71 ml. of gas at N.T.P.; this gas, which is mostly non-condensable and presumably hydrogen, was re-absorbed by the mixture until after 4 hr. only 1·3 ml. remained. Infrared analysis of the residual gas showed the presence of olefins.

The *mesitylenecyclopentadieneiron*, a deep-red oil, m. p. *ca.* −10°, was similarly prepared (Found: C, 69·1; H, 7·4%; *M*, 237·1. $C_{14}H_{18}Fe$ requires C, 69·4; 7·4%; *M*, 242).

Preparation of Benzene-(1-endo*deuterocyclopentadiene*)*iron.*—This derivative was made as above except that lithium aluminium deuteride was used. The yield was ~80% based on the deuteride. An estimate of the isotopic purity of the product by infrared measurement indicated over 95% purity.

Preparation of Norbornadieneiron Tricarbonyl.—Iron pentacarbonyl (5 g.) in excess of norbornadiene (~10 ml.) was gradually heated; at about 78° carbon monoxide was rapidly evolved, and the solution turned black. The mixture was then gently refluxed for 1 hr. and, after cooling, was transferred to a large column of alumina. The yellow petroleum eluate was evaporated to ~5 ml. and the solution cooled to −80°; the yellow crystals were recrystallised from isopentane. The *tricarbonyl* was a golden-brown liquid at normal temperatures; the crystals have m. p. −2° (Found: C, 51·2; H, 3·4%; *M*, 247. $C_{10}H_8O_3Fe$ requires C, 51·7; H, 3·4%; *M*, 232). The compound decomposes slowly in air but is stable in a vacuum.

Preparation of Reppe Compounds.—Iron pentacarbonyl (50 g.) in a solution of ethanol (150 ml.) and water (5 ml.) was heated with acetylene–nitrogen at 25 atmos. and 90° for 36 hr. Except for these slight differences, the method of preparation and isolation given by Reppe and Vetter [7] was used.

(*a*) $C_{11}H_6O_5Fe$. This compound was purified by fractional Soxhlet extraction of the residue from the reaction to give yellow crystals [yield 35% based on $Fe(CO)_5$], m. p. 125° (Found: C, 48·3; H, 2·3; O, 29·3; Fe, 20·1%; *M*, 264. Calc. for $C_{11}H_6O_5Fe$: C, 48·3; H, 2·2; O, 29·2; Fe, 20·4%; *M*, 273·9).

(*b*) $C_8H_4O_4Fe$. This compound was purified by sublimation in a vacuum to give bright yellow crystals (yield 70% based on $C_{11}H_6O_5Fe$), m. p. 113—114° (Found: C, 44·1; H, 2·1; O, 29·1; Fe, 25·1%; *M*, 220·8. Calc. for $C_8H_4O_4Fe$: C, 43·7; H, 1·8; O, 29·1; Fe, 25·4%; *M*, 220·0).

(*c*) $C_7H_4O_3Fe$. Purified by crystallisation from acetone this gave orange-brown crystals (yield 70%), decomp. 160° (Found: C, 43·5; H, 2·5; O, 25·4; Fe, 29·4%; *M*, 196·1. Calc. for $C_7H_4O_3Fe$: C, 43·8; H, 2·1; O, 25·4; Fe, 29·1%; *M*, 192·0).

(*d*) $C_4H_4Fe_2(CO)_6$. The crude reaction mixture (10 ml.) was placed on a column of alumina. The yellow petroleum eluate was evaporated and the residue crystallised from isopentane,

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[15] Piper, Cotton, and Wilkinson, *J. Inorg. Nuclear Chem.*, 1955, **1**, 165.

giving orange-yellow crystals (*ca.* 1 g.), m. p. 53° (Found: C, 36·4; H, 1·2; O, 28·7%; *M*, 322. $C_{10}H_4O_6Fe_2$ requires C, 36·1; H, 1·2; O, 28·9%; *M*, 332·1). The *compound* is very soluble in common organic solvents, and the solid is stable in air; in carbon tetrachloride some decomposition was noticeable after 1 day.

Infrared Spectra.—Measurements were made with a Perkin-Elmer Model 21 recording spectrophotometer having sodium chloride optics. The compounds were examined in carbon tetrachloride and carbon disulphide if sufficiently soluble or as mulls in Nujol and hexachlorobutadiene. Although the arenecyclopentadieneiron compounds decompose in solution, consecutive spectra taken during a 30-minute period immediately after the preparation of the solution were the same. The spectra of the cyclopentadienemesityleneiron and norbornadiene-iron tricarbonyl were also measured as thin films of the pure liquid. Details of the spectra not given in Tables 1 and 2 are as follows:

$C_6H_6(C_5H_6)Fe$ (in CCl_4, CS_2): 3850vw, 2525w, 2430w, 2055w, 2020w, 1981m, 1960m, 1882vw, 1837vw, 1798vw, 1772w, 1716w, 1688w, 1653m, 1624m, 1483m, 1445w, 1420w, 1394w, 1316w, 1290s, 1175w, 1138w, 1109s, 1053s, 1001s, 946m, 939m, 906vw, 843s.

$C_6H_6(C_5H_5D)Fe$ (in CCl_4, CS_2): 3800vw, 3720w, 2390w, 2245vw, 1943w, 1880vw, 1834w, 1771w, 1614w, 1480m, 1420m, 1392w, 1317m, 1307vw, 1294vw, 1263m, 1724vw, 1202vw, 1135w, 1107m, 1046w, 1011w, 998w, 927m, 914w, 899m, 865m, 659w.

$C_9H_{12}(C_5H_6)Fe$ (as a film): 1765w, 1707w, 1695w, 1617w, 1521vw, 1452m, 1438m, 1377m, 1370m, 1312w, 1250vw, 1177vw, 1165vw, 1103m, 1045m, 1036m(sh), 1017m(sh), 1006m, 1000m(sh), 972w, 923vw, 878m, 849w.

Nuclear Magnetic Resonance Spectra.—The spectra were obtained at 40 Mc./sec. on a Varian Associates model 4300B spectrometer. Measurements were made at 21° ± 1°, in strong solutions in benzene, carbon tetrachloride, acetone, dioxan, and nitromethane contained in 5-mm. (o.d.) spinning tubes. A small amount of tetramethylsilane was added as an internal reference and line positions reported in p.p.m. are referred to tetramethylsilane throughout. Line positions were measured by the conventional side-band technique.

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INORGANIC CHEMISTRY RESEARCH LABORATORIES,
IMPERIAL COLLEGE, LONDON, S.W.7.

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