# **119.** *Transition-metal Complexes of Seven-membered Ring Systems. Part III.*[1] *Cycloheptatrieneiron Carbonyl and Related Compounds.*

By R. Burton, L. Pratt, and G. Wilkinson.

The products from the reaction of iron pentacarbonyl and cycloheptatriene have been investigated chemically and by high-resolution nuclear magnetic resonance and infrared spectroscopy. The main products have been shown to be cycloheptatrieneiron tricarbonyl and cyclohepta-1,3-dieneiron tricarbonyl. The nuclear magnetic resonance spectra of cyclohexa-1,3-diene-iron tricarbonyl and bicyclo[4,2,0]octa-2,4-dieneiron tricarbonyl are also interpreted.

In Part I [2] we described the cycloheptatriene complexes of Group VI transition metals such as $C_7H_8Mo(CO)_3$. In these complexes the metal atom can be considered to attain a formal inert-gas configuration by use of $\pi$-electrons from all three double bonds of cycloheptatriene. A similar situation could hold for the seven-membered ring in the azulene-iron carbonyl complexes.[1] By analogy, a compound $C_7H_8Fe(CO)_2$ might have been expected to be obtained by reaction of cycloheptatriene with iron carbonyl.

The interaction of cycloheptatriene and iron carbonyl produces three organometallic complexes in yields which depend on the reaction conditions. If a mixture of the olefin and carbonyl is maintained at 110° ± 5° for about seven days and the unchanged materials are removed under a vacuum at room temperature, fractional distillation of the oily residue gives an orange-yellow liquid (A), $C_7H_8Fe(CO)_2$, $n_D^{20}$ 1·6277, b. p. 70°/0·4 mm. If the reactants are maintained at 135—140° for about seven days and the products separated as before, an orange-yellow liquid (B), $n_D^{20}$ 1·6184, of approximately the same boiling point (74°/0·4 mm.) as (A) is obtained. In this case there is a residue, which after crystallisation from ether gives yellow crystals whose analysis and molecular weight agree with those for a trinuclear complex, $C_{23}H_{16}Fe_3O_9$.

*Cycloheptatrieneiron Tricarbonyl.*—On the basis of analysis, the substance (A) was originally thought [3] to be cycloheptatrieneiron dicarbonyl; recently, Manuel and Stone [4] have provided preparative details and analytical data for such a dicarbonyl compound, $C_7H_8Fe(CO)_2$. However, this so-called dicarbonyl shows three strong bands in the carbonyl stretching region of its infrared spectrum, at 2050, 1989, and 1975 cm.$^{-1}$, and such a spectrum is inconsistent with a simple dicarbonyl for which only two carbonyl stretching frequencies can be expected. Very careful chromatography of this compound on an alumina column gives as major product a compound analysing as a tricarbonyl, $C_7H_8Fe(CO)_3$, m. p. *ca.* 5°. The infrared and nuclear magnetic resonance spectra of this compound, as discussed below, are also consistent with the structure (I), in which an $-Fe(CO)_3$ group is bound to two adjacent double bonds of the triene, while the third double bond remains unco-ordinated.

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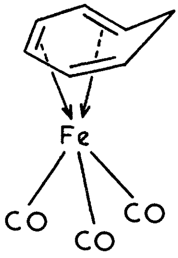
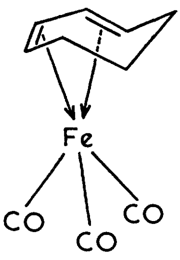
[1] Part II, Burton, Pratt, and Wilkinson, *J.*, 1960, 4290.
[2] Part I, Abel, Bennett, Burton, and Wilkinson, *J.*, 1958, 4559.
[3] Burton, Green, Abel, and Wilkinson, *Chem. and Ind.*, 1958, 1592.
[4] Manuel and Stone, *J. Amer. Chem. Soc.*, 1960, **82**, 366.

Although no experimental details have been given for its preparation, the infrared spectrum of a tropyliumiron dicarbonyl tetrafluoroborate has been given [5] and again three carbonyl stretching frequencies are observed. If this product was prepared from the compound we now know to be a tricarbonyl, by the method used to prepare $[C_7H_7Mo(CO)_3]BF_4$,[6] a reformulation of the iron complex cation as a tricarbonyl species, as its infrared spectrum indicates, will be necessary (see below and IV).

