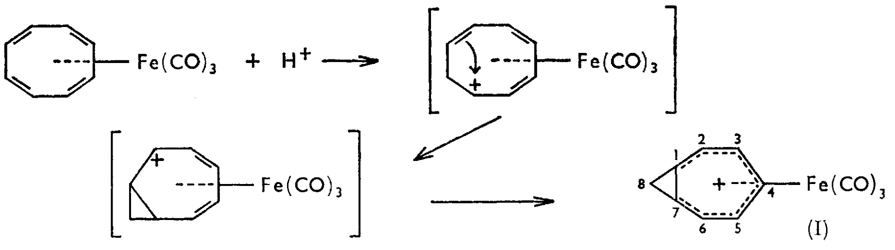
941. *The Protonation of Tricarbonylcyclo-octatetraeneiron and Some Related Compounds.*

By A. Davison, W. McFarlane, L. Pratt, and G. Wilkinson.

Tricarbonylcyclo-octatetraeneiron is protonated in strong acids to give the ion $[C_8H_9Fe(CO)_3]^+$, for which the proton magnetic resonance spectrum and a proton-spin decoupling study indicate the structure tricarbonylbicyclo-[5,1,0]octadieniumiron. Hydride-ion attack on the salt $C_8H_9Fe(CO)_3BF_4$ produces the olefin complex $C_8H_{10}Fe(CO)_3$, which is shown to be tricarbonylbicyclo[5,1,0]octa-2,4-dieneiron. Interaction of the complex $C_8H_8Fe(CO)_3$ with tetracyanoethylene gives a Diels–Alder adduct whose structure is discussed. The cyclo-octatetraene compounds π-$C_5H_5CoC_8H_8$ and π-$C_5H_5RhC_8H_8$ are shown to have olefin bound in a tub form; the protonated species are unstable. The proton magnetic resonance spectra of the tricarbonyl-cycloheptadieniumiron and mono-deuterocycloheptadieniumiron cations are discussed.

We have previously shown[1,2] that protonation of a number of transition-metal carbonyl complexes in strongly acid media leads to cationic species containing metal–hydrogen bonds, *e.g.*, $[HFe(CO)_4PPh_3]^+$ and $[\pi\text{-}C_5H_5W(CO)_3H_2]^+$. During this work a variety of carbonyl–olefin–metal complexes, such as $C_7H_8Mo(CO)_3$ and $C_4H_6Fe(CO)_3$, were investigated and different behaviour was observed on protonation. No transition-metal–hydrogen bond was formed; instead, the proton adds to the olefin ligand to give what can be regarded as " carbonium ions " bound to, and stabilised by, the carbonyl metal portion. This type of behaviour was first noticed by Burton *et al.*[3] in tricarbonylcycloheptatrieneiron. This compound, which contains a free double bond not involved in bonding to the metal atom, reacted with halogen acids, to give salts of the ion $[C_7H_9Fe(CO)_3]^+$. The proton magnetic resonance spectrum of this cation in concentrated sulphuric acid is interpreted below, although this paper deals mainly with the cyclo-octatetraene complexes of iron, cobalt, and rhodium. All these compounds have π-electrons on the bound olefin ligand which are not involved in bonding to the metal atom.

(A) *Tricarbonylcyclo-octatetraene iron.*—Recent *X*-ray measurements have shown[4] conclusively that tricarbonylcyclo-octatetraeneiron, in the solid state, has a free 1,3-diene system in its structure. Previously, protonation of the compound and its reaction with tetracyanoethylene had indicated that it behaved chemically as though it contained such a 1,3-diene group. This behaviour is not inconsistent with the observation that in solution the compound shows only one proton magnetic resonance line, even at —60°, since the complex spectrum expected for the 1,3-diene could be averaged out by chemical exchange. The compound is readily soluble in oxygen-free concentrated sulphuric acid,[5] giving a red



(I)

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[1] Davison and Wilkinson, *Proc. Chem. Soc.*, 1960, 356.

[2] Davison, McFarlane, Pratt, and Wilkinson, *J.*, 1962, 3653.

[3] Quoted by Winkhaus and Wilkinson, *Proc. Chem. Soc.*, 1960, 312; Burton, Pratt, and Wilkinson, *J.*, 1961, 594.

[4] Dickens and Lipscomb, *J. Amer. Chem. Soc.*, 1961, **83**, 4862.

[5] Davison, McFarlane, Pratt, and Wilkinson, *Chem. and Ind.*. 1961, 553.

solution which contains the tricarbonylbicyclo[5,1,0]octadieniumiron cation[6,7] (I). The evidence for this structure comes from a study of the proton magnetic resonance spectrum, and is in agreement with the chemical properties and infrared spectra which are discussed below.

