INTERACTION OF CUMULENE SYSTEMS WITH ORGANOMETALLIC π-COMPLEXES

I. CUMULENE COMPLEXES

AKIRA NAKAMURA, PU-JUN KIM AND NOBUE HAGIHARA
The Institute of Scientific and Industrial Research, Osaka University, Sakai, Osaka (Japan)
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INTRODUCTION

A good deal of interest has been focussed in recent years on the field of organometallic π-complexes of mono- and polyolefins[1]. However, the interaction of cumulene systems with organometallic compounds of the transition metals has not been investigated extensively. It would therefore be of interest to see whether or not cumulene type double bonds in a straight chain form stable π-complexes. In addition, π-electron clouds intersecting at right angles to each other in cumulene systems are also of interest in π-complex formation, because the system bears a close relationship to acetylenic triple bond systems which yield a number of stable π-complexes. Investigation of the interaction of the cumulene systems with organometallic compounds would also be of importance in connection with the known polymerization[2] and carbonylation[3] of allenic compounds. At the outset, we found that the cumulene systems did yield stable π-complexes with some transition metals. During the course of our study, allene has been reported by Green and Ariyaratne[4] as being found in a π-complexed form in a cation: $[C_5H_5Fe(CO)_2C_3H_4]^+$. Conclusive evidence of the presence of the π-complexed allene in the cation, however, is meagre. We have also investigated the interaction of cumulene systems with neighbouring groups containing organometallic π-complexes, *e.g.* ferrocenylbutatriene derivatives. The interaction was found to be of some importance in the stabilization of the cumulene linkage and will be the subject of a subsequent paper.

RESULT AND DISCUSSION

Tetraphenylallene iron tricarbonyl

Interaction of allenic compounds with cobalt carbonyl was first reported by Greenfield *et al.*[2a] but polymerization of the allenes was found to take place instead of the expected formation of π-complexes. We have found* that on refluxing tetraphenylallene with iron pentacarbonyl in isooctane interaction occurred to give red crystals (I); 29% yield after recrystallization from methanol. Compound (I) was quite stable in air and found to be diamagnetic. The molecular formula was found to be $(C_6H_5)_4C_3Fe(CO)_3$. Pyrolysis of (I) resulted in the evolution of 2.6 moles of carbon monoxide and gave tetraphenylallene and 1,1-diphenyl-3-phenylindene (identified

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* A preliminary communication of the preparation of (I) and (II) has been published[5].

by comparison of the infrared spectra of authentic samples). The substitution of the tetraphenylallene with triphenylphosphine was easily achieved as compared with the corresponding reaction for diene iron tricarbonyl complexes. Thus, the reaction of (I) with triphenylphosphine at 60° proceeded smoothly to give tetraphenylallene and bis(triphenylphosphine) iron tricarbonyl. The use of one molar equivalent of triphenylphosphine gave the same products together with the unchanged (I). A possible intermediate species such as tetraphenylallene triphenylphosphine iron tricarbonyl has not been isolated. The pyrolysis and the substitution reaction of (I) showed that the tetraphenylallene retained its skeletal structure on π-complex formation. Three strong infrared bands were observed (2060, 1999 and 1985 cm^{-1}) indicating terminal carbonyl groups are present in (I). In the visible region (I) exhibited a maximum at 468 mμ (log ε 2.91) and had a increasing absorption towards shorter wavelengths. The bonding and structure of (I) merit some discussions. The presence of three carbonyl groups in (I) suggests that the two double bonds in the allene system are both used in bonding with the iron tricarbonyl group. The two π-electron systems of the allenic double bonds are known to intersect at right angles to each other and bonding through one double bond in the same way as for ordinary olefin complexes leaves the other double bond in an unfavorable position for the π-complex formation. It is possible though that a d_π-p_π bond might be responsible for this latter bonding. The bonding through the phenyl groups of the tetraphenylallene, however, cannot be excluded at the present stage. An attempt to prepare an unsubstituted analog of (I) has been unsuccessful. Reaction of unsubstituted allene with triiron dodecacarbonyl at 120° gave mainly a mixture of two products: an orange oil of composition near $[(C_6H_8)Fe(CO)_3]_{1-2}$, and red crystals, $[(C_3H_4)Fe(CO)_3]_2$. Detailed investigation of these products will be necessary to establish the correct structures.

