The Interaction of Cumulene Systems with Organometallic π-Complexes.

III.[1] Iron Carbonyl Complexes of Hexapentaene and of Tetra- and Dimethylbutatriene*

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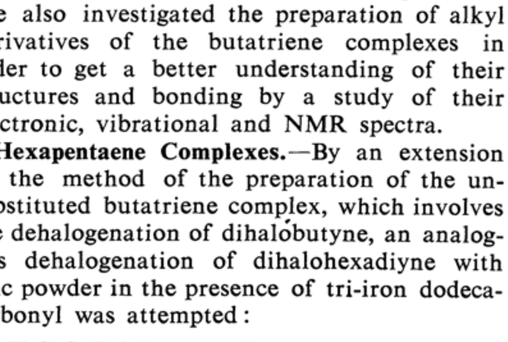
The stabilization of unstable organic compounds by the formation of organometallic π-complexes has provided a base for the occurrence of such unstable reaction intermediate species as cyclobutadiene.[2] We have reported the formation of a very stable tetraphenylcyclobutadiene complex of cobalt by the reaction of diphenylacetylene with some organocobalt compounds. In continuation of our study of the stabilization of unstable organic compounds by π-complex formation, we have found that the unsubstituted butatriene, a very unstable compound, can be stabilized by the formation of a stable iron carbonyl complex, $C_4H_4Fe_2(CO)_5$.[3] A brief communication describing the preparation of a tetraphenylbutatriene complex of iron carbonyl has also been published.[4] Unsubstituted hexapentaene, one of the unknown higher homologues of the butatriene, seems to be much more unstable than the unsubstituted butatriene. The successful isolation of the butatriene iron carbonyl complex led us to investigate the corresponding iron carbonyl complexes of the hexapentaene. We also investigated the preparation of alkyl derivatives of the butatriene complexes in order to get a better understanding of their structures and bonding by a study of their electronic, vibrational and NMR spectra.

Hexapentaene Complexes.—By an extension of the method of the preparation of the unsubstituted butatriene complex, which involves the dehalogenation of dihalobutyne, an analogous dehalogenation of dihalohexadiyne with zinc powder in the presence of tri-iron dodecacarbonyl was attempted:



$$\underset{\substack{|\\X}}{H_2C}-C\equiv C-\underset{\substack{|\\X}}{CH_2} + Fe_3(CO)_{12} + Zn \rightarrow (H_2C=C=C=CH_2)Fe_2(CO)_5$$

$$\underset{\substack{|\\X}}{H_2C}-C\equiv C-C\equiv C-\underset{\substack{|\\X}}{CH_2} + Fe_3(CO)_{12} + Zn \rightarrow (H_2C=C=C=C=C=CH_2)Fe_3(CO)_{7-8}$$

Thus, 1,6-dichlorohexadiyne was treated with an excess of zinc powder and tri-iron dodecacarbonyl in refluxing benzene. A vigorous gas evolution was observed during the reaction. From the reaction mixture, the product was purified by chromatography, followed by crystallization, to give deep purple-red crystals. The main difficulty in obtaining the product was its exceedingly small yield (1.2%) and the separation from the remaining tri-iron dodecacarbonyl. The product I was found to have the composition: $C_6H_4Fe_3(CO)_{7-8}$.

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[1] For previous paper of this series, A. Nakamura, P.-J. Kim and N. Hagihara, *J. Organometal. Chem.*, 3, (1965) in press.

[2] For review article, see, E. O. Fischer and H. Werner, *Angew. Chem.*, 75, 64 (1963). For the cyclobutadiene-cobalt complex, see, A. Nakamura and N. Hagihara, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **84**, 339 (1963); This Bulletin, **34**, 452 (1961).

[3] A. Nakamura, P.-J. Kim and N. Hagihara, *J. Organometal. Chem.*, **3**, 7 (1965).

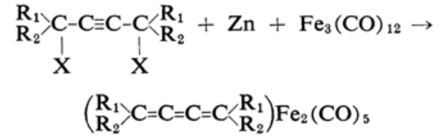
[4] A. Nakamura, P.-J. Kim and N. Hagihara, This Bulletin, **37**, 292 (1964).