Proton Magnetic Resonance Spectra.—The spectra of the protonated species $[C_8H_9Fe(CO)_3]^+$ and the deuterated species $[C_8H_8DFe(CO)_3]^+$ in concentrated sulphuric acid, together with a spectrum obtained in spin decoupling experiments, are shown in Fig. 1; details and assignments are given in the Experimental section. The component lines are all slightly broad, which may be due to the presence of small amounts of paramagnetic impurities and/or incomplete averaging of dipolar broadening in these viscous solutions. The low-field line (τ 2·26, relative intensity 1) is assigned to the proton H_4. The quintuplet structure arises from approximately equal spin coupling to the four protons H_2, H_3, H_5, and H_6. This interpretation was confirmed by a proton-spin decoupling experiment performed by Turner,[7] who showed that the chemical shift of the groups causing

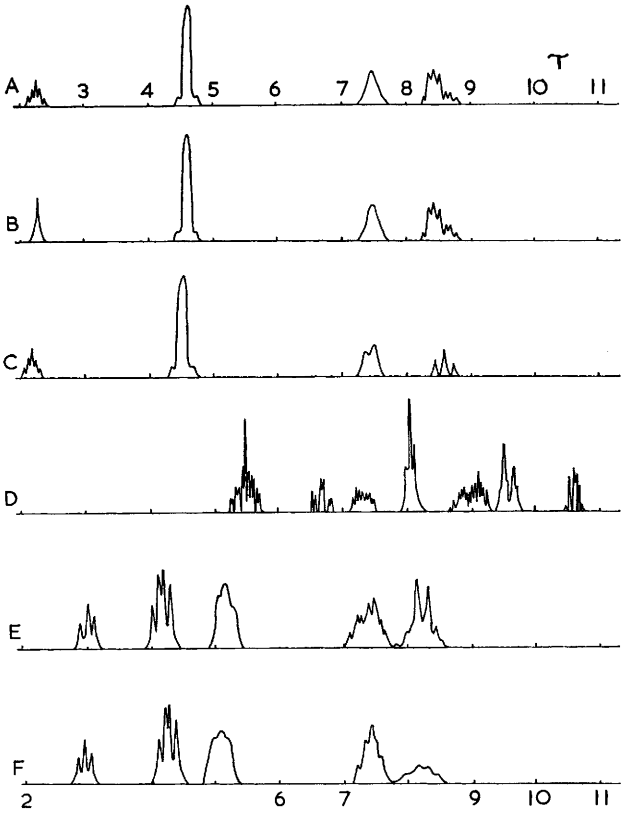

FIG. 1. Proton magnetic resonance spectra of the iron tricarbonyl complexes at 56·45 Mc./sec.

A, $[C_8H_9Fe(CO)_3]^+$ in H_2SO_4. B, The appearance of the low-field resonance in $[C_8H_9Fe(CO)_3]^+$ when the resonance at τ 4·62 is irradiated. C, $[C_8H_8DFe(CO)_3]^+$ in D_2SO_4. D, $C_8H_{10}Fe(CO)_3$ in benzene (solvent line not shown). E, $[C_7H_9Fe(CO)_3]^+$ in H_2SO_4. F, $[C_7H_8DFe(CO)_3]^+$ in D_2SO_4.

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[6] Wilkinson, 6th Internat. Conference on Coordination Chemistry, Detroit, September 1961.
[7] Quoted as an example of proton-spin decoupling by Turner, *J.*, 1962, 847.

the quintuplet splitting was 132 c./sec. on the high field of it, and therefore coincident with the band (τ 4·62, relative intensity 4) assigned to the protons, H_2, H_3, H_5, H_6. These protons appear to be nearly equivalent; they are spin-coupled to H_4, and probably also to H_1 and H_7, but none of this expected structure could be observed. The band at τ 7·48 (relative intensity 2) is assigned to the bridgehead protons, H_1 and H_7; and the high-field band (τ 8·56, relative intensity 2) is assigned to the two non-equivalent methylene protons on C-8, which can be regarded as an " AB " pair. The " AB " part of the spectrum can be analysed to give the values τ_A 8·65 and τ_B 8·47, J_{AB} 4·86 c./sec. These parameters alone would give a quartet, but the observed spectrum can be reproduced satisfactorily (as a quartet of overlapping doublets) if allowance is made for the additional coupling from the bridgehead protons H_1 and H_7. These have different coupling constants from the protons " A " (J ~8 c./sec.) and " B " (J ~4·5 c./sec.), suggesting that the methylene-hydrogen atoms make different dihedral angles with the bridgehead hydrogen atoms. This interpretation of the spectrum is confirmed by measurement of the spectrum of $C_8H_8Fe(CO)_3$ dissolved in concentrated deuterosulphuric acid. Except for a small solvent shift, the spectrum differs from that of the protonated species only in the appearance of the two high-field lines. The band at τ 7·44 (relative intensity 2), from H_1 and H_7, is now an incompletely resolved unsymmetrical doublet. The other band (τ 8·59) is an unsymmetrical triplet (relative intensity 1). The two bands can be regarded approximately as an " AB_2 " group with a value of 7·9 c./sec. for the coupling between the bridgehead protons and the remaining methylene-proton. Comparison of this spectrum with that of the protonated species shows that the proton taken up by $C_8H_8Fe(CO)_3$ in strong acids becomes a methylene-proton and gives rise to the part of the spectrum at τ 8·47. The spectrum in deuterosulphuric acid is unchanged after three days, indicating that the other protons in the compound do not undergo exchange with the solvent.