*Cyclohepta-*1,3-*dieneiron Tricarbonyl.*—Infrared and nuclear magnetic resonance measurements suggested that the liquid product (B) was a mixture of cycloheptatrieneiron tricarbonyl and some other closely similar compound or compounds. Vapour-phase chromatography indeed showed the presence of two closely related components in the mixture. Careful liquid-phase chromatography on alumina allowed satisfactory separations to be obtained. The more strongly absorbed component was shown by nuclear magnetic resonance measurements to be cycloheptatrieneiron tricarbonyl. Analysis of the less strongly absorbed component gave a stoicheiometry $C_7H_{10}Fe(CO)_3$. The product, m. p. 23°, although similar to the triene complex, showed differences in both the infrared and the nuclear magnetic resonance spectrum. The latter indicated the presence of four olefinic and six aliphatic protons in the molecule, and was consistent with the other evidence in favour of the formulation cyclohepta-1,3-dieneiron tricarbonyl (II). This compound must be formed by hydrogen transfer to the co-ordinated triene system from excess of the triene under the reaction conditions. Confirmation of the nature of the compound was obtained by direct synthesis from cycloheptadiene and iron pentacarbonyl and also by catalytic reduction of $C_7H_8Fe(CO)_3$ (see below).



(I)



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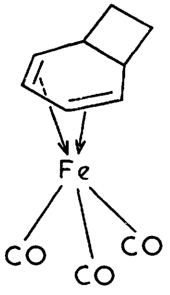

(III)

*Spectroscopic Measurements.*—In order to assist in the assignments of lines in the infrared and particularly the high-resolution nuclear magnetic resonance spectra of $C_7H_8Fe(CO)_3$ and $C_7H_{10}Fe(CO)_3$ some closely related compounds, which have a conjugated diene system bound to iron, were also examined. The compound obtained from cyclooctatriene and iron pentacarbonyl [7] has been conclusively shown by its nuclear magnetic resonance spectrum to be bicyclo[4,2,0]octa-2,4-dieneiron tricarbonyl (III) in agreement with the suggestion made on the basis of indirect evidence.[4] Cyclohexa-1,3-dieneiron tricarbonyl [8] has also been studied and the nuclear magnetic resonance spectrum [9] of butadieneiron tricarbonyl re-measured at 56·4 Mc./sec.

The infrared spectrum of $C_7H_8Fe(CO)_3$ shows a band of medium intensity at *ca.* 1660 cm.$^{-1}$. No bands are found in the 1800—1500 cm.$^{-1}$ region for $C_7H_{10}Fe(CO)_3$ or the iron carbonyl derivatives of cyclohexa-1,3-diene or bicyclo-octadiene. It therefore seems reasonable to assign the 1660 cm.$^{-1}$ band to the C=C frequency of the non-co-ordinated double bond

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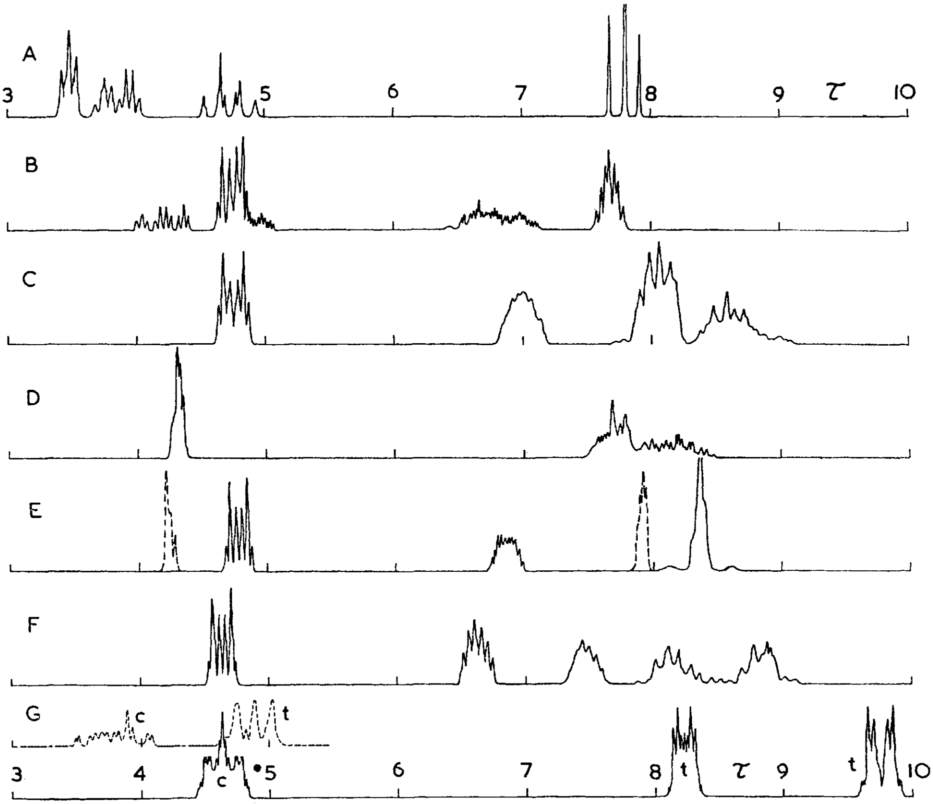
[5] Fischer, *Chem. Ber.*, 1960, **93**, 165.
[6] Dauben and Honnen, *J. Amer. Chem. Soc.*, 1958, **80**, 5570.
[7] Fischer, Palm, and Fritz, *Chem. Ber.*, 1959, **92**, 2645.
[8] Hallam and Pauson, *J.*, 1958, 642.
[9] Green, Pratt, and Wilkinson, *J.*, 1959, 3753; *J.*, 1960, 989.