The number of carbonyl groups in the complex is rather ambiguous considering the accuracy of the elemental analysis. Moreover, the molecular weight of I is not very accurate as a result of its slight solubility in many organic solvents. The infrared spectrum of I was found to have very strong carbonyl bands at 2088, 2065, 2045 and 2005 cm^{-1}, thus indicating some similarity with that of the corresponding butatriene complex. The electronic spectrum of I had its maximum at 567 mμ. The position of this maximum is, significantly, at a longer wavelength than that of the butatriene complex. The NMR spectrum was very similar to that of the butatriene complex in that it showed two signals at 5.20 and 5.71 τ, although the very low solubility of I prevented the obtaining of a well-resolved spectrum. Therefore, no splitting of the signals were observed.

The most interesting property of I is its thermal and air stability. For example, it is stable up to 250°C in nitrogen, stable in air as crystals, and also stable as a solution in carbon tetrachloride. Since unsubstituted butatriene has been reported[5] to be stable only at very low temperatures in nitrogen, unsubstituted hexapentaene, if prepared, will probably be much more unstable than the butatriene. Hence, the preparation of unsubstituted hexapentaene has not been reported to date and a comparison of the stability of the free and the complexed hexapentaene is impossible. However, the stabilization of the hexapentaene by means of the π-complex formation is apparent; it is another example of such stabilization.

In order to furnish further evidence for the presence of a hexapentaene system in the complex, tetraphenylhexapentaene was reacted with iron pentacarbonyl and with tri-iron dodecacarbonyl. A very deep brown solid II was obtained; it was stable in air. However, it was very difficult to obtain the product in a crystalline state, and attempts to purify it by chromatography on activated or deactivated alumina resulted in decomposition in the column. The infrared spectrum of II showed a similarity with that of I in the absorption pattern of the terminal metal carbonyl-stretching region (maxima at 2071, 2036, 2009 and 2001 cm^{-1}). The absence of an uncomplexed tetraphenylhexapentaene system in the product was shown by the absence of any maxima in the visible region. The structures of these hexapentaene complexes are difficult to infer, but they are probably similar to those of the butatriene complexes described below. Attempts to prepare analogous hexapentaene complexes of cobalt and chromium have all failed. Now, however, it may be said with considerable certainty that the interaction of cumulene systems with iron carbonyls is great enough to give stable π-complexes generally.

1, 1, 4, 4-Tetramethyl- and 1, 4-Dimethylbutatriene Iron Carbonyl Complexes.—Unsubstituted butatriene and tetraphenylbutatriene complexes of iron carbonyl have already been prepared and described in detail in a previous paper of this series.[3] We have here attempted to prepare methyl-substituted analogues by the application of the dehalogenation method to methyl-substituted dihalobutynes. The preparation of the methyl analogues will allow us to compare the electronic and vibrational spectra of the complexes and will give us very interesting NMR spectra, which might in turn lead to the determination of the correct structure of the complexes. 2, 5-Dichlorohexyne-3 (1, 4-dimethyl-1, 4-dichlorobutyne-2) was reacted with an excess of zinc powder in the presence of tri-iron dodecacarbonyl in just the same way as in the preparation of butatriene di-iron pentacarbonyl (III). A reddish-orange, air-stable crystalline compound IV was obtained in a 4.1% yield (based on the iron carbonyl used). It was very similar to the butatriene complex III in appearance, solubility, volatility and stability. The close similarity to III in its infrared metal carbonyl-stretching absorption pattern and also in its electronic spectrum, together with the elemental analysis and molecular weight data, showed it to be a dimethyl derivative of III.



$$\mathrm{{}^{R_1}_{R_2}\!\!>\!\underset{|\atop X}{C}\text{-}C{\equiv}C\text{-}\underset{|\atop X}{C}\!<\!{}^{R_1}_{R_2} + Zn + Fe_3(CO)_{12} \rightarrow}$$

$$\mathrm{\left({}^{R_1}_{R_2}\!\!>\!C{=}C{=}C{=}C\!<\!{}^{R_1}_{R_2}\right)Fe_2(CO)_5}$$