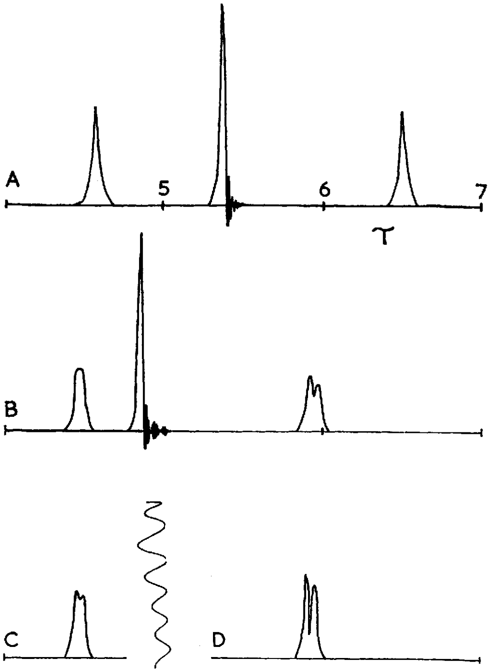


FIG. 2. Proton magnetic resonance spectra of π-$C_5H_5MC_8H_8$ (M = Co or Rh) complexes in CCl_4 at 56·45 Mc./sec.

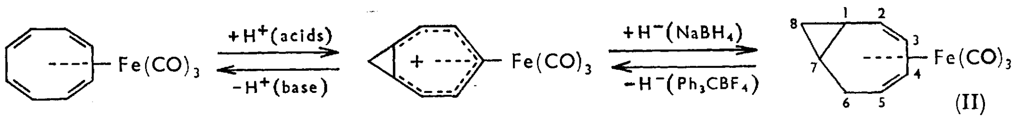
A, π-$C_5H_5CoC_8H_8$.
B, π-$C_5H_5RhC_8H_8$.
C, Appearance of low-field resonance in π-$C_5H_5RhC_8H_8$ when high-field resonance is irradiated.
D, Appearance of high-field resonance when the low-field resonance is irradiated.

Chemical Properties of the $[C_8H_9Fe(CO)_3]^+$ *Ion.*—Careful dilution of sulphuric acid solutions containing the $[C_8H_9Fe(CO)_3]^+$ cation gives unstable yellow solutions which slowly evolve carbon monoxide and give precipitates with the salts of large anions such as

$[PtCl_6]^{2-}$. Neutralisation of the diluted acid solution produces some tricarbonylcyclo-octatetraeneiron. Tricarbonylbicyclo[5,1,0]octadieniumiron tetrafluoroborate has been obtained by mixing cold acetic anhydride solutions of $C_8H_8Fe(CO)_3$ and a 2—3-fold excess of aqueous hydrogen tetrafluoroborate. The resultant pale yellow solution was poured into a large excess of diethyl ether, giving a yellow precipitate $C_8H_9Fe(CO)_3BF_4$; the proton magnetic resonance spectrum of this salt in solution in liquid sulphur dioxide is the same as that of tricarbonylcyclo-octatetraeneiron in sulphuric acid. The infrared spectrum of the salt has intense absorption bands at 2108 and 2055 cm.$^{-1}$ which are assigned to the terminal C–O groups and show the increase in wavenumber expected in a positively charged carbonyl complex. There is no absorption in the free-olefin region, but there is a strong band at 1060 cm.$^{-1}$ which is assigned to the tetrafluoroborate asymmetric stretching mode.

The bicyclic structure of the $[C_8H_9Fe(CO)_3]^+$ cation is confirmed by the fact that the compound is reduced in anhydrous tetrahydrofuran by sodium borohydride to tricarbonylbicyclo[5,1,0]octa-2,4-dieneiron. This is a pale yellow, low-melting crystalline complex which can be purified by sublimation under reduced pressure. The assignment of the seven complex bands in its proton magnetic spectrum (Fig. 1) can be made satisfactorily for the bicyclic structure (II). The bonding of the iron atom to the conjugated diene system leads to a separation of the co-ordinated-olefin resonances into high- and low-field groups; their positions are close to those observed in similar diene complexes of iron, as discussed previously.[3] The band at τ 5·49 arises from the " central " diene protons (H_3 and H_4) which are almost equivalent. The terminal diene protons are not equivalent: one of them (τ 6·68) is next to the single bridgehead-proton H_1 and shows less fine structure than the other (τ 7·3) which is next to the 6-methylene group. This methylene group gives a band at τ 8·06. The complex bands at high τ values are assigned to the four protons of the cyclopropane ring, two of which are bridgehead protons. The non-equivalence of the 8-methylene protons may be due to long-range shielding effects which are associated with the bonded diene group and have been suggested to explain the separation of methylene-proton resonance in similar types of organometallic complex.[8] The infrared spectrum of the complex $C_8H_{10}Fe(CO)_3$ is fully consistent with its proposed structure. There are absorptions in the region 3100—2700 cm.$^{-1}$ that can be ascribed to tertiary and secondary CH groups, but there are no absorptions in the region associated with free double bonds. The very strong absorptions at 2025, 1965, and 1920 cm.$^{-1}$ are attributed to the terminal C–O stretching of the $Fe(CO)_3$ grouping.

