405. *Cyclo-octatriene and Related Complexes of Iron and Cobalt.*

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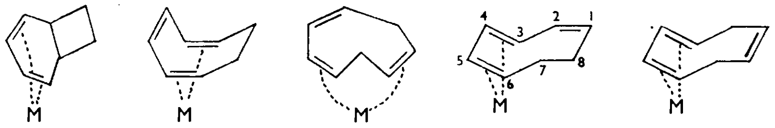
The formation, in the reduction of tricarbonylcyclo-octatetraeneiron(0), of compounds which can be regarded as cyclo-octatriene derivatives has led to further study of the direct interaction of the isomeric cyclo-octatriene mixture with dodecacarbonyltri-iron and π-cyclopentadienyldicarbonyl-cobalt.

New compounds and species formed from them by protonation in concentrated sulphuric acid are characterised by infrared and high-resolution nuclear magnetic resonance spectroscopy.

The organometallic complexes obtained in the direct reaction between iron and cobalt carbonyl compounds and the isomeric mixture of cyclo-octatrienes (obtained by reduction of cyclo-octatetraene) have been studied by a number of workers.[1-5] During our studies [6] on the reduction of tricarbonylcyclo-octatetraeneiron, we obtained several compounds which can be regarded as derivatives of cyclo-octatriene and this led us to re-investigate the above direct reactions more closely, particularly in view of the previous discordant results.

The reduction of cyclo-octatetraene with zinc dust and sodium hydroxide in alcohol gives a mixture of cyclo-octa-1,3,5-triene, cyclo-octa-1,3,6-triene, and bicyclo[2,4,0]octa-2,4-diene in proportions which vary from preparation to preparation but which are not important in the present context since isomerisation takes place readily when the mixture is heated with metal carbonyl compounds.

Formulæ [I—V; M = $Fe(CO)_3$ or $Co-\pi-C_5H_5$] show some of the complexes which might be formed when one of the octatrienes becomes associated with a metal able to combine with a diolefin. Certain of these olefin complexes will have a double bond not involved in bonding to the metal atom, as first shown for tricarbonyl cycloheptatrieneiron.[7] Since no rules so far exist for distinguishing in such cases between bound and free double bonds we use the nomenclature illustrated under (I—V) where (*a*) the free double bond is designated in bold type, (*b*) the free double bond is given the smallest number in cases where there is no conflict with standard organic nomenclature for such ring systems, and (*c*), if a choice remains, the sum of bold face numbers is minimised.



(I) (II) (III) (IV) (V)

(I) Bicyclo[4,2,0]octa-2,4-diene-. (II) Cyclo-octa-1,**3**,5-triene-. (III) Cyclo-octa-**1**,3,6-triene-. (IV) Cyclo-octa-**1**,3,5-triene-. (V) Cyclo-octa-1,3,**6**-triene-.

π-Cyclopentadienylcobalt Complexes.—In contrast to previous work,[3] we find that the reaction between the cyclo-octatriene mixture and dicarbonyl-π-cyclopentadienylcobalt gives two products, which can be separated by chromatography, in proportions which depend on the temperature and duration of the reactions.

Under mild conditions or with short reaction times the principal product is a deep-red

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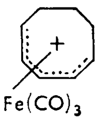
[1] Fischer, Palm, and Fritz, *Chem. Ber.*, 1959, **92**, 2645.
[2] Manuel and Stone, *J. Amer. Chem. Soc.*, 1960, **82**, 6240.
[3] King, Treichel, and Stone, *J. Amer. Chem. Soc.*, 1961, **83**, 3593.
[4] Nakamura and Hagihara, *J. Chem. Soc. Japan*, 1961, **82**, 1389.
[5] Nakamura and Hagihara, *J. Chem. Soc. Japan*, 1961, **82**, 1392.
[6] Davison, McFarlane, Pratt, and Wilkinson, *J.*, 1962, 4821.
[7] Burton, Pratt, and Wilkinson, *J.*, 1961, 594.