III : $R_1=R_2=H$, $X=Br$
IV : $R_1=H$, $R_2=CH_3$, $X=Cl$
V : $R_1=R_2=CH_3$, $X=Cl$

2, 5-Dichloro-2, 5-dimethylhexyne-3(1, 1, 4, 4-tetramethyl-1, 4-dichlorobutyne-2) was used to prepare an analogous tetramethyl derivative in the same way. The reddish-orange, air-stable compound V obtained in this way, in a 4.4% yield, was also very similar to III and IV in many ways. Apart from the similarity in the infrared and electronic spectra of these compounds, their NMR spectra provided the confirmation of IV and V as, respectively, di- and tetramethyl derivatives of III.

Discussion

The method of preparation, the yield and various physical constants of the cumulene

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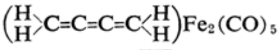
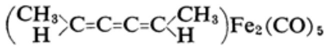
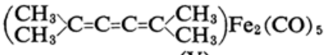
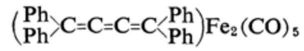
[5] W. M. Schubert, T. H. Liddicoet and W. A. Lanka, *J. Am. Chem. Soc.*, 76, 1929 (1954).

TABLE I

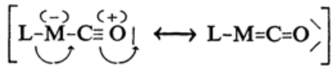
	 $\left(\substack{H\\H}\!>\!C=C=C=C\!<\!\substack{H\\H}\right)Fe_2(CO)_5$ (III)	 $\left(\substack{CH_3\\H}\!>\!C=C=C=C\!<\!\substack{CH_3\\H}\right)Fe_2(CO)_5$ (IV)
Method of preparation	Dehalogenation	Dehalogenation
Color	Red-orange	Red-orange
Yield, %	16.7	4.1
M. p. °C	69—70 (air)	104 (air)
Decomposition (°C)	230 (air)	240—250 (N$_2$)
Sublimation temp., °C/mmHg	40—50/3	80/3
Infrared, νC≡O, cm^{-1}	2090 2052 2022/1995 1963	2088 2051 2020 1958
Visible and ultraviolet, mμ, (log ε)*1	448 (3.356) 346 (3.734) 286 sh	452 (3.303) 342 (3.728) 298 (3.83)
NMR, τ	5.22 (d)*2 1*3 5.85 (d) 1	8.17 (d) 3 4.42 (q) 1
Coupling constant	J=1.5 c. p. s.	J=6.0 c. p. s.

	 $\left(\substack{CH_3\\CH_3}\!>\!C=C=C=C\!<\!\substack{CH_3\\CH_3}\right)Fe_2(CO)_5$ (V)	 $\left(\substack{Ph\\Ph}\!>\!C=C=C=C\!<\!\substack{Ph\\Ph}\right)Fe_2(CO)_5$ (VI)
Method of preparation	Dehalogenation	Direct reaction
Color	Red-orange	Red
Yield, %	4.4	26
M. p. °C	118 (N$_2$)	Decomp.
Decomposition (°C)	240—250 (N$_2$)	200 (air)
Sublimation temp., °C/mmHg	90—100/3	180/3 (decomp.)
Infrared, νC≡O, cm^{-1}	2087 2039 2010 1953	2072 2035 1998 1988
Visible and ultraviolet, mμ, (log ε)*1	470 (3.299) 340 sh 299 (3.86)	No maximum
NMR, τ	7.81 (s) 1 7.98 (s) 1	—
Coupling constant	—	—

*1 Measured in ethanol *2 s : singlet, d : doublet, q : quartet. *3 ratio of area

complexes prepared by us are listed in Table I. The successful preparation of the di- and tetramethyl derivatives of III showed that the preparation of such derivatives is possible by the same dehalogenation route and that the alkyl derivatives have a stability similar to that of the unsubstituted compound III. The preparation of the tetraphenyl derivative VI, as has been reported previously, also shows that the tetra-aryl derivatives will be similarly stable and can be prepared by the direct route in good yields.