of the cycloheptatriene ring. The carbonyl stretching region for all the mononuclear iron carbonyl–olefin complexes is very similar, three bands being found under high resolution.

The high-resolution nuclear magnetic resonance spectra are shown in the Figure, and details of the spectra and assignments are given in the experimental section. Chemical shifts are expressed as $\tau$ values.*

All four iron compounds show two bands which are attributed to the four protons of the conjugated diene group bound to the iron atom, in addition to the lines in the region 7·5—9·0, which are assigned to aliphatic protons. In contrast to their positions in the olefins themselves, where the olefinic proton resonances lie at low fields, one of the co-ordinated "olefinic" bands occurs at high fields (7·0—6·5) and the other remains at low fields. A similar separation of the co-ordinated olefinic resonances into high- and low-field groups has been previously found for other conjugated olefin–metal complexes,[1,9] and it was shown that the low-field band arises from the "central" protons of the diene grouping while the high-field band arises from the "terminal" protons. The spectra of the present iron tricarbonyl complexes show that a similar assignment is valid for them also. The centre of the low-field band occurs at exactly the same position, 4·76, for $C_7H_8Fe(CO)_3$ and $C_7H_{10}Fe(CO)_3$ and is very close to this position in the hexadiene and

*Proton resonance spectra of iron tricarbonyl derivatives of olefins at* 56·45 Mc/sec. *Magnetic field increases from left to right.* A, *Cycloheptatriene.* B, *Cycloheptatrieneiron tricarbonyl.* C, *Cyclohepta*-1,3-*dieneiron tricarbonyl.* D, *Cyclohepta*-1,3-*diene.* E, *Broken lines, cyclohexa*-1,3-*diene; full lines, cyclohexa*-1,3-*dieneiron tricarbonyl.* F, *Bicyclo*[4,2,0]*octa*-2,4-*dieneiron tricarbonyl.* G, *broken lines, butadiene; full lines, butadieneiron tricarbonyl* (*c = central protons*; t = *terminal protons*).



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* $\tau = 10{\cdot}00 - x$, where $x$ is the line position in p.p.m. on the low-field side relative to tetramethylsilane as internal reference.

bicyclo-octadiene compounds. The symmetrical fine structure is the same at 40 and 56·4 Mc./sec. and is produced by the electron-coupled spin–spin interaction among the four diene protons. The coupling constants can be evaluated by standard methods [10] if these protons are treated as an $A_2X_2$ group, an approximation which is adequate when considering the " central " protons. The coupling between the " terminal " positions is very small or zero; the coupling of one " central " proton with the other " central " proton is ~4·8 c./sec., with the adjacent " terminal " proton is 6·6—7·6 and with the distant terminal proton is 1·2—1·6 c./sec. These values are consistent with the proposed structures.

The position of the high-field band changes from one compound to another more than does that of the low-field band, probably because the " terminal " protons are more affected by the different groups attached to the co-ordinated conjugated diene system. The structure of the high-field band should be similar to that of the low-field band, but it is made complicated by the additional coupling of the " terminal " protons of the diene grouping with the adjacent aliphatic [and in $C_7H_8Fe(CO)_3$, cycloalkene] protons.

In the bicyclo-octadiene complex, the resultant structure is fairly simple, since there is only one (tertiary) proton adjacent to each " terminal " proton, producing mainly an additional doublet splitting. In the cyclohexa-1,3-diene complex and in $C_7H_{10}Fe(CO)_3$, the additional splitting will be in the form of triplets due to the adjacent $>CH_2$ groups and the resultant structure could not be resolved. In $C_7H_{10}Fe(CO)_3$, the width of this band is independent of the measuring frequency, suggesting that the " terminal " protons of the diene grouping are equivalent, as would be expected. The corresponding band in $C_7H_8Fe(CO)_3$ is wider and its width decreases with the measuring frequency, indicating a chemical shift of *ca.* 0·2 p.p.m. between the two non-equivalent " terminal " protons. This again would be expected on the basis of structure (I) since one of these " terminal " protons is adjacent to a $>CH_2$ group and the other to an olefinic group. These two groups will also produce different additional splittings on the " terminal " protons and although the band in $C_7H_8Fe(CO)_3$ shows considerable fine structure it is not easy to interpret it.