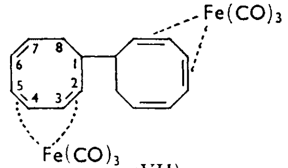
solid (m. p. 46°) which was formulated with structure (I; $M = Co\text{-}\pi\text{-}C_5H_5$) although the nuclear magnetic resonance spectra of the compound were ill-resolved and not wholly conclusive.[3] Present measurements conclusively confirm structure (I) for the compound, the spectrum being almost identical with that of the corresponding tricarbonyliron derivative[7] with the addition of an extra line of intensity five due to the π-C_5H_5 group. Further, there is no absorption in the infrared spectrum in the region normally associated with free olefinic groups.

If the reaction is allowed to proceed for a longer time or the conditions are more severe, the main product is a golden-brown air-stable solid (m. p. 98°). The infrared spectrum of this compound shows a weak band at 1618 cm.$^{-1}$ which can be assigned to a free double bond, while the nuclear magnetic resonance spectrum is consistent uniquely with structure (II; $M = Co\text{-}\pi\text{-}C_5H_5$). The compound is soluble in concentrated sulphuric acid, giving a dark-brown solution. The nuclear magnetic resonance spectrum shows that protonation of the free double bond has occurred. The protonated species is, however, unstable as a result of the inability of the positive charge to be delocalised. This behaviour may be compared with that shown by cyclo-octatetraene derivatives of π-cyclopentadienylcobalt and -rhodium[6] in which the olefin ligand also is present in the tub conformation and contrasted with that shown by tricarbonylcycloheptatrieneiron[7] and tricarbonylcyclo-octatetraeneiron[6] where delocalisation to give dienyl systems occurs.

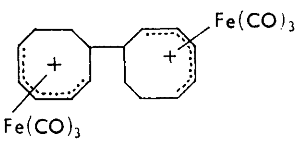
Tricarbonyliron Complexes.—Two products have been obtained from the interaction of dodecacarbonyltri-iron and the cyclo-octatriene mixture. In this case, the bicyclo-octadiene complex [I; $M = Fe(CO)_3$] appears to be the more stable isomer, since it is produced under vigorous conditions or with longer reaction times. The other product, also of stoicheiometry $C_8H_{10}Fe(CO)_3$, is formed under milder conditions and has been observed previously[2,4] although its constitution has not been established. The second complex is a yellow-orange oil whose infrared spectrum shows a band attributable to a free double bond. The original suggestion[1] that the more stable product was a derivative of cyclo-octa-1,3,6-triene [whether (III) or (V) was not specified] was disputed[2] on the grounds that cyclo-octa-1,3,6-triene is the least, and bicyclo[2,4,0]octa-2,4-triene the most, thermodynamically stable of the three isomers and that the iron complexes should have similar stabilities. Our observations on the π-cyclopentadienylcobalt compounds show that this argument is of doubtful validity. The same reasoning was used[2] to assign structure [IV; $M = Fe(CO)_3$] to the less stable iron complex containing the free double bond. Our proton magnetic resonance data, including a spin–spin decoupling study, show that this assignment is in fact correct since the spectrum is consistent with structure (IV) and not with any of the others. Furthermore, solutions of the compound in trifluoroacetic and sulphuric acid are stable and their proton magnetic resonance spectra are consistent with protonation of the free double bond, followed by delocalisation of the positive charge, to give the tricarbonylcyclo-octadienyliron cation (VI). The stable pale-yellow tetrafluoroborate salt containing this ion can be obtained by treatment of solutions of the olefin compound in propionic anhydride with a mixture of fluoroboric acid in an excess of propionic anhydride. The infrared spectrum of the salt shows that the carbonyl frequencies are raised by *ca.* 70 cm.$^{-1}$, as expected for the influence of the positive charge on the complex ion. The proton resonance spectrum of a solution of the salt in liquid



(VI)



(VII)



(VIII)

sulphur dioxide is identical with that of the parent compound dissolved in trifluoroacetic acid.