A comparison of the infrared spectra of butatriene complexes, III—VI, also seems of interest. A small but significant lowering of the metal carbonyl-stretching frequency in the III to VI series is apparent. This lowering is obviously caused by the introduction of the substituents into the butatriene system. A lowering of the metal carbonyl-stretching frequency has been attributed to the increase in electron density around the metal atom,⁶⁾ because such an increase results in the enhanced contribution of the resonance species of M=C=O, as is shown below:



$$\left[L-\overset{(-)}{M}-C\equiv\overset{(+)}{O}| \longleftrightarrow L-M=C=O\rangle \right]$$

It is conceivable that, in the case of the substituted butatriene complexes, electron-donating methyl groups on the butatriene part push the electron to the iron atom through the butatriene part and cause the lowering of the metal carbonyl-stretching frequency. Phenyl groups are known to have an electron-attracting inductive effect, but they are also known to have an electron-releasing resonance polar effect. The tetraphenylbutatriene complex VI has the lowest metal carbonyl-stretching

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6) R. D. Fischer, *Chem. Ber.*, **93**, 165 (1960); E. O. Fischer and H. Werner, *Angew. Chem.*, **75**, 60 (1963).

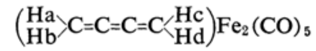
frequency among the butatriene complexes prepared heretofore. Therefore, the electron-releasing resonance polar effect may be operating here. The complexes, III—VI, resemble each other in metal carbonyl-stretching pattern so closely that only difference in the frequency distinguish them.

The electronic spectra of the butatriene compounds are also very similar. Here again, only small differences in the position of the absorption maxima are observed. The longest wavelength maxima of these complexes shift towards even longer wavelengths upon the successive introduction of methyl groups. The introduction of two methyl groups shifts the maximum by 4 mμ, and that of four methyl groups, by 22 mμ. This shifts reminds us of the mell-known Woodward rule,[7] which states that the introduction of one methyl group into the conjugated diene system results in a shift of 5 mμ in the K-band.

The NMR spectrum of III has already been discussed in the previous paper. No definite conlusion concerning the structure of III was there obtained, however. The spectrum indicated that two kinds of protons are present and that the coupling constant of the two protons is small (ca. 1.5 c. p. s.). As expected, two kinds of methyl signals were observed in the NMR spectrum of the tetramethyl derivative V. The difference in the chemical shift (0.17 p. p. m.) between the methyl signals is significantly smaller than that between the two proton signals of III (0.63 p. p. m.). In the NMR spectrum of the corresponding dimethyl derivative IV, only one methyl signal is observed; it is split into a doublet by an adjacent olefinic proton. The olefinic proton signal is split into a symmetrical quartet (ratio of areas: 1 : 3 : 3 : 1) by the adjacent methyl group. The coupling constant between these methyl and olefinic protons was, as expected, found to be 6.0 c. p. s. These results show that the two methyl groups are equivalent, and so are the two olefinic protons.

From an examination of the NMR spectra of these three compounds, III—V, the following conclusions can be drawn:

i) The Ha and Hb protons (also Hc and Hd) are not equivalent.



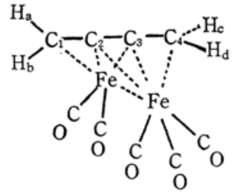
$$\left(\begin{matrix}Ha\\Hb\end{matrix}\!\!>\!C{=}C{=}C{=}C\!<\!\!\begin{matrix}Hc\\Hd\end{matrix}\right)Fe_2(CO)_5$$

(III)

ii) The splitting observed in the spectrum of III probably arises from the geminal coupling between Ha and Hb.

iii) No appreciable long-range coupling is observed between the terminal protons of III.

A planar structure of the butatriene part and a symmetrical attachment of the iron carbonyl groups do not easily explain the difference between Ha and Hb. A twisted structure, as shown below, explains the observed NMR spectrum more easily than the other possible



structures. In the twisted structure, the two terminal protons are not equivalent because of the unsymmetrical attachment of the two iron carbonyl groups, $Fe(CO)_3$ and $Fe(CO)_2$. However, a repeated intramolecular transfer of one of the CO groups from the iron tricarbonyl group to the iron dicarbonyl group would make the two terminal protons equivalent. The Ha and Hb protons are made non-equivalent by the attachment of the iron carbonyl group on one side of the plane defined by Hc–C_4–Hd. Therefore, Hb and Hd may be expected to be nearer to the iron carbonyl groups than Ha and Hc. The difference in the environment will make the protons, Ha and Hb, non-equivalent. For the tetramethyl compound V, the situation is quite similar, and two methyl signals are observed. In the dimethyl compound IV, the two methyl groups probably occupy the positions of Ha and Hc because of the bulkiness of the methyl group, and they remain equivalent.