The remaining bands at *ca.* 8·05 and 8·6 p.p.m. in the spectrum of $C_7H_{10}Fe(CO)_3$ can be assigned to the two $>CH_2$ groups severally; these bands are similar to those of the aliphatic protons in the parent olefin. The $>CH_2$ group in $C_7H_8Fe(CO)_3$ gives rise to the band at 7·7 p.p.m. The overall width of this band decreases slightly with frequency, indicating that the two methylene protons are not equivalent, possibly because one of them is closer to the metal atom. Consequently the $>CH_2$ protons will split each other into doublets. In addition they will each experience doublet splittings from the adjacent " terminal " proton, and from each proton of the unco-ordinated olefin group. Since the band is slightly unsymmetrical, the total splitting of one $>CH_2$ proton is not identical with that of the other.

The protons of the unco-ordinated double bond in $C_7H_8Fe(CO)_3$ are not equivalent, one of them (Ha), which is probably adjacent to the diene group, giving the band at *ca.* 4·25 p.p.m. The other (Hb) gives a band at *ca.* 4·85 p.p.m. which is mostly hidden by the low-field band. Comparison of the spectra at 40 and 56·4 Mc./sec. shows that all of the structure of Ha is due to coupling. Ha and Hb each split the other into a doublet (10·6 c./sec.) and since the splitting is of the same order of magnitude as the shift between them (*ca.* 0·6 p.p.m.), the inner component of each doublet is more intense than the outer. Each component of Ha is then split into a doublet (7·7 c./sec.) by the " terminal " proton and each of the resulting four components is split further into a triplet (2·2 c./sec.) by the two protons of the $>CH_2$ group. The two inner triplets overlap partially to give the appearance of a quartet. Hb must also experience a doublet splitting by the " terminal " proton, and a triplet splitting (1·2 c./sec.), possibly by the $>CH_2$ group, can be observed on two of the unobscured components at 5·0 p.p.m.

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[10] Pople, Schneider, and Bernstein, " High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., New York, 1959, p. 140.

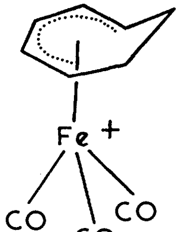
Hence the nuclear magnetic resonance data can be interpreted satisfactorily on the basis of structure (I) and (II) for $C_7H_8Fe(CO)_3$ and $C_7H_{10}Fe(CO)_3$, respectively.

As mentioned previously in the discussion on the structures of the other olefin complexes,[1,9] the shift of the " terminal " protons to a higher field (almost in the aliphatic region of the spectrum) could be consistent with a structure involving $\sigma$-bonds from the " terminal " carbon atoms to the metal atom. However, an investigation of the infrared spectra [9] of the complexes did not support such a structure. An up-field shift of olefin-proton resonances is also found in the nuclear magnetic resonance spectrum of cycloheptatrienemolybdenum tricarbonyl,[11] whose structure, which has been determined by *X*-ray analysis,[12] again does not appear to have $\sigma$-bonds to the metal atom. Hence the latter two methods of structure determination support the $\pi$-bonded structures for the metal–olefin complexes and these methods are sufficiently well established to provide more reliable criteria of bond type than is nuclear magnetic resonance of organometallic compounds at the present time.

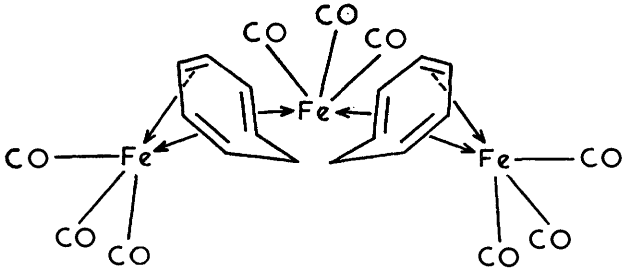
The shifts of the co-ordinated conjugated diene protons can, in fact, be explained on the basis of the $\pi$-bonded structure if allowance is made for the long-range shielding contribution to the shift which arises from the anisotropic magnetic polarisation of electrons in the metal–olefin bonds.[11]