We have also observed the formation of the compound [IV; M = $Fe(CO)_3$] in low yield during the reduction of tricarbonylbicyclo-octa[5,1,0]dienyliron tetrafluoroborate[6] with sodium borohydride in tetrahydrofuran in the presence of lithium chloride and a small amount of water. When this reaction is performed under vigorous conditions, there is obtained a sparingly soluble yellow compound $C_{22}H_{18}Fe_2O_6$, in addition to the complexes of lower molecular weight. This binuclear species is also formed in the reactions between the tetrafluoroborate and methyl- or phenyl-lithium, but it is best made by treatment of the tetrafluoroborate with zinc dust in boiling tetrahydrofuran. Its infrared spectrum shows the presence of a free double bond(s) and symmetrically situated tricarbonyliron residues, while a satisfactory assignment of its proton magnetic resonance spectrum can be made on the basis of structure (VII). The formulation as hexacarbonylbi(cyclo-octa-2,4,**6**-trienyl)di-iron is confirmed by proton resonance study of the deep yellow-brown solution which the substance gives in concentrated sulphuric acid. The spectrum is similar to that of tricarbonylcyclo-octa-**1**,3,5-trieneiron in the same acid and is clearly consistent with the structure (VIII) for the ion.

EXPERIMENTAL

Microanalyses and molecular-weight determinations (ebullioscopic in benzene) are by the Microanalytical Laboratory, Imperial College.

The mixture of isomeric cyclo-octatrienes was made by Jones's method[8] except that the product was not steam-distilled; it was shown spectroscopically to contain less than 5% of cyclo-octatetraene and this was most conveniently removed (as metal complex) by chromatography after the reactions were complete. Dicarbonyl-π-cyclopentadienylcobalt[9] was chromatographed in light petroleum (b. p. 40—60°) on alumina (Brockmann's grade III) before use.

Interaction of Dicarbonyl-π-cyclopentadienylcobalt and Cyclo-octatrienes.—Dicarbonyl-π-cyclopentadienylcobalt (7 g., 39 mmoles) and the mixture of cyclo-octatrienes (5 ml., 38 mmoles) was refluxed in light petroleum (b. p. 120—130°; 50 ml.) under nitrogen for 15 hr. The solution was cooled, filtered, and transferred to an alumina (grade III) column. Elution with light petroleum (b. p. 40—60°) gave two bands. Band A was deep red and on evaporation and crystallisation [to remove a small amount of unchanged π-$C_5H_5Co(CO)_2$] from light petroleum (b. p. 30—40°) at −30° gave π-cyclopentadienylbicyclo[4,2,0]octa-2,4-dienecobalt (0·7 g., 8%) as dark-red needles, m. p. 46°, which were very soluble in organic solvents. Band B on evaporation followed by crystallisation at −78° from light petroleum (b. p. 40—60°) and sublimation (60°/0·01 mm.) gave *π-cyclopentadienylcyclo-octa-*1,**3**,5*-trienecobalt* as golden-brown needles, m. p. 98° (1·1 g., 11·5%) (Found: C, 67·0; H, 6·8%; *M*, 225. $C_{13}H_{15}Co$ requires C, 67·8; H, 6·5%; *M*, 230·1). The compound is moderately soluble in common organic solvents, and light petroleum solutions are stable in air for weeks.

Interaction of Dodecacarbonyltri-iron and Cyclo-octatrienes.—Dodecacarbonyltri-iron (6·36 g., 13 mmoles) was refluxed in light petroleum (b. p. 100—120°; 50 ml.) with cyclo-octatrienes (5 ml., 38 mmoles) for 35 min. under nitrogen. The cooled mixture was filtered and chromatographed in de-aerated light petroleum (b. p. 40—60°) on alumina (grade III). The first band to be eluted contained pentacarbonyliron and was rejected. The second band was evaporated and the residue crystallised from light petroleum (b. p. 30—40°) at −78°, to give *tricarbonylcyclo-octa-***1**,3,5*-dieneiron* (1·9 g., 20%) as a somewhat air-sensitive yellow-orange oil, f. p. −10° (Found: C, 54·3; H, 4·1%; *M*, 241·3. $C_{11}H_{10}FeO_3$ requires C, 53·7; H, 4·1%; *M*, 245·0). If either the stated time or the temperature of the reaction is exceeded, the main product is tricarbonylbicyclo[4,2,0]octa-2,4-dieneiron.

Tricarbonylcyclo-octadienyliron Tetrafluoroborate.—A solution of tricarbonylcyclo-octa-**1**,3,5-dieneiron (1·23 g., 5 mmoles) in propionic anhydride (5 ml.) was mixed with ice-cold propionic anhydride (15 ml.) containing fluoroboric acid (5 ml. of 40% aqueous acid). The mixture

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[8] Jones, *J.*, 1954, 1808.

