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The Interaction of Cumulene Systems with Organometallic π-Complexes. IV.[1] Novel π-Allyl Complexes Obtained from the Reactions of Allene with Iron and Cobalt Carbonyls

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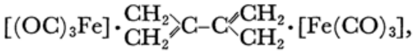
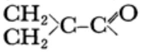
2, 2′-Bi-π-allylene(hexacarbonyl)di-iron,  $[(OC)_3Fe]\cdot\begin{matrix}CH_2\\CH_2\end{matrix}\!\!>C-C<\!\!\begin{matrix}CH_2\\CH_2\end{matrix}\cdot[Fe(CO)_3]$, was found to be a product of the reaction of allene with $Fe_3(CO)_{12}$. A study of the NMR spectrum, however, showed that a rapid valence tautomerisation takes place, even at −10°C between the 2, 2′-bi-π-allylene structure and the related butadiene-type structure. In the presence of an excess of $Co_2(CO)_8$, allene yielded the $[(C_3H_4)Co(CO)_3]_2$ complex. The structure of this complex in which a  $\begin{matrix}CH_2\\CH_2\end{matrix}\!\!>C-C<^{O}$ skeleton was bound to two $Co(CO)_2$ groups via π-allyl and acyl groups, was suggested.

In a previous paper,²⁾ we have described the interaction of cumulene systems with organometallic π-complexes such as iron carbonyls to give a variety of stable π-complexes. As the first member of the cumulene system, allenic systems were examined for their ability to form π-complexes. Tetraphenylallene gave a stable iron tricarbonyl complex, $(Ph_4C_3)Fe(CO)_3$ and a cobalt complex, $(C_5H_5)Co(CO)(Ph_4C_3)$. Unsubstituted allene gave complexes of the compositions $[(C_3H_4)Fe(CO)_3]_2$ (I) and $[(C_3H_4)_2Fe(CO)_3]_{1-2}$. The structure of these complexes was not, however, clear. In this report, an investigation of the structure of the complex I will be described. A novel complex obtained from the reaction of allene with dicobalt octacarbonyl will also be reported.

Results and Discussion

The reaction of unsubstituted allene with tri-iron dodecacarbonyl at 120°C under pressure has been described in the previous paper.²⁾ The same reaction at atmospheric pressure in *n*-hexane, using an excess of tri-iron dodecacarbonyl gave a similar product, except that in this case the amount of the complex I increased and a new red compound was isolated in a small amount. When iron pentacarbonyl was used under the pressure of carbon monoxide at 140°C, no reaction was observed. In order to get a clue about the skeletal structure of the complexed organic part of complex I, the bromination of complex I was studied.[*2] It gave colorless crystals upon bromination at room temperature. The crystal exhibited a reaction typical of allylic bromide, but it did not add another molecule of bromine. The presence of a double bond was shown by the permanganate test. The infrared spectrum of the crystals was found to be superimposable upon that of the authentic 2, 3-bis(bromomethyl)-1, 4-dibromobutene-2 prepared by the literature method.³⁾ If no coupling

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1) For the previous paper of this series, cf. A. Nakamura, This Bulletin, **38**, 1868 (1965).

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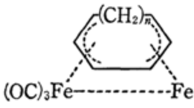
2) A. Nakamura, P.-J. Kim and N. Hagihara, *J. Organometal. Chem.*, **3**, 7 (1965).

[*2] The preliminary results of the study have already been reported; cf. A. Nakamura and N. Hagihara, *J. Organometal. Chem.*, **3**, 480 (1965).

3) A. C. Cope and F. Kagan, *J. Am. Chem. Soc.*, **80**, 5499 (1958).

of the C_3H_4 moiety occurs during the bromination, the structure of the bromination product suggests that the skeletal structure of the organic part is $\substack{C\\C}{>}C{-}C{<}\substack{C\\C}$. Therefore, the 2, 2-bi-π-allylene structure may be present in I.[*3] The infrared spectrum of I had strong maxima at 2068, 2030, 2003 and 1990 cm^{-1}, indicating the presence of terminal metal carbonyl groups. The infrared spectrum as a whole supported the π-allyl type structure. Recently, Emmerson et al.4) reported the preparation of cyclic bi-π-allylene type iron carbonyl complexes such as are shown below.