*Structural Isomerism in Cycloheptatrieneiron Tricarbonyl Complexes.*—Compounds possessing a structure similar to that of $C_7H_8Fe(CO)_3$ derived from unsymmetrically substituted cycloheptatrienes can in principle exist as two geometrical isomers, each of these having optically active forms as would be expected for $C_7H_8Fe(CO)_3$ itself. The situation is analogous to that found for the azuleneiron carbonyls.[1] So far, attempts to prepare such isomeric compounds by using methyl thujate have been unsuccessful because of the extensive polymerisation of this triene in the reaction with iron carbonyl. It may be noted, however, that two isomeric forms of cycloheptatrienoneiron tricarbonyl have been reported.[13]

*Some Chemical Reactions of Cycloheptatrieneiron Tricarbonyl.*—The above evidence clearly shows that in $C_7H_8Fe(CO)_3$ one of the double bonds is not co-ordinated to the metal atom. Attempts have been made to determine whether the compound retains any chemical properties of a normal olefin. In general, the reactions typical of the carbon–carbon double bond do not take place with $C_7H_8Fe(CO)_3$.



(IV)



(V)

Oxidation of the compound with osmium tetroxide, a reaction which gives 1,2-diols from normal olefins, causes immediate decomposition of the iron complex. Oxidation by perphthalic acid, normally giving an epoxide, likewise produces immediate decomposition. It has been suggested that the $-Cr(CO)_3$ group in the arenechromium tricarbonyls has

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[11] Bennett, Pratt, and Wilkinson, unpublished work.

[12] Dunitz and Pauling, *Helv. Chim. Acta*, 1960, **43**, 2188.

[13] Hübel and Weiss, *Chem. and Ind.*, 1959, 703.

an electron-withdrawing power on the ring system.[14] The possibility that the $-Fe(CO)_3$ group in $C_7H_8Fe(CO)_3$ might also have a similar effect on the cycloheptatriene ring, with subsequent deactivation of the unco-ordinated double bond towards the normal electrophilic reagents, was taken into account, but reactions with nucleophilic reagents were also unsuccessful. For example, treatment of $C_7H_8Fe(CO)_3$ with either phenyl-lithium or phenylmagnesium bromide under a variety of conditions gave none of the expected products. An attempt to brominate the $>CH_2$ group, using *N*-bromosuccinimide, also caused extensive decomposition.

Although treatment with zinc and acetic or hydrochloric acid caused no apparent change, the high-pressure reduction of $C_7H_8Fe(CO)_3$ has been more rewarding. Reduction in the presence of Raney nickel and hydrogen at 130°/100 atm. caused complete decomposition, and cycloheptane was obtained in high yield. Reduction at room temperature for 24 hours gave a 20% yield of cycloheptadieneiron tricarbonyl.

Halogens react rapidly with $C_7H_8Fe(CO)_3$ but the reactions have not yet been studied in detail. Dry hydrogen chloride and hydrogen bromide are absorbed by the compound in inert solvents, and yellow precipitates obtained. The latter are soluble in water to give yellow solutions which quite rapidly decompose with evolution of carbon monoxide; the solutions give precipitates with large anions such as silicotung-state, Reineckate, etc. The cation has been isolated as yellow crystals of the tetrachloroferrate, stable in air as the solid, and as a hygroscopic bromide. The addition of halogen acid across the unco-ordinated double bond in $C_7H_8Fe(CO)_3$ could be expected to lead to a cation $C_7H_9Fe(CO)_3^+$. The analyses and diamagnetism of the bromide are in accord with this stoicheiometry, and the bromide shows three strong carbonyl stretching frequencies, at 2119, 2061, 1986 $cm.^{-1}$.

Since it has been shown [15] that cyclohexa-1,3-diene can give rise to a π-cyclohexadienylmanganese tricarbonyl, $C_6H_7Mn(CO)_3$, where the $C_6H_7$ radical is iso-π-electronic with the cyclopentadienyl radical, other cyclic 1,3-dienes can be expected to behave similarly. In the present case the ion, which we now formulate as π-cycloheptadienyliron tricarbonyl, $\pi$-$C_7H_9Fe(CO)_3^+$ (IV) is thus similar to the neutral manganese compound.

*The Trinuclear Iron Complex.*—In view of the structure of $C_7H_8Fe(CO)_3$, it seems reasonable to assign to the trinuclear complex $C_{23}H_{16}Fe_3O_9$ the structure (V), in which an $-Fe(CO)_3$ group is bound to two adjacent double bonds of the cycloheptatriene rings and the two units are bridged by a third $-Fe(CO)_3$ group bound to the remaining double bond of each triene ring. An analogous complex has been obtained by reaction of bi(cycloheptatrienyl) with iron pentacarbonyl, and the polynuclear azuleneiron carbonyl [1] may also be similarly constituted.