Hydride abstraction from tricarbonylbicyclo[5,1,0]octa-2,4-dieneiron by triphenylmethyl tetrafluoroborate in dichloromethane gives pale yellow crystals of bicyclo[5,1,0]-octadienium fluoroborate whose infrared and proton magnetic resonance spectra are identical with those of a sample produced by protonation of the complex $C_8H_8Fe(CO)_3$. It has been shown[9] that tricarbonylcyclo-octatetraeneiron cannot be hydrogenated to give organometallic compounds directly, unlike tricarbonylcycloheptatrieneiron.[3] The production of tricarbonylbicyclo[5,1,0]octa-2,4-dieneiron by protonation of the complex $C_8H_8Fe(CO)_3$ to give the tricarbonylbicyclo[5,1,0]octadieniumiron cation, followed by hydride ion attack at position 2 or 6 of this cation, constitutes a two-stage stereospecific reduction of tricarbonylcyclo-octatetraeneiron.



(II)

The tetracyanoethylene adduct of tricarbonylcyclo-octatetraeneiron. Additional evidence that tricarbonylcyclo-octatetraeneiron contains a " non-bonded " 1,3-diene system is that

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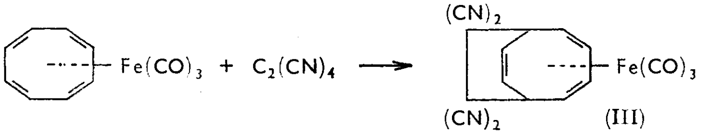
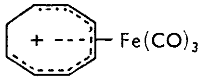
[8] Bennett, Pratt, and Wilkinson, *J.*, 1961, 2037.

[9] Manuel and Stone, *J. Amer. Chem. Soc.*, 1960, **82**, 366.

it readily forms a Diels–Alder adduct (III) with tetracyanoethylene. This is a pale yellow diamagnetic solid which is insoluble in organic solvents. Its infrared spectrum shows no bands attributable to methylene-protons; weak absorption at 2254 cm.$^{-1}$ can be assigned to the cyanide groups. Intense absorption at 2072 and 2012 cm.$^{-1}$ is due to the terminal C–O stretching modes of the $Fe(CO)_3$ grouping, and a very weak band at 1670 cm.$^{-1}$ is probably due to the free double bond. When it was shown [5] that tricarbonylcyclo-octatetraeneiron could be protonated to give $[C_8H_9Fe(CO)_3]^+$ it was suggested by Schrauzer [10] that the protonated species had the structure (IV) in which only four of the six delocalised π-electrons were used in bonding to iron. This structure is not compatible with the proton magnetic resonance spectrum, with our chemical evidence, or with the molecular structure of the complex $C_8H_8Fe(CO)_3$.



(III)



(IV)

(B) *Cyclo-octatetraene Derivatives of Cobalt and Rhodium.*—The behaviour of tricarbonylcyclo-octatetraeneiron is in strong contrast to that exhibited by the cyclo-octatetraene-π-cyclopentadienyl-cobalt and -rhodium complexes, π-$C_5H_5MC_8H_8$. The proton magnetic resonance spectra of these compounds (Fig. 2) agree with structures containing the cyclo-octatetraene ligand in a tub conformation, bonded to the metal by the non-conjugated 1,5-diene groups. The two compounds have very similar spectra; each shows three proton resonances of relative intensities 4 : 5 : 4. The central line, of intensity 5, is very sharp and is assigned to the protons of the π-bonded C_5H_5 ring. This line is a singlet in the cobalt compound, and a closely spaced doublet (J 0·7 c./sec.) as a result of coupling of the protons to the ^{103}Rh nucleus in the rhodium complex. The other bands, which are broad, arise from the protons on the cyclo-octatetraene group. In contrast to behaviour in the parent olefin, the protons in the complex occur in two non-equivalent groups, each containing four protons. This non-equivalence can be understood on the basis of the tub conformation of the bonded olefin ligand. The resonances of the four non-bonded olefinic protons H_3, H_4, H_7, and H_8 occur on the low-field side of the π-C_5H_5 resonance, and the protons H_1, H_2, H_5, and H_6 of the metal-bonded olefin occur on the high-field side. The width of the lines is due, in part at least, to spin coupling between the protons. This was demonstrated by means of proton-spin decoupling; in each case, irradiation of the low-field group resulted in a sharpening of the high-field group, and *vice versa.* When the high-field band of the rhodium complex was irradiated the sharpening of the low-field band revealed a residual doublet structure; this represents the coupling (J ~1·4 c./sec.) of the non-bonded olefinic protons to the ^{103}Rh nucleus. The high-field resonance shows a larger (J 2·4 c./sec.) doublet structure, detectable in the normal spectrum, which arises from the coupling of the rhodium nucleus to the four protons of the bonded-olefin groups. Irradiation at the resonant frequency of the low-field protons, which removes their spin coupling to the high-field ones, makes the high-field doublet better resolved without changing the separation of its component lines.