Tetraphenylbutatriene diiron pentacarbonyl

Tetraphenylbutatriene was reacted with iron pentacarbonyl by refluxing in ethylcyclohexane for 14 h and red crystal (II) were obtained in 26% yield after recrystallization. The compound (II) was found to have a composition, $(C_6H_5)_4C_4Fe_2(CO)_5$. The infrared spectrum showed four bands (2072, 2035, 1998 and 1988 cm^{-1}) attributable to terminal metal carbonyl groups. No maxima were observed in the visible and ultraviolet region. (II) was stable in air and diamagnetic. Pyrolysis of (II) gave tetraphenylbutatriene and 1-(diphenylmethylene)-3-phenylindene (identified by comparison of the infrared spectra of authentic samples) and 5 mole-equivalents of carbon monoxide were evolved. The possibility of the presence of the tetraphenylbutatriene in the form of 1-(diphenylmethylene)-3-phenylindene was rejected as a result of failure to obtain the same compound starting from the indene and iron pentacarbonyl. Therefore, (II) must contain the tetraphenylbutatriene without changes in its structure. The fact that the strong absorption maximum of tetraphenylbutatriene at 420 mμ was not observed in (II) indicates that the butatriene chromophore is destroyed by bonding with the iron carbonyl group. The bonding of the butatriene system, however, might involve the phenyl groups of (II). This possibility was completely eliminated by the preparation of an unsubstituted derivative as described in the later part of this paper. The reaction of (II) with triphenylphosphine in benzene at 80° was attempted, and the starting materials were recovered unchanged. The conditions of the reaction were almost the same as those for the reaction of (I) with triphenylphosphine as described above. The enhanced stability of the butatriene complex over the allene complex was clearly demonstrated.

Butatriene diiron pentacarbonyl

Unsubstituted cumulenes are generally thought to be unstable substances. For example, unsubstituted butatriene[6] was reported to polymerize violently near 0° and tetrafluorobutatriene[7] to detonate at 0°. It seemed that it would be impossible to react such compounds with metal carbonyls. However, the debrominating ability of zinc powder and of triiron dodecacarbonyl was utilized to debrominate 1,4-dibromo-2-butyne to butatriene. This reaction of 1,4-dibromo-2-butyne with triiron dodecacarbonyl in the presence of an excess of zinc powder at 60° resulted in a red crystalline product (III) which was very stable in air and found to have the molecular formula: $C_4H_4Fe_2(CO)_5$. The yield was 13% based on the dibromobutyne and 18% based on the iron carbonyl. The best yield was obtained by using an excess of zinc powder, but (III) could be obtained without zinc powder. No complexes were obtained using iron pentacarbonyl. (III) could also be obtained in poor yields using 1,4-dichloro-2-butyne or 1,4-diacetoxy-2-butyne in place of the dibromobutyne. (III) showed five bands (2090, 2052, 2025, 2015 and 1995 cm^{-1}) in the terminal metal carbonyl stretching region and the absorption pattern is similar to that of (II) as shown in Fig. 1 indicating a similarity in the bonding. In the visible region (III) showed maxima at 448 $m\mu$ ($\log \varepsilon$ 3.356) and 346 $m\mu$ ($\log \varepsilon$ 3.734). The stability of (III) is in marked contrast to the instability of uncomplexed butatriene. Thus, a solution of (III) in an organic solvent was stable in air for a few days and thermal decomposition of (II) occurred at