$n=1, 2$

These complexes can be regarded as derivatives of unknown 1, 1′-bi-π-allylene(hexacarbonyl)diiron. 2, 2′-Bis-π-allylenemetal complexes also have been unknown. If one assumes the 2, 2′-bi-π-allylene structure for I, the NMR spectrum would have two singlets, with a separation of ca. 1. p.p.m., corresponding to the syn and anti protons of the π-allylic group. The actual NMR spectrum in carbon tetrachloride at 35°C had two peaks, separated by only 0.07 p.p.m. and centered at 8.34 τ. The separation became smaller when the temperature was lowered, until finally the two peaks condensed into a sharp singlet at −10°C. This NMR behavior can be understood on the assumption that the following valence tautomerism occurs rapidly, even at −10°C in the solution. This rapid tautomerism averages out all the protons, and the NMR spectrum will have a single peak. The τ-value can be calculated approximately as follows on the assumption of this tautomerism. The calculation, which involves averaging out all the τ-values5) of the terminal protons of butadiene-(tricarbonyl)iron and the hypothetical τ-values for π-allyl(tricarbonyl)iron, results in a value of 8.35 τ. π-Allyl(tricarbonyl)iron is reported to be paramagnetic in a solution, and the NMR spectrum can not be obtained.6) The hypothetical τ-value was calculated by averaging the known τ-values of the terminal protons in π-allyl(tetracarbonyl)-manganese and in π-allyl(tricarbonyl)cobalt.7) At much lower temperature, e. g., at −55°C in chloroform, the compound I showed three broad signals centered at about 8.3 τ; these may correspond to the tautomers slowly exchanging at the temperature. At higher temperatures, such as at 65°C, two peaks are observed. However, the oxidative degradation of the compounds I was occurring during the measurement by the solvent, carbon tetrachloride, and no satisfactorily accurate result could be obtained. These two NMR peaks at higher temperatures appeared to us to arise from the π-allylic tautomer (A). This fact suggests that the π-allylic form might be predominant at higher temperatures. The possible intervention of the π-allylic complex at higher temperatures has already been suggested in the deuterium exchange study8) of polymethylcyclopentanes using such metal catalysts as palladium. Therefore, the predominance of the π-allylic form at higher temperatures is not unreasonable.

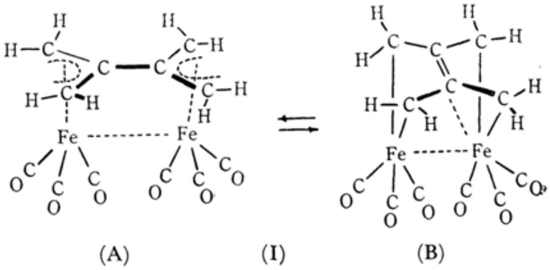


Fig. 1

Rapid valence tautomerism has been postulated in the interpretation of the NMR spectra of some cyclic polyene-metal carbonyl complexes. For example, cyclooctatetraene(tricarbonyl)iron has only one sharp NMR signal.9) This NMR behavior was once taken as evidence for the planar structure and aromaticity of the cyclooctatetraene ring on π-complex formation.9a) X-ray structure analysis10) of the compound, however, has shown that the ring is not planar in the crystalline state. The appearance of only one NMR signal has been understood as due to rapid valence tautomerism in the solution. More recently, two other similar examples11) have been added to this type of tautomerism. It is of interest to regard compound I as the first example of rapid tautomerism occurring in the chain structure. Valence tautomerism now

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[*3] The author at first called this system "2, 2′-bis-π-allyl" to indicate two π-allyl systems connected at the center carbon atoms. However, it was later recommended that the system be called "2, 2′-bi-π-allylene" because of its bifunctional character. A confusion may indeed arise because allylene is a common name for 1-propyne. The author nevertheless prefers to use the latter nomenclature for the system, as he used it in the preliminary note.