The NMR results obtained so far can be explained, as above, on the assumption of a straight C4 chain, but there is no clear indication of the straightness of the C4 chain. Actually, it might well be a bent structure. The NMR results are not very sensitive to such a deformation, and, unfortunately, they do not definitely establish the correct structure for the butatriene complexes. Therefore, an X-ray structure analysis of these complexes is necessary in order to establish the correct structure.*

Experimental

All melting points are uncorrected; they were measured by a micro-melting point apparatus, Yanagimoto Model MP-S2. The melting points and decomposition points in nitrogen were measured in a sealed capillary filled with nitrogen. The infrared spectra were obtained by Hitachi Model EPI-2

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[7] R. B. Woodward, *J. Am. Chem. Soc.*, **64**, 72 (1942).

* A private communication from Professor O. S. Mills told us that he and his co-workers were carrying out an X-ray analysis of the tetraphenyl butatriene iron carbonyl complex.

and Jasco Model DS-402G grating spectrophotometers. The visible and ultraviolet spectra were taken by a Beckman DK-2 spectrophotometer. The NMR spectra were recorded by a Varian Model A-60 instrument using tetramethylsilane as an internal standard in carbon tetrachloride. The alumina used for the chromatography had an activity grade of I and was of a 200—300 mesh size. The elemental analysis was performed by Mr. T. Shibano of this Institute. The elemental analysis for oxygen was performed by Mr. I. Shimidzu of the Japan Synthetic Rubber Company. The molecular weights were measured in a benzene solution using a Mechrolab Vapor Pressure Osmometer Model 301A.

Materials.—Dichloro- and dibromohexadiyne-2, 4,[8] 2, 5-dichlorohexyne-3,[9] 2, 5-dimethyl-2, 5-dichlorohexyne-3,[10] tetraphenylhexapentaene,[11] butatriene di-iron pentacarbonyl[3] and tetraphenylbutatriene di-iron pentacarbonyl[3] were prepared in manners described in the literature.

The Preparation of the Hexapentaene Iron Carbonyl Complex (I).—A mixture of 3.0 g. of freshly prepared and distilled dichlorohexadiyne-2, 4, 4.2 g. of tri-iron dodecacarbonyl, 5.0 g. of zinc powder in 25 ml. of isooctane and 20 ml. of benzene was heated, with vigorous magnetic stirring, under nitrogen for 4 hr. at 80—90°C. During the reaction period, a total of about 1250 ml. of a gas evolved. The deep green solution was then filtered by gravity in air, and the brown precipitates were washed well with benzene. The evaporation of the filtrate and the wash gave almost black crystalline solids, which were then dissolved again in benzene and purified by chromatography on alumina. Elution with benzene gave a deep purple-red eluate. (A considerable decomposition of the product was observed when the elution was carried out with *n*-hexane.) The evaporation of the eluate gave almost black crystals (0.1 g.), which were purified further by crystallization from benzene (5 ml.) to give deep purple-red crystals (45 mg.) (I). The insoluble part in benzene consists mainly of tri-iron dodecacarbonyl

Found: C, 35.73; H, 1.19; O, 30.05±3%; mol. wt., 500—700. Calcd. for $C_{14}H_4Fe_3O_8$: C, 35.94; H, 0.87; O, 27.36%; mol. wt. 467.6.