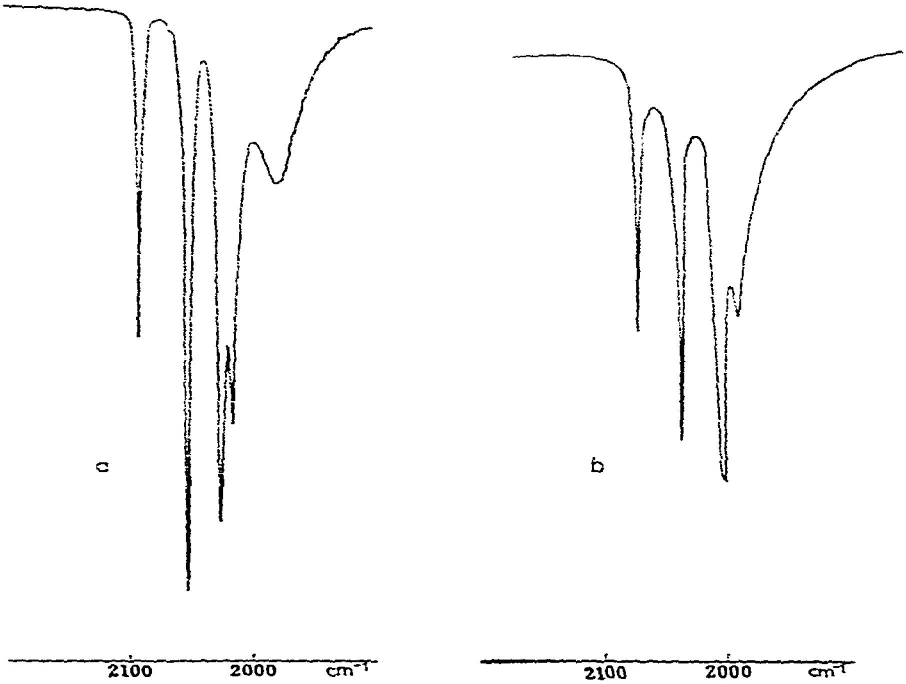

Fig. 1. Infrared spectra in carbon tetrachloride in the 2100–2000 cm^{-1} region of: (a), $C_4H_4Fe_2(CO)_5$; (b), $(C_6H_5)_4C_4Fe_2(CO)_5$.

200–230° in air. The stabilization of butatriene by π-complex formation is as great as in the case of cyclobutadiene. The NMR spectrum of (III) showed two peaks at 5.22 and 5.85 τ of equal intensity as shown in Fig. 2. Each peak is slightly split (*ca.* 1.5 cps) and this is probably due to a doublet, a fact which should be important in structure elucidation. The split, however, is so small and possibilities other than doublet formation exist.