4) G. F. Emmerson, J. E. Mahler, R. Pettit and R. Collins, ibid., **86**, 3590 (1964).

5) M. L. H. Green, L. Pratt and G. Wilkinson, *J. Chem. Soc.*, **1959**, 3753.

6) H. D. Murdoch and E. A. C. Lucken, *Helv. Chim. Acta*, **47**, 1517 (1964).

7) W. R. McClellan, H. H. Hoehn, H. N. Cripps, E. L. Muetterties and B. W. Howk, *J. Am. Chem. Soc.*, **83**, 1601 (1961).

8) J. J. Rooney and G. Webb. *J. Catalysis*, **3**, 488 (1964) and references therein.

9) a) T. A. Manuel and F. G. A. Stone, *Proc. Chem. Soc.*, **1959**, 90 (1959); b) M. D. Rausch and G. N. Schrauzer, *Chem. & Ind.*, **1959**, 957; c) A. Nakamura and N. Hagihara, This Bulletin, **32**, 880 (1959).

10) W. N. Lipscomb and B. Dickens, *J. Am. Chem. Soc.*, **83**, 4862 (1961).

11) a) R. B. King, *Inorg. Chem.*, **3**, 785 (1964); b) R. Pettit, J. E. Mahler and D. A. K. Jones, *J. Am. Chem. Soc.*, **86**, 3589 (1964).

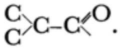
seems to be possible not only in the cyclic polyene ligand, but also in the chain structure.

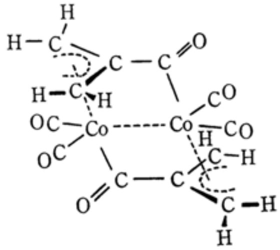
Our investigation suggests that a comparison of the thermodynamic stability between the π-allylic form (A) and the π-complexed butadiene form (B) is possible by means of the measurement of the NMR spectrum.

The 2, 2′-bi-π-allylene structure may yield compounds with many other transition metals, and other interesting properties may be found. We therefore intend to explore the chemistry of 2, 2′-bi-π-allylene complexes and related compounds further.

The Allene Complex of Cobalt Carbonyl.—The polymerization of allenic compounds by dicobalt octacarbonyl at room temperature was first reported by Greenfield et al.[12] The presence of metal carbonyl stretching bands in the infrared spectrum of the polymer attracted our interest. So far, only the formation of rather unstable diene-cobalt carbonyl complexes has been reported. However, the considerable stability of the metal carbonyl species in the allene polymer prepared by means of the cobalt carbonyl catalyst suggests the possibility of the formation of a stable allene complex of cobalt carbonyl. Thus, allene was slowly bubbled into a solution of dicobalt octacarbonyl in benzene at room temperature. A slight change in color to reddish brown and an evolution of heat was observed.

The sublimation of the reaction mixture gave air-sensitive yellow and black crystals. The black crystals were identified as tetracoblat dodecacarbonyl by means of their infrared spectrum. The yellow crystals were further purified and found to have the composition: $[(C_3H_4)Co(CO)_3]_2$ (II). A well-crystallized pure sample was stable in air for a few days, but the solution in organic solvents was unstable. Decomposition usually begins after the solution has stood in air at room temperature for about 10 min. The infrared spectrum showed two very strong bands at 2050 and 2010 cm^{-1}, indicating the presence of terminal metal carbonyl groups. The presence of a strong band at 1620 cm^{-1} suggests the presence of a keto carbonyl with an unusually low stretching frequency. This keto carbonyl may be of the acyl cobalt type. The NMR spectrum in carbon tetrachloride showed two singlets, at 6.39 and 7.72 τ, of equal intensity. The position of the peaks may be well accounted for by assuming the presence of a π-allyl group with an electro-negative group at the 2-position. For example, π-allyl cobalt tricarbonyl shows its NMR peak at 6.93 and 7.85 τ.[7] The peak at 6.93 τ has been assigned to the syn proton and the one at 7.85 τ, to the anti protons. The chemical shifts of the syn and anti protons in the known π-allyl cobalt tricarbonyl are, therefore, similar to those observed for the complex, except for the presence of a shift towards a lower field, which is probably due to an electron-withdrawing substituent at the 2-position.