The Preparation of the Tetraphenylhexapentaene Iron Carbonyl Complex (II).—Tetraphenylhexapentaene was reacted with an excess of iron pentacarbonyl in *p*-xylene for 3.5 hr. under nitrogen. The color turned deep brown upon heating at 140°C. The reaction mixture was then evaporated under reduced pressure to give a deep-reddish-brown semisolid (II), m. p. (decomp.) ca. 220°C in air. This semisolid did not crystallize from the solution in benzene or in a *n*-hexane-benzene mixture. A similar reaction using tri-iron dodecacarbonyl in benzene at 90°C for 3 hr. gave similar results.

Tetramethylbutatriene Di-iron Pentacarbonyl (V).—A mixture of 1.2 g. of freshly distilled 2, 5-dimethyl-2, 5-dichlorohexyne-3, 2.2 g. of tri-iron dodecacarbonyl and 3.0 g. of zinc powder in 20 ml. of dry isooctane was stirred magnetically under nitrogen and heated at 90—100°C on a water bath. During the 3 hr. of the reaction, the evolution of a gas continued. After 150 ml. of the gas had evolved, however, the evolution almost stopped. The brownish suspension was filtered by gravity in air, and the precipitates were washed with a small amount of benzene. The deep brown filtrate was then evaporated under reduced pressure at room temperature to give a deep brown semisolid.

The semisolid was then dissolved in a small amount of *n*-hexane and chromatographed on alumina. Elution with *n*-hexane gave a deep red eluate, which in turn gave a red viscous oil upon evaporation under reduced pressure. Most of the oil crystallized when the mixture was chilled to −20°C in a refrigerator overnight. The red crystals (52 mg.) (V) were collected on a clay plate and washed well with a small amount of *n*-hexane. The crystals were purified further by sublimation at 80°C/3 mmHg to afford an analytical sample. A further crop (12 mg.) of the crystals could be obtained from the oily part of the eluate through fractional sublimation and through drying on a clay plate.

Found: C, 43.56; H, 3.35; mol. wt., 357. Calcd. for $C_{13}H_{12}Fe_2O_5$: C, 43.38; H, 3.36%; mol. wt., 360.

Dimethylbutatriene Di-iron Pentacarbonyl (IV).—The title compound IV was obtained by essentially the same method as that described for the tetramethyl compound V, using 0.9 g. of 2, 5-dichlorohexyne-3, 2.0 g. of tri-iron dodecacarbonyl and 3.0 g. of zinc powder in 20 ml. of isooctane. The analytical sample (31 ml.) was obtained from 38 mg. of the crude product by sublimation. A further crop (16 mg.) was obtainable by working up the oily part in the manner described above for V.

Found: C, 40.22; H, 2.33; O, 23.04; mol. wt., 360. Calcd. for $C_{11}H_8Fe_2O_5$: C, 39.85; H, 2.43; O, 24.10%; mol. wt., 332.

Summary

The reaction of 1, 6-dihalohexadiyne-2, 4 with tri-iron dodecacarbonyl in the presence of an excess of zinc powder have given a hexapentaene iron carbonyl complex, $C_6H_4Fe_3(CO)_{7-8}$, as deep purple-red, air-stable crystals in a 1.2% yield. Essentially the same reaction using methyl-substituted 1, 4-dichlorobutyne-2 have given substituted butatriene iron carbonyl complexes, $(R_1R_2C{=}C{=}C{=}CR_1R_2)Fe_2(CO)_5$, where $R_1=R_2=CH_3$ (V), $R_1=H$, and $R_2=CH_3$ (IV), in low yields. The vibrational, electronic and NMR spectra of these new complexes have been discussed in connection with their structures.

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[8] J. B. Armitage and M. C. Whiting, *J. Chem. Soc.*, **1952**, 2005.

[9] C. L. Cook, E. R. H. Jones and M. C. Whiting, ibid., **1952**, 2883; R. Ya. Levina and Yu. S. Shabarov, *Doklady Acad. Nauk. SSSR.*, **84**, 709 (1952); *Chem. Abstr.*, **47**, 3219 (1953).

[10] W. Reppe, *Ann.*, **596**, 25 (1955); A. I. Zhakharova and G. D. Ilina, *Zhur. Obshchei. Khim.*, **24**, 2144 (1954).

[11] H. D. Hartzler, *J. Am. Chem. Soc.*, **83**, 4996 (1961).

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