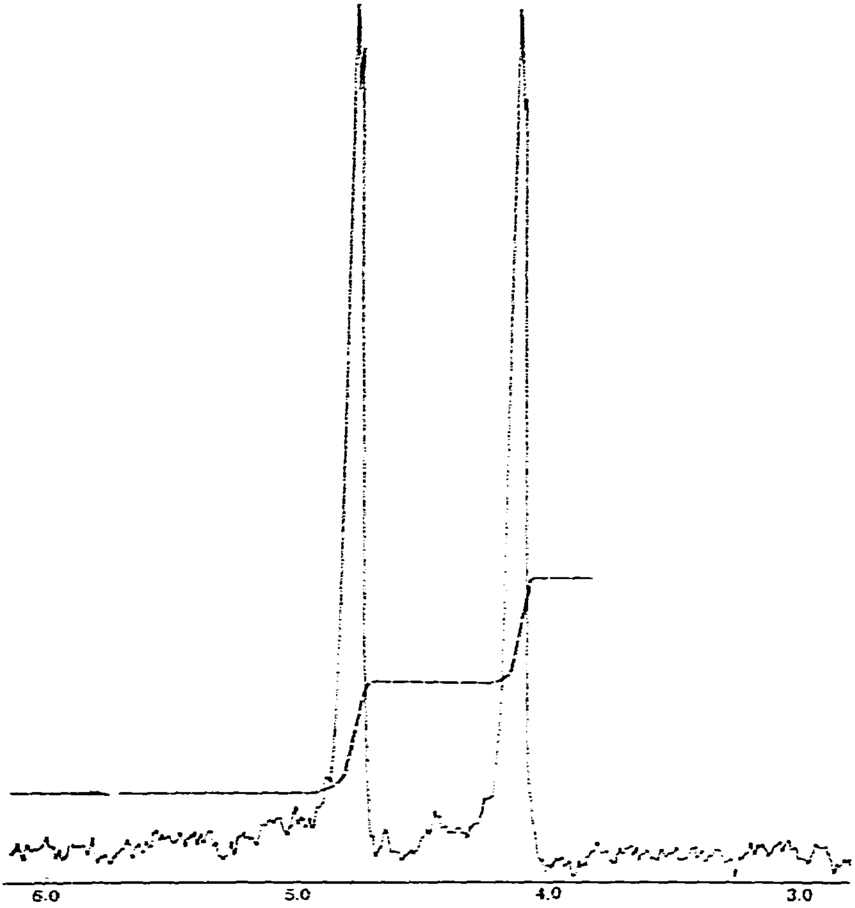

Fig. 2. NMR spectrum of $C_4H_4Fe_2(CO)_5$ in carbon tetrachloride. Chemical shifts are recorded in ppm downfield from tetramethylsilane.

Several structures are conceivable for (III). Some of the probable structures are illustrated in Fig. 3. Structure (a) involves a straight C_4 chain as in the free butatriene. Double bonds at the 1- and 2-position form a bond with one iron tricarbonyl group just like the bonding assumed for the allene complex (I). The double bond at the 3-position forms a bond with another iron dicarbonyl group. There may be a metal–metal bond between the two iron carbonyl groups. Two kinds of protons are expected and the splitting is quartet in this structure. An analogous long range coupling of protons has been observed in similar types of compounds, such as dimethylbutadiyne[8] and methylhexatrienal[9]. The coupling across the conjugated double

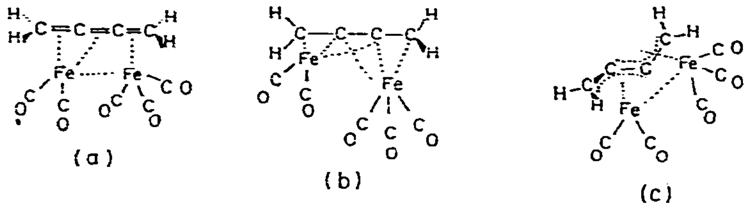

Fig. 3. Some of the probable structures of $C_4H_4Fe_2(CO)_5$.

bonds seems to be somewhat reduced by the interference of the attached iron carbonyl groups.

Structure (b) involves a straight C_4 chain, but the terminal methylene groups are in a twisted position with respect to each other. Three *p*-orbitals at C_1, C_2 and C_3 form an electron system similar to that of the π-allyl system and the other three at C_2, C_3 and C_4 form another three electron system. The two systems are at right angles to each other. An iron tricarbonyl group and an iron dicarbonyl group are attached to the systems and form a metal–metal bond between them. Two kinds of protons are expected and the coupling is triplet (A_2X_2 system). However, examination of the model shows that the coupling may not be equal between the methylene protons and the splitting may not be triplet because of the attachment of the iron carbonyl groups on one side of the butatriene. Therefore, a quartet splitting might be expected. The structure involving two π-allyl systems superimposed at right angles to each other and having a bent butatriene system is shown in structure (c). In this structure the terminal methylene protons are not equivalent and will appear at considerably higher fields (at *ca.* 8–9 τ) than olefinic protons usually do. The observed τ-values for the butatriene complex (III) are far from the expected values for the π-allyl system; four peaks having doublet splitting would be expected in the NMR spectrum of the structure (c). A rapid interchange of the carbonyl groups may be occurring which reduces the number of the NMR peaks in the present case. Therefore, the correct structure cannot be deduced from the evidence at hand and an X-ray structure analysis of the cumulene complexes is hoped for.