Evidence in support of the ability of the unco-ordinated double bond in $C_7H_8Fe(CO)_3$ to be co-ordinated to another metal atom is provided by the reaction of the compound with a concentrated aqueous solution of silver nitrate. A pale yellow, insoluble adduct is obtained but this decomposes quite quickly, the silver ion being reduced to metallic silver, so that analysis could not be undertaken.

## EXPERIMENTAL

Microanalyses and molecular weights by the Microanalytical Laboratory, Imperial College.

*Interaction of Iron Pentacarbonyl and Cycloheptatriene.*—*Method* (*a*). The olefin (20 g.) and carbonyl (30 ml.) were kept at 110° for 7 days. The unchanged reactants were then removed at 20°/0·4 mm. and an orange-yellow liquid (A) (24 g.), b. p. 70°/0·4 mm., $n_D^{20}$ 1·6277, distilled from the residue. Chromatography of this material in light petroleum on an alumina column gave *cycloheptatrieneiron tricarbonyl*, m. p. *ca.* 5° (Found: C, 52·1; H, 3·9; O, 20·7%; *M*, 230. $C_{10}H_8O_3Fe$ requires C, 51·7; H, 3·5; O, 20·7%; *M*, 232), as an orange-yellow liquid which decomposes in air on prolonged storage.

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[14] Nicholls and Whiting, *J.*, 1959, 551.

[15] Winkhaus and Wilkinson, *Proc. Chem. Soc.*, 1960, 311.

*Method* (*b*). Cycloheptatriene (20 g.) and iron pentacarbonyl (30 ml.) were heated together at 135—140° for 7 days. The unchanged reactants were removed at 20°/0·4 mm. and an orange-yellow liquid (B) (11 g.), b. p. 74°/0·4 mm., $n_D^{20}$ 1·6184, was distilled from the residue. Chromatography in light petroleum on an alumina column gave approximately equal quantities of two complexes. The first complex eluted was *cyclohepta*-1,3-*dieneiron tricarbonyl*, m. p. 23° (Found: C, 51·6; H, 4·4; O, 20·4%; *M*, 230. $C_{10}H_{10}O_3Fe$ requires C, 51·3; H, 4·3; O, 20·5%; *M*, 234), and the second, cycloheptatrieneiron tricarbonyl. The residue remaining after the distillation of compound (B) was washed with light petroleum (3 × 100 c.c.) and crystallisation from ether of the remaining solid gave *di*(*cycloheptatriene*)*tri*(*iron tricarbonyl*) (Found: C, 46·5; H, 2·87; O, 23·5%; *M*, 666. $C_{23}H_{16}O_9Fe_3$ requires C, 45·7; H, 2·65; O, 23·8%; *M*, 604) as yellow crystals.

*Other Preparations.*—Cyclohexa-1,3-dieneiron tricarbonyl and "cyclo-octatriene"iron tricarbonyl were made by published methods [7,8] and purified by chromatography on alumina.

*Reduction of* $C_7H_8Fe(CO)_3$ *at Room Temperature.*—A mixture of the compound (3·7 g.) and Raney nickel (0·5 g.) in ethanol (20 ml.) was continuously agitated for 24 hr. under 100 atmospheres of hydrogen. The contents of the autoclave were washed out with ethanol. After filtration, the ethanolic solution was diluted with water, and the aqueous mixture extracted with light petroleum (3 × 50 c.c.). The petroleum extracts were dried ($MgSO_4$) and the solvent was removed at 20°/14 mm. Chromatography of the residual liquid in light petroleum on an alumina column gave $C_7H_{10}Fe(CO)_3$, m. p. 23° (0·74 g., 20%), confirmed by its nuclear magnetic resonance spectrum.

*Reduction of* $C_7H_8Fe(CO)_3$ *at Elevated Temperature.*—A mixture of the compound (5·5 g.) and Raney nickel (0·5 g.) in ethanol was continuously agitated for 24 hr. at 130° under 100 atmospheres of hydrogen. The contents of the autoclave were washed out with ethanol and after filtration the ethanolic solution was diluted with water. The aqueous mixture was extracted with light petroleum (2 × 50 ml.), and the combined extracts were dried ($MgSO_4$). The solvent was removed and distillation of the residual liquid gave cycloheptane (1·0 g., 40%), $n_D^{20}$ 1·4439, confirmed by its nuclear magnetic resonance spectrum.