The structure of the complex was investigated by bromination. The action of bromine at room temperature in carbon tetrachloride evolved 4 mol. of carbon monoxide. The composition of the complex indicates that six carbon monoxide groups are incorporated into the structure. Therefore, two carbon monoxide groups are bound to the organic part, and four such groups are present as terminal metal carbonyl groups. The bromination product was a complicated one. It contained an acid bromide of an unknown structure and other materials. The bromination in methanol at about 15°C gave a colorless crystals in a good yield. The elemental analysis and the molecular weight measurement, together with the infrared evidence, favor a diketone structure: $(\mathrm{BrCH_2})_2\text{-}\underset{\mathrm{Br}}{\mathrm{C}}\text{–CO–CO–}\underset{\mathrm{Br}}{\mathrm{C}}(\mathrm{BrCH_2})_2$. The bromination in methanol at higher temperatures resulted in a reduced yield of the diketone and in a mixture of bromoesters. The bromination product suggests that the skeletal structure of the organic part is  ${}^{\mathrm{C}}_{\mathrm{C}}{>}\mathrm{C}\text{–}\mathrm{C}{<}^{\mathrm{O}}$. In addition, the presence of an acyl cobalt linkage is indicated by the isolation of an acid bromide, and also by the infrared band of II at 1620 cm^{-1}. The accumulated evidence suggests the following π-allyl-acyl cobalt carbonyl structure for the complex.



(II)

Fig. 2

A dimeric structure with a Co–Co bond, as indicated by its molecular weight, is necessary in explaining the diamagnetism of the compound. An alternative structure, in which one cobalt atom is bound to the π-allyl and the acyl groups simultaneously, is possible. However, this structure might allow dissociation in the solution, as in the case of the π-allyl-(tricarbonyl)iron dimer.[6] The considerable stability of the complex in solution and its diamagnetism in carbon tetrachloride makes the latter structural possibility less probable.

The reaction of II with triphenylphosphine occurred readily when the solution of the reactants was warmed in benzene; orange air-stable crystals

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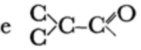
[12] a) H. Greenfield and I. Wender and J. H. Wotiz, *J. Org. Chem.*, **21**, 875 (1956); b) I. W. Stolz, G. R. Dobson and R. K. Sheline, *Inorg. Chem.*, **2**, 1264 (1963).

were thus obtained. The crystals have strong infrared bands at 2002 cm^{-1} and at 1964 cm^{-1} and its NMR peaks mainly in the phenyl proton range. The composition was nearly $(C_3H_4)_2$-$Co_2(CO)_2(Ph_3P)_3$. The structure of the phosphine derivative is not clear at present.

The isolation of the iron and cobalt compounds is closely connected with the known polymerization[13] and carbonylation[14] of allene by organometallic catalysts. The π-allylic iron carbonyl compound (I) can be regarded as the stabilized form of the initiation step of the allene polymerization. The importance of π-allyl complexes of nickel and cobalt in the polymerization of butadiene and allene has already been shown.[13] In the reaction with allene, iron(0) in the iron carbonyl group ($Fe(CO)_3$) forms a stable complex, as has been described above, whereas nickel(0) does not. Possibly for this reason, nickel(0) complexes polymerize allene to a 1, 2-polymer with a very regular structure at room temperature.[13] The isolation of a stable complex of cobalt carbonyl with the  skeletal structure shows that this form might be the stabilized initial step of the carbonylation of allene. The catalytic carbonylation[14] of allene has been reported using a ruthenium(II) or a platinous chloride-stannic chloride system. In all cases, carbon monoxide adds to the central carbon atom of the allene system. The close similarity of the structure shows that the carbonylation of allene may be possible by means of a cobalt carbonyl catalyst.