Hexapentaene π-complexes

It is interesting at this point to examine the possibility of trapping hexapentaene in the form of a π-complex. Since unsubstituted butatriene has been found to be a very unstable compound, no attempt has been recorded for the isolation of unsubstituted hexapentaene. The reaction of 1,6-dichloro-2,4-hexadiyne with triiron dodecacarbonyl in the presence of zinc powder at 80° proceeded with evolution of gas. Almost black, air-stable crystals were obtained through chromatography followed by sublimation at 120°. The infrared spectrum of the product showed strong peaks (2088, 2065, 2047 and 2005 cm^{-1}) in the metal carbonyl stretching region. It was sparingly soluble in *n*-hexane and soluble in benzene with a deep red color. Exceedingly poor yield (*ca.* 1 %) of this compound made detailed characterization very difficult. The reaction of tetraphenylhexapentaene with triiron dodecacarbonyl was also investigated. The deep red-brown semisolid obtained from the reaction defied attempts at crystallization. Purification by chromatography on deactivated alumina caused decomposition of the compound. The infrared spectrum of the crude product showed several bands

(2071, 2036, 2009 and 2001 cm^{-1}) in the terminal metal carbonyl stretching region. The infrared pattern in this region was found to be similar to that of the product from the reaction of the dichlorohexadiyne with the iron carbonyl. So far only preliminary evidence for the presence of π-complexes of hexapentaene systems has been obtained and further study is in progress to establish the correct structures of these π-complexes.

Interaction of tetraphenylallene and tetraphenylbutatriene with various metal carbonyls

The ability of tetraphenylallene and -butatriene to form organometallic π-complexes was examined using various metal carbonyls. The photochemical reaction of cyclopentadienylvanadium tetracarbonyl with tetraphenylallene and with tetraphenylbutatriene evolved only a small amount of carbon monoxide, and the starting materials were recovered unchanged. In contrast to the behaviour of the cumulenes, acetylene and its derivatives react easily with cyclopentadienylvanadium tetracarbonyl on irradiation with sun-light to give acetylene complexes*.

Thermal reaction of bis(triphenylphosphine) nickel dicarbonyl with tetraphenylallene and with tetraphenylbutatriene in inert solvents proceeded with the development of a deep red color. The color, however, faded on cooling and the starting materials were recovered. It is conceivable that the appearance of the red color is due to the formation of a charge transfer complex. The interaction of chromium hexacarbonyl with the allene and with the butatriene yielded complexes having chromium tricarbonyl groups attached at the phenyl groups and will be described in a subsequent paper. Photochemical reaction of cyclopentadienylmanganese tricarbonyl with tetraphenylallene indicated π-complex formation. Infrared investigation of the reaction product showed that one of the carbonyl groups had been replaced by the allene. The yield was poor and further study is now under way. Cyclopentadienylcobalt dicarbonyl reacted with tetraphenylallene on refluxing in isooctane to give a compound of composition: $(C_5H_5)Co(CO)[(C_6H_5)_4C_3]$ (IV) in poor yield. The deep red compound (IV) was stable in air and purified by repeated chromatography. The presence of one terminal metal carbonyl group is indicated by an absorption at 2002 cm^{-1} in the infrared. (IV) showed a maximum at 266 mμ (log ε 4.435) in the ultraviolet. It is interesting to note that tetraphenylallene acts as a monodentate ligand in this case whereas the tetraphenylallene in its iron tricarbonyl complex formally acts as a bidentate ligand as described above. Thermal reaction of dicobalt octacarbonyl with tetraphenylallene and -butatriene has so far given no π-complexes. These results are not unexpected because Greenfield *et al.*[2] previously found that tetraphenylallene did not react with dicobalt octacarbonyl at room temperature whilst the unsubstituted allene polymerized under these same conditions. No interaction has been observed between dimanganese decacarbonyl and tetraphenylallene and between nickel tetracarbonyl and tetraphenylallene.