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

darkened and after 30 sec. was poured into diethyl ether (500 ml.). The pale-yellow precipitate of the *salt* was filtered off, washed with ether and light petroleum (b. p. 30—40°), and dried *in vacuo* (Found: C, 40·0; H, 3·5; F, 23·0. $C_{11}H_{11}BF_4FeO_3$ requires C, 39·6; H, 3·3; F, 22·8%). The solid is stable in air and decomposes at 120°.

Hexacarbonylbi(cyclo - octa - 2,4,6 - dienyl)di - iron.—Tricarbonylbicyclo[5,1,0]octadienyliron tetrafluoroborate [6] (3·22 g., 10 mmoles) and zinc dust (6·5 g., 50 mg.-atoms) were suspended in de-aerated tetrahydrofuran which was refluxed and stirred vigorously under nitrogen. The tetrafluoroborate slowly dissolved, and after 10 hr. the mixture was filtered and the filtrate evaporated. Treatment of the oily residue with light petroleum (b. p. 30—40°), followed by crystallisation of the solid from benzene, gave yellow crystals of the *compound* (0·98 g., 40%) (Found: C, 54·0; H, 3·6; O, 19·3%; *M*, 485. $C_{22}H_{18}Fe_2O_6$ requires C, 53·9; H, 3·7; O, 19·1%; *M*, 490·1). The air-stable compound is soluble in carbon tetrachloride, carbon disulphide, and benzene but is sparingly soluble in light petroleum. It decomposes without melting at 120—130°.

Infrared Spectra.—Spectra were recorded on a Perkin-Elmer Model 21 in both carbon tetrachloride and carbon disulphide solutions where feasible; where mulls are specified, these are in both Nujol and hexachlorobutadiene.

π-Cyclopentadienylcyclo-octa-1,3,5-trienecobalt: 3090w, 2960s, 2895m, 2845w, 2812w, 1618w, 1425w, 1402w, 1365w, 1342w, 1180w, 1160sh, 1121w, 1107w, 1009w, 989w, 952w, 929w, 885sh, 861m, 843w, 809sh, 800s, 781m, 748w.

Tricarbonylcyclo-octa-1,3,5-trieneiron: 3045m, 2970s, 2941s, 2846m, 2065vs, 1980vs, 1945sh, 1673sh, 1636w, 1442m, 1428w, 1385w, 1362w, 1330m, 1310m, 1256m, 1225w, 1215sh, 1194w, 1168w, 1133w, 1088w, 1044m, 999m, 962w, 956w, 934w, 914w, 890vw, 863m, 847m, 828w, 809m, 776m, 722s, 704s.

Hexacarbonylbi(cyclo-octa-2,4,6-trienyl)di-iron: 2995vs, 2910ms, 2870m, 2040vs, 1980vs, 1965sh, 1640w, 1442m, 1370m, 1322m, 1308m, 1258w, 1220w, 1192m, 1094m, 1058m, 1023m, 956w, 932m, 904w, 872w, 848ms, 832m, 798ms, 705s.

Tricarbonylcyclo-octadienyliron tetrafluoroborate (mull): 3080w, 3030m, 2925w, 2880w, 2840w, 2105vs, 2040vs, 1442m, 1432ms, 1420m, 1333w, 1282w, 1231w, 1199w, 1144w, 1080sh, 1060vs, 1046vs, 1032vs, 950w, 928w, 896w, 872w, 843m, 828w, 776w.

High-resolution Proton Magnetic Resonance Spectra.—Spectra were measured in Pyrex tubes of 5 mm. outside diameter, at 22° ± 2°, on a Varian Associates model 4300B spectrometer at 56·45 Mc./sec. Line positions are given in τ values. The spin–spin decoupling experiment was performed with the apparatus constructed by Turner.[10]

π-Cyclopentadienylbicyclo[2,4,0]*octa-2,4-dienecobalt* (in carbon tetrachloride solution): 4·92, unsymmetrical quadruplet (area 2), " inner " protons of bound diene system; 5·34, sharp singlet (area 5), π-C_5H_5 group; 6·86, incompletely resolved multiplet (area 2), " outer " diene protons, split by " inner " protons and also by the adjacent bridgehead protons; 7·69, complex band (area 2), bridgehead protons, split by adjacent " outer " diene and methylene protons; 8·92, complex doublet (area 4), broad maxima at 8·24 and 9·02, methylene protons, A_2B_2 group with additional splitting from bridgehead protons.