Unlike $C_8H_8Fe(CO)_3$, these complexes in concentrated sulphuric acid give very unstable solutions, whose proton magnetic resonance spectra show very broad lines that give little information about the protonated species. This instability is probably due to the inability of the cyclo-octatetraene ligand to give on protonation a [5,1,0]bicyclo-system without rearrangement. Instead, protonation probably produces a cyclo-octatrienium complex in which the positive charge is not delocalised in the π-orbitals of the ligand. An unstable solid was produced by the treatment of π-$C_5H_5CoC_8H_8$ in acetic anhydride

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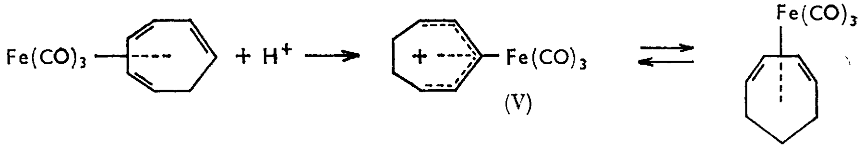
[10] Schrauzer, *J. Amer. Chem. Soc.*, 1961, **83**, 2966.

with hydrofluoroboric acid. The infrared spectrum of this solid indicated that it was an ionic fluoroborate π-$C_5H_5CoC_8H_9BF_4$; it showed a strong absorption due to the BF_4^- ion, and some of the lines characteristic of a π-bonded C_5H_5 group. Further evidence of the absence of a non-bonded 1,3-diene system in the olefin ligand of these neutral complexes π-$C_5H_5MC_8H_8$ (M = Co or Rh) is their inability to give Diels–Alder adducts with tetracyanoethylene.

(C) *Tricarbonylcycloheptatrieneiron and Related Species.*—As mentioned earlier,[3] tricarbonylcycloheptatrieneiron can be protonated to give the $[C_7H_9Fe(CO)_3]^+$ cation. This cation was subsequently prepared by Dauben *et al.*[11] as a tetrafluoroborate salt, both by protonation of $C_7H_8Fe(CO)_3$ with hydrogen tetrafluoroborate in propionic anhydride, and by hydride abstraction from tricarbonylcycloheptadieneiron by triphenylmethyl tetrafluoroborate in dichloromethane. Reduction of the protonated species with sodium borohydride gives tricarbonylcycloheptadieneiron, this being another example of a two-stage stereospecific reduction. The proton magnetic resonance spectra of tricarbonylcycloheptatrieneiron in concentrated sulphuric and deuterosulphuric acid (Fig. 1) are those of the cycloheptadienium cation (V) and the monodeutero-derivative. The spectrum of the protonated species shows five bands; the three at low field, of relative intensities 1 : 2 : 2, are assigned to the protons H_4, H_3, and H_5, and H_2 and H_6, respectively, in the delocalised group. The two bands at high field are assigned to the methylene protons on C-1 and C-7. In the deutero-species the band at highest field is of unit intensity, showing that the proton (deuteron) which becomes attached by protonation (deuteration) of the free double bond of $C_7H_8Fe(CO)_3$ to give one of the methylene groups is not involved in chemical exchange with the solvent protons (deuterons), at least for several hours. Since the parent complex $C_7H_8Fe(CO)_3$ is not regenerated by dilution of the solutions in concentrated acid, but only when these dilute solutions are neutralised by base (cf. the behaviour of the tricarbonylbicyclo[5,1,0]octadieniumiron cation in concentrated sulphuric acid), we have been able to confirm that exchange does not occur even in dilute acid solution. Thus when $C_7H_9Fe(CO)_3^+$ in concentrated sulphuric acid and $C_7H_8DFe(CO)_3^+$ in concentrated dideuterosulphuric acid are diluted (to *ca.* 1N) with deuterium oxide and water, respectively, and the corresponding hexafluorophosphates are precipitated after *ca.* 30 min., the high-resolution nuclear magnetic resonance spectra of these salts in liquid sulphur dioxide are identical with those of the original cations in the concentrated acids. The resonance line of the added proton lies at highest field (τ 8·2), and by analogy with previous cases (see ref. 8 and references quoted therein) it must be *endo* with respect to the metal atom; the protonation is thus irreversible in acid media and is stereospecific.