EXPERIMENTAL

All the melting points given are uncorrected and were measured by a micromelting point apparatus made by Yanagimoto company. Polarized light was sometimes used to examine the crystallinity. Infrared spectra were obtained by a Hitachi Model

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* R. TSUMURA AND N. HAGIHARA, presented at *17th Annual Meeting of the Chemical Society of Japan*, Tokyo, 1964.

EPI-2, a Jasco Model DS-402G grating spectrophotometer and a Jasco Model IR-S spectrophotometer. Visible and ultraviolet spectra were measured by a Beckman DK-2 spectrophotometer. NMR spectra were obtained with a Varian Model A-60 spectrometer, tetramethylsilane being used as external standard. Magnetic measurements were made by the Gouy method in glass tubes. Elemental analysis was performed by Messrs. T. SHISHIDO and T. SHIBANO of this Institute. Molecular weights were measured cryoscopically in benzene or by using a Mechrolab Vapor Pressure Osmometer Model 301A, a benzene solution of the compound being used. Alumina used for chromatography had activity grade I and was of 200–300 mesh size. All reactions involving organometallic compounds were carried out under nitrogen.

Materials

Iron pentacarbonyl[10], triiron dodecacarbonyl[11], cyclopentadienylcobalt dicarbonyl[12], cyclopentadienylvanadium tetracarbonyl[13], 1,4-dibromo-2-butyne[14], 1,4-dichloro-2,4-hexadiyne[15], tetraphenylallene[16], tetraphenylbutatriene[17], tetraphenylhexapentaene[18], 1,1-diphenyl-3-phenylindene[19] and 1-(diphenylmethylene)-3-phenylindene[20] were prepared by the respective methods described in literature.

Tetraphenylallene iron tricarbonyl (I)

Tetraphenylallene (2.0 g, 5.8 mmole), iron pentacarbonyl (2.5 ml, 18 mmole) and isooctane (10 ml) were mixed and heated under reflux for 13 h. The volume of gas evolved amounted to 140 ml, and a deep red color developed during the reaction. The solution was evaporated *in vacuo* and the red semisolid was crystallized from methanol. After removal of a small amount of deep red gummy material, red crystals were obtained The product was purified further by recrystallization from methanol. A 29% yield of analytically pure sample was obtained. (Found: C, 74.00; H, 4.45; mol. wt. cryoscopic, 518. $C_{30}H_{20}FeO_3$ calcd.: C, 74.39; H, 4.16%, mol. wt. 484.) Magnetic susceptibility; $X_g = 0.18 \times 10^{-6}$ cgsu.

Reaction of allene with triiron dodecacarbonyl

A solution containing *ca.* 0.8 g of allene (20 mmole) in *n*-hexane and triiron dodecacarbonyl (1.0 g, 5.9 mmole) were placed in a 100-ml autoclave. The mixture was heated at 120° for 3 h. The deep orange solution was filtered from brown solid matter and evaporated *in vacuo*. The red-orange semisolid was chromatographed. Elution with *n*-hexane–benzene (10:1) gave an orange oil (0.2 g) which was distilled at 60–80°/3 mm. (Found: C, 48.21; H, 3.74; mol. wt. v.p.o.*, 357. $C_9H_8FeO_3$ calcd.: C, 49.13; H, 3.67%; mol. wt. 220.) Elution with *n*-hexane–benzene (10:2) gave red crystals which were purified by recrystallization from *n*-hexane to give red needles. M.p. 88–89°, yield 0.2 g. (Found: C, 39.96; H, 2.33; mol. wt. v.p.o., 387. $C_6H_4FeO_3$ calcd.: C, 40.05; H, 2.24%; mol. wt., 360.)