*The Reaction of* $C_7H_8Fe(CO)_3$ *with Hydrogen Chloride and Bromide.*—$C_7H_8Fe(CO)_3$ (3·6 g.) in ethanol (20 ml.), chloroform (20 ml.), and concentrated hydrochloric acid (20 ml.) was left for 6 days in air. Addition of excess of chloroform to the yellow solution produced yellow crystals which were removed and washed with alcohol and ether (0·7 g.) {Found: C, 27·9; H, 2·4; O, 13·5; Fe, 25·4; $Cl^-$, 32·8. $[C_7H_9Fe(CO)_3][FeCl_4]$ requires C, 27·9; H, 2·1; O, 11·2; Fe, 26·1; $Cl^-$, 33·1%}. The crystals are readily soluble in water and from a 6N-hydrochloric acid solution the tetrachloroferric acid can be extracted with ether, leaving a pale yellow rather unstable cation in solution. The isolation of the tetrachloroferrate must arise from partial decomposition of the $C_7H_8Fe(CO)_3$ under the reaction conditions. To $C_7H_8Fe(CO)_3$ in light petroleum was added dropwise a solution of hydrogen bromide in light petroleum. The yellow precipitate was centrifuged and washed with light petroleum and dried in a stream of nitrogen; the dry solid is very hygroscopic.

*Reduction of the Bromide Salt.*—The bromide (*ca.* 2 g.) was dissolved in ethanol (20 ml.), and sodium borohydride added to the solution in small portions. After 15 min. the mixture was diluted with water and extracted with light petroleum. After drying ($MgSO_4$), the solvent was removed and the residual brown oil chromatographed. Cycloheptadieneiron tricarbonyl (0·1 g.) was obtained and its nature confirmed by nuclear magnetic resonance and infrared spectra.

*Dipole Moment.*—The dipole moment of $C_7H_8Fe(CO)_3$ was measured in a manner similar to that described [1] for the azuleneiron carbonyl. We obtained a value $\mu = 2·43 \pm 0·04$ D.

*Infrared Spectra.*—Spectra were taken on a Perkin-Elmer model 21 spectrophotometer with sodium chloride and calcium fluoride optics. Details of the spectra in thin films of the pure liquid are as follows (cm.$^{-1}$):

$C_7H_8Fe(CO)_3$: 3026s, 2992m, 2921w, 2872m, 2841m, 2796m, 2050vs, 1989vs, 1975vs, 1668m, 1665m, 1471m, 1446m, 1419s, 1404s, 1356m, 1346m, 1214s, 1189m, 1153w, 1000m, 943m, 933m, 893m, 864w, 834s, 804m, 704s.

$C_7H_{10}Fe(CO)_3$: 3026m, 2975s, 2918s, 2875s, 2840s, 2046vs, 1977vs, 1458s, 1447s, 1442s, 1404s, 1372m, 1348s, 1338s, 1262w, 1225w, 1194w, 1163m, 1090m, 1060s, 958m, 933w, 868s, 860s, 843m, 803w, 790m.

$C_6H_8Fe(CO)_3$: 3044w, 3004m, 2928s, 2904s, 2884s, 2844s, 2050vs, 1976vs, 1469s, 1454w, 1432m, 1429w, 1403m, 1337s, 1318w, 1267m, 1237w, 1179s, 1142w, 1118w, 1072m, 1028m, 1008m, 937m, 877m, 862m, 844m, 799w, 641m.

*High-resolution Nuclear Magnetic Resonance Spectra.*—These were recorded at 22° ± 1° at frequencies of 56·45 and 40 Mc./sec. with Varian Associates spectrometers V4311 and 4310C, respectively. The samples were in 5-mm. (outside diameter) Pyrex spinning tubes, usually in solution in $CCl_4$. A little tetramethylsilane was added as an internal reference. Line positions were determined by the conventional side-band technique, using a Muirhead–Wigan D695A low-frequency oscillator. Data for each line are presented in the following order: centre position of line in $\tau$ values; relative intensity; splitting in c./sec.; assignment and source of observed splitting. The data at 40 and 56·4 Mc./sec. were in full agreement, and in all cases the values of the splittings are the same at the two frequencies.

*Cycloheptatriene.* ($CH_2$ group = position 1.) 3·49, two identical protons, $H_4$ and $H_5$, structure complex but appears as a " triplet " (3·1 c./sec. between components); 3·91, centre (calculated for A of an AB pair) of two identical protons, $H_3$ and $H_6$, each split into a doublet (9·0 c./sec.) by $H_2$ and $H_7$, respectively, each component split into a triplet (3·1 c./sec.) by $H_4$ and $H_5$; 4·73, centre (calculated for B of an AB pair) of two identical protons, $H_2$ and $H_7$, each split into a doublet (9·0 c./sec.) by $H_3$ and $H_6$, respectively, each component split into a triplet (6·7 c./sec.) by the $CH_2$ group, the two triplets overlap to give the appearance of a quartet under moderate resolution; 7·806, two identical protons, $CH_2$ group, split into a triplet (6·7 ± 0·1 c./sec.) by $H_2$ and $H_7$.