EXPERIMENTAL

Microanalyses are by the Microanalytical Laboratory of this College.

Tricarbonylcyclo-octatetraeneiron. This compound has been made by direct interaction of cyclo-octatetraene and pentacarbonyliron,[9, 14, 15] but the following procedure was more satisfactory. Dodecacarbonyltri-iron (8·4 g.) and cyclo-octatetraene (6 ml.) were refluxed in light

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[11] Dauben and Bertelli, *J. Amer. Chem. Soc.*, 1961, **83**, 497.
[12] Nakamura and Hagihara, *Bull. Chem. Soc. Japan*, 1960, **33**, 425.
[13] Fischer and Bittler, *Z. Naturforsch.*, 1961, **16*b***, 225.
[14] Nakamura and Hagihara, *Bull. Chem. Soc. Japan*, 1959, **32**, 880.
[15] Rausch and Schrauzer, *Chem. and Ind.*, 1959, 957.

petroleum (30 ml.; b. p. 120—130°) under nitrogen for 1 hr. The mixture was filtered and evaporated at 50°/0·1 mm. The residue was crystallised from ethanol and sublimed at 50°/0·01 mm. in 90% yield; small amounts of the complex $C_8H_8Fe_2(CO)_6$ were also produced.

Tricarbonylbicyclo[5,1,0]*octadieniumiron Tetrafluoroborate.*—Tricarbonylcyclo-octatetraeneiron (12·2 g., 0·1 mole) in acetic anhydride (75 ml.) was treated with 40% aqueous hydrogen tetrafluoroborate (40 ml., 0·3 mole) in ice-cold acetic anhydride (100 ml.). The mixture at once became pale yellow and was immediately poured into diethyl ether (1½ l.). The yellow precipitate was washed with ether (8 × 100 ml.) and dried under a vacuum, to give pale yellow crystals of the *compound*, decomp. 150°, which was analysed immediately (Found: C, 39·75; H, 3·0; F, 22·4. $C_{11}H_9BF_6FeO_3$ requires C, 39·8; H, 2·7; F, 22·9%).

The fluoroborate was dissolved in air-free water and a slight excess of potassium hydroxide was added. Extraction with diethyl ether gave a quantity of tricarbonylcyclo-octatetraeneiron, but yields were variable on account of the instability of the aqueous fluoroborate solution, and hydrated ferric compounds and organic materials were also produced.

Tricarbonylbicyclo[5,1,0]*octa-*2,4-*dieneiron.*—The following operations were performed in an atmosphere of nitrogen. The salt $C_8H_9Fe(CO)_3BF_4$ (10 g.) was suspended in anhydrous tetrahydrofuran (75 ml.) and powdered sodium borohydride (3 g., excess) was added during 1 hr. There was vigorous evolution of gas and when the fluoroborate had dissolved, light petroleum (100 ml.; b. p. 60—80°) was added. The tetrahydrofuran and excess of borohydride were removed by repeated washing with air-free water and the petroleum solution was dried ($CaCl_2$) and chromatographed on alumina (Brockmann, grade III). Two bands were eluted with light petroleum (b. p. 40—60°), the second giving the complex $C_8H_8Fe(CO)_3$ (0·5 g.). The first fraction was evaporated and gave, after recrystallisation from light petroleum (b. p. 30—40°) at −78° and sublimation at room temperature, deep yellow crystals of the *complex*, m. p. 36·5° (1·2 g., 16%) (Found: C, 53·5; H, 4·2. $C_{11}H_{10}FeO_3$ requires C, 53·7; H, 4·1%), very soluble in organic solvents, giving solutions which are somewhat unstable in air although the solid itself is fairly stable.

Hydride-abstraction from Tricarbonylbicyclo[5,1,0]*octa-*2,4-*dieneiron.*—Solutions of triphenylmethyl tetrafluoroborate (0·62 g., 1·9 mmoles) in dichloromethane (4 ml.) and the iron complex (0·463 g., 1·9 mmoles) in dichloromethane (2 ml.) were mixed. The initial dark colour faded in ~30 sec. and the yellow crystals which separated were washed with diethyl ether (2 × 50 ml.) and dried under a vacuum. Their proton magnetic resonance spectrum was identical with that of an authentic specimen of tricarbonylbicyclo[5,1,0]octadieniumiron tetrafluoroborate made from $C_8H_8Fe(CO)_3$ and hydrogen tetrafluoroborate.