π-Cyclopentadienylcyclo-octa-1,3,5-trienecobalt (in carbon tetrachloride solution): 4·62, sharp band (splitting <1 c./sec.) (area 2), two equivalent protons of " free " olefinic bond. On this assignment the coupling in the group =CH–CH=, *i.e.*, between each proton and the adjacent proton of the bound olefin groups is small. This could occur if the dihedral angle between the C–H bonds is about 80°; models show that this is likely. An example of a small coupling constant which arises in this way is in the π-cyclopentadienylcyclo-octatetraenecobalt and rhodium complexes; [6] 5·45, sharp singlet (area 5), π-C_5H_5 group; 6·46, complex band (area 4), 4 " bonded " olefinic protons, each split by the other proton of the same bond and by the methylene protons; 7·2—8·5, complex band (area 4), with principal maxima at 7·46 and 8·30, methylene protons, A_2B_2 group with additional splitting from the bound olefin protons.

Tricarbonylcyclo-octa-1,3,5-trieneiron (in carbon disulphide solution). 4—5, complex, well-resolved band (area 4), " free " olefinic protons coupled to adjacent " bound " diene proton and methylene protons, and " inner " bound diene protons; 6·51, unsymmetrical triplet (area 1), displaying further splitting, " outer " bound diene proton [H_6] adjacent to methylene protons. The spin–spin decoupling experiment showed that this proton is coupled to the remaining

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[10] Turner, *J.*, 1962, 847.

bound olefinic protons and also to *one* of the adjacent methylene protons on C_7; 6·86, well-resolved unsymmetrical triplet (area 1), " outer " diene proton [H_3] adjacent to double bond, spin–spin decoupling showed this proton to be coupled to the lone olefinic protons [H_1, H_2] but not the methylene protons; 7·9—8·5, complex band (area 4), methylene protons, one (on C_7) coupled to an " outer " diene proton [H_6] and two of them to free olefin protons [H_1, H_2] in addition to being coupled to each other.

*Hexacarbonylbi(cyclo-octa-*2,4,6*-trienyl)di-iron* (in carbon disulphide solution): 4·27, multiplet (area 2), " free " olefinic protons [H_6, H_7]; 4·78, multiplet (area 2), " inner " bound diene protons [H_3, H_4]; 6·81, doublet (area 1), " outer diene " proton not adjacent to " free " double bond [H_2]; 7·04, unsymmetrical triplet (area 1), " outer " diene proton adjacent to " free " double bond [H_5]; 8·45, complex band (area 3), methylene protons.

Tricarbonylcyclo-octadienyliron tetrafluoroborate (in liquid sulphur dioxide): All lines were rather broad. 2·73, triplet (area 1), H_4 coupled to H_3 and H_5; 4·27, multiplet (area 2), H_3 and H_5, each coupled to H_4 and either H_2 or H_6; 5·53, complex band (area 2), H_2 and H_6 coupled to H_3 and H_1 or H_5 and H_7; 7·5—8·5, complex band (area 5), protons on C_1 and C_7 and one proton on C_8; 9·54, quadruplet (area 1), other proton on C_8.

*Hexacarbonylbi(cyclo-octa-*2,4,6*-trienyl)di-iron* (in concentrated sulphuric acid with dimethyl sulphate as internal reference): All lines were broad. 2·71, triplet (area 1), H_4 coupled to H_3 and H_5; 4·27, multiplet (area 2), H_3 and H_5 coupled to H_4 and to either H_2 or H_6; 5·51 and 6·11, pair of overlapping doublets (total area 2), H_2 (coupled to H_1 and H_3) and H_6 (coupled to H_5 and protons on C_7); 7·5—10·0, complex band (total area 5), methylene protons on C_1, C_7, and C_8.

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