*Cycloheptatrieneiron tricarbonyl.* (Numbering of positions as for cycloheptatriene itself with the iron atom bonded to the diene group 4, 5, 6, 7, so that non-bonded olefin group is 2 and 3.) 4·845, centre (calculated for A of an AB pair) of one proton, $H_3$, split by $H_2$ into an unsymmetrical doublet (10·6 c./sec.) of which the components centred at 331·3 c./sec. (on the low-field side of tetramethylsilane at 56·45 Mc./sec.) are less intense than those at 320·7 c./sec., each component split further into a doublet (7·6 c./sec.) by $H_4$ and into a triplet (2·2 c./sec.) by the $CH_2$ group, of the four triplets; the inner two overlap to give the appearance of a quartet; 4·76, two identical protons, $H_5$ and $H_6$, the " central " diene protons, approximate analysis for these as one half of an $A_2X_2$ group gives values for the splitting of each proton by the other (4·74 c./sec.), by the nearest of $H_4$ or $H_7$ (7·7 c./sec.) and by the furthest of $H_7$ or $H_4$ (1·5 c./sec.); about 4·87, centre of $H_2$ (calculated for B of an AB pair), split into a doublet (10·6 c./sec.) by $H_3$, components centred at 293·4 c./sec. (the more intense) and 282·3 c./sec., each with further fine structure, including (probably) triplets (3·8 c./sec.) by the $CH_2$ group; about 6·70, $H_4$ split into doublet by $H_2$, $H_3$, $H_5$, and $H_6$, but the fine structure is complex being partly obscured by $H_7$; about 7·04, $H_7$ split into triplet by $CH_2$ group and doublets by $H_5$ and $H_6$, fine structure complex and overlapped by $H_4$; about 7·73 and 7·62, two protons, not identical, $CH_2$ group, split into doublets by $H_3$ (2·2 c./sec.) and also by $H_2$ and $H_7$.

*Cyclohepta*-1,3-*diene.* 4·31, four olefinic protons, almost identical, structure unresolved but unsymmetrical; about 7·69, four protons, two $CH_2$ groups next to the olefinic groups, complex structure; about 8·08, two protons, central $CH_2$ group.

*Cyclohepta*-1,3-*dieneiron tricarbonyl.* 4·76, two identical protons, " central " diene protons, splittings calculated for $A_2X_2$ group, each split by the other (4·75 c./sec.) by the nearest " terminal " proton (7·6 c./sec.) and by the furthest " terminal " proton (1·2 c./sec.); 6·99, two identical " terminal " diene protons, each split by the " central " protons (7·6 and 1·2 c./sec.) and into triplets by adjacent $CH_2$ group, total structure unresolved; about 8·05, four protons, two identical $CH_2$ groups next to diene group, split by " terminal " proton into doublets and by central $CH_2$ group into triplets; about 8·55, two protons, central $CH_2$ group, split by other two $CH_2$ groups.

*Cyclohexa*-1,3-*diene.* 4·22, four olefinic protons, very nearly equivalent, slight unsymmetrical splitting (about 2 c./sec.) by aliphatic groups; 7·92, four aliphatic protons, very nearly equivalent, slight unsymmetrical splitting (about 4 c./sec.) by olefinic protons.

*Cyclohexa*-1,3-*dieneiron tricarbonyl.* 4·775, two identical " central " diene protons, splittings calculated (for $A_2X_2$ group), giving each split by other (4·1 c./sec) and by nearest (6·6 c./sec.) and farthest (1·5 c./sec.) " terminal " protons; 6·86, " terminal " protons, identical or nearly so, each split by " central " diene protons and also into a triplet by the adjacent $CH_2$ group although structure is not resolved; 8·37, four protons of $CH_2$ groups, structure not resolved.

*Bicyclo*[4,2,0]*octa*-2,4-*dieneiron tricarbonyl.* 4·64, two identical " central " diene protons, on $A_2X_2$ assumption each is split by the other (4·8 c./sec.) and by the nearest (6·8 c./sec.) and furthest (1·6 c./sec.) " terminal " diene protons; 6·63, two " terminal " protons, identical or nearly so, each split by " central " diene protons and also into a doublet by the adjacent tertiary proton; 7·45, two tertiary protons; 8·16 and 8·83, four $CH_2$ protons, possibly each an AB pair giving an $A_2B_2$ group, *i.e.*, the two protons of each $CH_2$ group may not be identical.

The data for butadiene and butadieneiron tricarbonyl have been recorded previously at 40 Mc./sec.;[9] the spectrum of the latter compound at 56·4 Mc./sec. is very similar to that at 40 Mc./sec. apart from the difference in chemical shifts.

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