The Interaction of Allene with Other Metal π-Complexes.—The interaction of allene with molybdenum hexacarbonyl with ultraviolet irradiation formed an orange solution under nitrogen. The attempt to isolate the allene complex failed, however, because of its instability. The orange complex may be stable only in the solution. We regard it as similar to the unstable olefin and acetylene complexes reported by Sheline et al.[12] No reaction of allene was observed in the thermal reaction with molybdenum hexacarbonyl at 70°C at atmospheric pressure or with dimanganese decacarbonyl at 150—160°C under pressure. No stable π-complexes have been isolated from the photochemical reaction of allene with cyclopentadienyl vanadium tetracarbonyl or with cyclopentadienyl manganese tricarbonyl. The polymerization of allene was observed, in the thermal reaction with nickelocene at 150—200°C to give a polymer with an irregular structure, together with a small amount of an unstable red compound. Tetraphenylallene was recovered unchanged in the reaction with nickelocene at 140°C.

Experimental

All melting points are uncorrected and 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 a Hitachi Model EPI-2 and a Jasco Model DS-402G grating spectrometer. The NMR spectra were recorded by a Varian Model A-60 instrument and a Jeol JNM 4H-100 instrument using tetramethylsilane as an internal standard. The elemental analysis for carbon and hydrogen was performed by Mr. Shibano of this Institute. The molecular weights were measured in a bezene solution using a Mechrolab Vapor Pressure Osmometer, Model 301A.

Materials.—Allene was prepared by the debromination of 2, 3-dibromo-propene-1 with zinc dust. Tri-iron dodecacarbonyl and dicobalt octacarbonyl were prepared by the literature method.[15]

The Preparation of I.—a) The preparation of I in an autoclave under an autogeneous pressure of allene has been described in a previous paper.

b) In a 100 ml. round-bottomed flask, tri-iron dodecacarbonyl (1.5 g.) and a *n*-hexane solution of allene (1 ml. in 30 ml.) were placed. The mixture was then refluxed by stirring it for 3 hr. under nitrogen, using a condenser cooled with dry ice - acetone. At all times there was an excess of iron carbonyl. When the reaction mixture was treated in a way similar to that described previously, about 70 mg. of I was obtained. In addition to this I, a small amount of orange oil and red crystals were obtained.

The Bromination of I.—In a carbon tetrachloride solution of I (0.1 g. in 5 ml.), an excess of bromine (1 ml.) in carbon tetrachloride was slowly added at room temperature in air. An instant reaction occurred, with the evolution of a gas. The ferric bromide formed was removed by an addition of water, and the product was obtained after the evaporation of the solution. The crude product was purified by sublimation at 70°C/3 mmHg, followed by washing with *n*-hexane, to give 0.1 g. of colorless crystals. M. p. 174°C (in sealed tube).

The Preparation of II.—Into a solution of dicobalt octacarbonyl (3.0 g.) in benzene (50 ml.), 1 ml. of liquid allene was slowly introduced in the gaseous state with stirring at 40°C during a 30 min. period under nitrogen. The evolution of a gas and slight heat was observed. After the reaction mixture had stood for 2 hr., then the solvent was evaporated under reduced pressure. A dark brown solid containing a yellow solid was thus obtained. The crude product was obtained by slow sublimation at 80°C/3 mmHg under nitrogen. The sublimate was a mixture of dark brown and yellow crystals. The dark brown sublimate consisted of di-cobalt octacarbonyl and teracobalt dodecacarbonyl and was sensitive towards air. The sublimate was stored under nitrogen for several days. During this period, the di-cobalt octacarbonyl decomposed. The product was then extracted with benzene.

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[13] a) S. Otsuka, M. Mori and F. Imaizumi, ibid., **87**, in press and references therein; b) R. E. Benson and R. V. Lindsey, Jr., ibid., **81**, 4247, 4250 (1959).