Cyclo-octatrienium-π-cyclopentadienylcobalt Tetrafluoroborate.—Cyclo-octatetraene-π-cyclopentadienylcobalt was prepared by Nakamura and Hagihara's method [12] except that the reaction mixture was chromatographed and yields of 25—30% were obtained. The product was treated with hydrogen tetrafluoroborate in the same way as $C_8H_8Fe(CO)_3$, but the yellow-brown solid obtained was too unstable for satisfactory analysis.

Cyclo-octatetraene-π-cyclopentadienylrhodium.—Dicarbonylcyclopentadienylrhodium [13] (from 4·6 g. of chlorodicarbonylrhodium, 4·6 g. of sodium, and 18 ml. of cyclopentadiene) was refluxed under nitrogen with cyclo-octatetraene (4 ml.) in light petroleum (b. p. 120—160°; 25 ml.) for 18 hr. The solution was filtered and chromatographed in light petroleum (b. p. 40—60°) on alumina (Brockmann, grade III). A yellow band was eluted which on evaporation and crystallisation from light petroleum gave yellow air-stable crystals of the *compound*, m. p. 106° (0·7 g., 11%) (Found: C, 57·5; H, 5·4. $C_{13}H_{13}Rh$ requires C, 57·4; H, 4·8%).

*Tricarbonyl-*9,9,10,10-*tetracyanobicyclo*[4,2,2]*deca-*2,4,7-*trieneiron.*—Benzene solutions of tricarbonylcyclo-octatetraeneiron (0·52 g., 2·1 mmoles; in 10 ml.) and tetracyanoethylene (0·27 g., 2·1 mmoles; in 25 ml.) were mixed at room temperature. Pale yellow crystals which slowly formed were collected after 1 hr., washed with benzene and then light petroleum, and dried under a vacuum. The diamagnetic *adduct* darkens at 150°, is stable in air, and is insoluble in common organic solvents and water (Found: C, 55·25; H, 2·8; Fe, 15·2; N, 15·5; O, 15·6. $C_{17}H_8FeN_6O_3$ requires C, 55·0; H, 2·2; Fe, 15·1; N, 5·1; O, 12·9%).

Infrared Spectra.—Spectra were measured on a Perkin-Elmer model 21 instrument, with sodium chloride or calcium fluoride optics where appropriate, and in carbon disulphide or carbon tetrachloride solution where possible; otherwise Nujol, hexachlorobutadiene, or Fluorolube mulls were used.

Tricarbonylbicyclo[5,1,0]octadieniumiron tetrafluoroborate: (3087sh), 3060w, (3011sh), 2055vs, 2018vs, 1060vs.

Tricarbonylbicyclo[5,1,0]octa-2,4-dieneiron: (3040sh), 2935s, 2900ms, 2855m, 2820ms, 2025vs, 1965vs, 1920vs, 1460sh, 1435m, 1416m, (1375sh), 1362m, (1340sh), 1320m, 1242w, 1226m, 1198w, 1162w, 1120m, 1035s, 1020ms, 993s, 966ms, (937sh), 928m, 896ms, 872m, 850m, 828s, 802m, 758m. 722m, 710ms, 673ms.

Cyclo-octatetraene-π-cyclopentadienylrhodium: 3015s, 2985s, 1640m, 1405w, 1380w, 1340ms, 1140w, 1120ms, 1100w, 1006m, 980m, 948w, 908s, 836w, (822sh), 803vs, 783vs, 752m, 722m.

Tricarbonyl-9,9,10,10-tetracyanobicyclo[4,2,2]deca-2,4,7-trieneiron: 3030w, 2995w, 2978w, 2950w, 2250w, 2072vs, 2012vs, 1670w, 1405w, 1344w, 1320m, (1306sh), 1286w, 1270w, 1240w, 1222w, 1180w, 1139w, 1113m, (1080sh), 1062w, 1024w, 985w, 960m, 928m, 898ms, 855m, 838w, 827m, 774ms, 750m, 693w.

Proton Magnetic Resonance Spectra.—Spectra were measured in tubes of 5 mm. outside diameter on a Varian Associates model V4311 spectrometer at 56·45 Mc./sec. at 22° + 2°. Line positions were measured by conventional side-band techniques relative to tetramethylsilane or dimethyl sulphate (in sulphuric acid solutions). Dimethyl sulphate was referred to tetramethylsilane in trifluoroacetic acid and has τ 5·97. The sulphuric acid solutions were prepared from ice-cold oxygen-free "AnalaR" sulphuric acid. Solutions in liquid sulphur dioxide were made by condensing sulphur dioxide on to the solid contained in a thick-walled Pyrex tube (5 mm. in outside diameter) sealed under a vacuum. The proton–proton spin decoupling experiments were performed with the apparatus constructed by Dr. Turner of this College.[7] Line positions, in τ values, were as follows.