Tetraphenylbutatriene diiron pentacarbonyl (II)

Tetraphenylbutatriene (1.1 g, 3.1 mmole) and iron pentacarbonyl (2.2 ml, 15.7 mmole) were placed in a flask with 5 ml of ethylcyclohexane and heated under reflux for 14 h. During the reaction about 400 ml of gas was evolved. The reaction product was purified by repeated recrystallization from *n*-hexane–benzene mixtures. Brownish red crystals (0.5 g) were obtained in 26% yield. (Found: C, 64.90; H, 3.55; mol. wt.

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* Measured by a vapor pressure osmometer.

v.p.o., 683. $C_{33}H_{20}Fe_2O_5$ calcd.: C, 65.16; H, 3.31%; mol. wt., 608.) Magnetic susceptibility, $X_g = 0.06 \times 10^{-6}$ cgsu.

Butatriene diiron pentacarbonyl (III)

1,4-Dibromo-2-butyne (0.8 g, 3.75 mmole), triiron dodecacarbonyl (1.0 g, 5.9 mmole) and zinc powder (1.0 g) were placed in a round bottomed flask with 10 ml of isooctane. The mixture was heated at 80° and agitated with a magnetic stirrer. The evolution of gas was measured by use of a gasometric apparatus. After the evolution of *ca.* 300 ml of gas, in 5 h, the evolution ceased practically. The initial deep green color of the mixture turned to red. The solution was filtered by gravity in air and the precipitates were washed with benzene. The combined filtrate and the wash were evaporated *in vacuo* and the red solid remained was sublimed at 60–80°/3 mm. The red sublimate was purified further by chromatography. Elution with *n*-hexane–benzene (1:1) and evaporation of the red eluate gave red crystals, m.p. 69–70° in 18% yield based on the iron carbonyl. (Found: C, 35.85; H, 1.27; mol. wt. cryoscopic, 303. $C_9H_4FeO_5$ calcd.: C, 35.57; H, 1.33%; mol. wt., 305.)

Cyclopentadienylcobalt carbonyl tetraphenylallene (IV)

Tetraphenylallene (1.5 g, 4.4 mmole) and cyclopentadienylcobalt dicarbonyl (1.3 g, 7.2 mmole) were refluxed in 15 ml of isooctane for 20 h, during which *ca.* 34 ml of gas was evolved. The brown precipitate (1.4 g) which was obtained, was purified by chromatography. Elution with *n*-hexane–benzene (1:1 to 1:2) gave a deep red eluate. The eluate contained a considerable amount of unchanged tetraphenylallene. The chromatography was repeated and a red solid obtained from the red eluate was recrystallized from *n*-hexane. Finally the crystals were purified again by chromatography followed by recrystallization from *n*-hexane to give *ca.* 20 mg of deep red crystals (*ca.* 2% yield), m.p. 135° (in nitrogen). (Found: C, 80.50; H, 5.41; mol. wt. v.p.o., 488. $C_{33}H_{25}CoO$ calcd.: C, 79.83; H, 5.08%; mol. wt., 496.)

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SUMMARY

The reaction of tetraphenylallene and -butatriene with iron pentacarbonyl gave $(C_6H_5)_4C_3Fe(CO)_3$ and $(C_6H_5)_4C_4Fe_2(CO)_5$, as red and brownish red crystals, respectively. The unsubstituted butatriene complex, $H_4C_4Fe_2(CO)_5$ was also prepared by the reaction of 1,4-dibromo-2-butyne with triiron dodecacarbonyl in the presence of zinc powder. The interaction of cumulene systems with a variety of metal carbonyls has been examined.

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