[14] a) T. J. Kealy and R. E. Benson, *J. Org. Chem.*, **26**, 3126 (1961); b) E. L. Jenner and R. V. Lindsey, Jr., U. S. Pat. 2876254 (1959).

[15] a) R. B. King and F. G. A. Stone, "Inorganic Syntheses," Vol. 7, McGraw Hill, New York (1963), p. 193; b) I. Wender, ibid., Vol. 5, McGraw Hill, New York (1959), p. 190.

The evaporation of the solvent under nitrogen, followed by sublimation, gave pure II as yellow crystals. The purified crystals were stable in air for a few days, and a slight decomposition was observed when it was stored in air for a longer period. The solution of II in benzene or in carbon tetrachloride began to decompose in air in 10—20 min.

The preparation of II can be performed under the pressure of carbon monoxide. A cooled *n*-hexane solution (20 ml.) of allene in an ampoule and dicobalt octacarbonyl in benzene (20 ml.) were placed in an autoclave at about 10°C. The carbon monoxide pressure was raised to 50 atm., and then the contents of the ampoule and the cobalt carbonyl solution were mixed. The autoclave was heated with rocking to 50—60°C for 1 hr. The product (0.7 g.) was isolated in this case by the evaporation of the solvent, followed by extraction with *n*-hexane and recrystallization. The purification of the product could be achieved by alumina chromatography under nitrogen.

Found: C, 39.76; H, 2.29. Calcd. for $[C_6H_4CoO_3]_2$: C, 39.37; H, 2.20%. mol. wt. 322: calcd. 366.

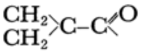
The Bromination of II.—a) In methanol: A suspension of II in methanol was mixed slowly with a solution of bromine in carbon tetrachloride at 10—15°C until the bromine was in excess. Water was then added to separate the cobaltous bromide formed, and the carbon tetrachloride layer was extracted with benzene. The evaporation of the solvent gave crude colorless crystals, which were further purified by recrystallization; m. p. 130—132°C in a sealed capillary.

Found: C, 15.6; H, 2.1. Calcd. for $C_4H_4Br_3O$: C, 15.60; H, 1.3%. mol. wt. 556. calcd. 615. infrared max., 1720cm^{-1} (strong, –CO–CO–).

The vicinal bromide structure was shown by the reaction with potassium iodide in acetone to give iodine.

b) In carbon tetrachloride: A solution of II in carbon tetrachloride was mixed with a solution of bromine at room temperature. The reaction occurred immediately. The product was isolated by distillation on a small scale and gave a colorless liquid. The characteristic smell and acidity of the liquid suggested the presence of an acid bromide. The presence of strong infrared band at 1780 cm^{-1} showed this compound to be acid bromide. The product hydrolyzed in air, and analysis was impossible. Another bromination, in a mixture of ethanol and carbon tetrachloride, gave a mixture of bromoesters (b. p. 100°C/3 mmHg), as evidenced by the presence of 1735 cm^{-1} band in the infrared spectrum.

Summary

The product with the $[C_3H_4Fe(CO)_3]_2$ composition obtained from the reaction of allene with tri-iron dodecacarbonyl has been found to be the first metal complex with a 2, 2′-bi-π-allylene structure. A study of the NMR spectrum has, however, shown an extensive valence tautomerism occurring, even at $-10°C$ between the bi-π-allylene structure and the related butadiene-type structure. The reaction of allene with an excess of dicobalt octacarbonyl gave yellow crystals with the $[(C_3H)_4\text{-}Co(CO)_3]_2$ composition. A structure has been proposed in which a  $\begin{matrix}CH_2\\CH_2\end{matrix}\!\!>\!C{-}C\!\!\begin{matrix}\nearrow O\\ \searrow\end{matrix}$ skeleton is bound to cobalt atoms via π-allyl and acyl groups. The relation between the structures of these complexes and the catalytic reaction of allene have been discussed.

The author is grateful to Professor Nobue Hagihara for his invaluable discussions and encouragement during this study. He also wishes to express his appreciation of the advice and cooperation of Professor Sei Otsuka in the preparation of this report.