$[C_8H_9Fe(CO)_3]^+$ in sulphuric acid: band A, 2·26, quintuplet, H_4 split by $H_2 + H_3 + H_5 + H_6$, $J \sim 3{\cdot}8$ c./sec.; band B, 4·62 (broad), H_2, H_3, H_5, H_6; band C, 7·48 (broad), "bridgehead" protons H_1 and H_7; band D (complex), 8·56 (calc. for centre of "AB" pair), "A" component 8·65, "B" component 8·47 ($J_{\text{“AB”}}$ 4·8 c./sec.), 8-methylene protons, additional structure on the "A" component, spin coupled to $H_1 + H_7$ ($J \sim 8$ c./sec.), and on the "B" component, spin-coupled to $H_1 + H_7$ ($J \sim 4{\cdot}5$ c./sec.). The spectrum in liquid sulphur dioxide is identical.

$[C_8H_8DFe(CO)_3]^+$ in dideuterosulphuric acid: band A, 2·18, H_6 (same as band A above); band B, 4·55, H_2, H_3, H_4, and H_6 (same as band B above); band C, 7·44, H_1 and H_7 (unsymmetrical doublet); band D, 8·59, H_8 in $>$CHD group (unsymmetrical triplet); bands C and D were analysed as an "AB_2" group with J/Δ 0·122 ($J_{\text{“AB”}}$ 7·96 c./sec.).

$C_8H_{10}Fe(CO)_3$ in benzene: band A, 5·49 (complex), H_3 and H_4; band B, 6·68, "triplet" of doublets (main splitting 5 c./sec., smaller splitting $\sim$2 c./sec.), H_2; band C, $\sim$7·3 (complex), H_5; band D, 8·06 (complex), 6-methylene protons; bands E, 8·7—9·8, and F, 10·61 (both complex), protons H_1, H_7, and the two-equivalent methylene protons on C_8.

$[C_7H_9Fe(CO)_3]^+$ in sulphuric acid: band A, 3·03, unsymmetrical triplet, H_4 split by $H_3 + H_5$ ($J = 6{\cdot}5$ c./sec.); band B, 4·81, unsymmetrical quartet (double doublet), H_3 and H_5, each split by H_4 (J 6·5 c./sec.) and by H_2 or H_6 (J 9·9 c./sec.); band C, 5·15 (broad), H_2 and H_6; bands D, $\sim$7·4, and E, $\sim$8·2, 1- and 7-methylene protons.

$[C_7H_8DFe(CO)_3]^+$ in dideuterosulphuric acid: band A, 2·96, unsymmetrical triplet, H_4 (same as band A above); band B, 4·07, unsymmetrical quartet, H_3 and H_5 (same as band B above); band C, 5·08 (broad), H_2 and H_6; band D, $\sim$7·4 (complex), two of the 1- and 7-methylene protons; band E, 8·21, incompletely resolved doublet, one of the 7-methylene protons, analysed as a double doublet (main splitting $\sim$16·5 c./sec., smaller splitting $\sim$7·5 c./sec.) coupled to the other H_7 proton and also to H_1 and H_6.

π-$C_5H_5CoC_8H_8$ in carbon tetrachloride: band A, 4·56 (broad), H_3, H_4, H_7, and H_8, each proton coupled to at least two of H_1, H_2, H_5, and H_6; band B, 5·3, singlet, the five equivalent protons of the π-C_5H_5 group; band C, 6·50 (broad), H_1, H_2, H_5, and H_6, each proton coupled to at least two of H_3, H_4, H_7, and H_8.

π-$C_5H_5RhC_8H_8$ in carbon tetrachloride: band A, 4·47 (broad), H_3, H_4, H_7, and H_8 (as in corresponding band above in Co compound); band B, 4·85, the five protons in the π-C_5H_5 group, doublet (J 0·71 c./sec.) since these protons are spin-coupled to the ^{103}Rh (spin ½, abundance 100%); band C, 5·94, H_1, H_2, H_3, H_5, and H_6 (as in corresponding band above in Co compound), incompletely resolved doublet as a result of ^{103}Rh splitting ($J \sim 2{\cdot}4$ c./sec.).

Proton–Proton Spin-decoupling Studies on Cobalt and Rhodium Complexes.—Irradiation of either band A or band C produced marked sharpening of the other. In the rhodium complex, in addition to this sharpening, a small residual doublet splitting became evident (*J* ~1·4 c./sec.) in band A when band C was irradiated. The doublet structure displayed by band C (*J* ~2·4 c./sec.) was resolved more clearly by irradiation of band A.

We thank the Department of Scientific and Industrial Research, the Hercules Powder Co. (A. D.), and the United States Rubber Co. (W. McF.) for financial assistance; Messrs. Johnson Matthey and Co., Ltd., for the loan of rhodium; and the International Nickel Co. (Mond), Ltd., E. I. du Pont de Nemours and Co., and Shell Chemical Co. for gifts of iron carbonyl tetracyanoethylene, and cycloheptatriene, respectively.

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[*Received, April* 16*th*, 1962.]