ORGANOMETALLIC COMPLEXES

XV*. TROPONEIRON CARBONYLS AND OTHER COMPLEXES FROM PHENYLACETYLENES AND IRON CARBONYLS

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(Received June 4th, 1964)

The reaction of alkynes with iron carbonyls[1-4] gives a variety of organoiron carbonyls having cyclic organic ligands. Thus tricarbonyliron complexes of cyclopentadienones[5] and cycloheptatrienone[6] have been obtained and characterized. The present paper deals with iron carbonyl complexes of substituted tropones and with other new complexes resulting from the reaction of phenyl- and (*p*-bromophenyl)acetylene with iron carbonyls in inert solvents.

TRICARBONYL(2,4,6-TRIPHENYLTROPONE)IRON COMPLEXES

The main products of the reaction of PhC≡CH with $Fe_3(CO)_{12}$ at 80–85° are two isomeric complexes of formula $(PhC_2H)_3COFe(CO)_3$ [(I) and (II); 20%] having very similar properties[2] (Table 1). Both compounds are also formed by decomposition of $(PhC_2H)_3COFe_2(CO)_5$[2,7] under mild conditions, such as by refluxing it in benzene (50%) or by chromatography on Al_2O_3 (60%), suggesting it to be their precursor. Indeed, $(PhC_2H)_3COFe_2(CO)_5$ is practically the only complex formed in the reaction between PhC≡CH and $Fe_3(CO)_{12}$ when carried out below 60°.

Complexes (I) and (II) liberate the same triphenyltropone in high yields, when reacted with PPh_3 in a closed system, whereas by thermal decomposition only 1,3,5-triphenylbenzene is obtained[2,4] in about 50% yield. The formation of the symmetrical triphenylbenzene shows the phenyl groups to be in the 2-, 4- and 6-positions on the tropone ring. On the other hand, by reacting 2,4,6-triphenyltropone with $Fe_3(CO)_{12}$, the mixture of (I) and (II) is again obtained. Compounds (I) and (II) are therefore two isomeric tricarbonyl(2,4,6-triphenyltropone)iron complexes[6]. The isomerism can only be understood by assuming localized bondings of the tricarbonyliron group to two double bonds of the tropone ring (Fig. 1), in contrast to the assumption made by Brown[8] from molecular-orbital considerations. In the case of symmetrically substituted tropones this type of bonding gives rise to optical isomers, as has been discussed previously[6] in the case of tricarbonylcycloheptatrienoneiron, whereas with unsymmetrically substituted tropones positional isomers are obtained; each of these should exist in two optically active forms. Of the three double bonds of the tropone system only the conjugated pair is involved as indicated in Fig. 1. A structure using both

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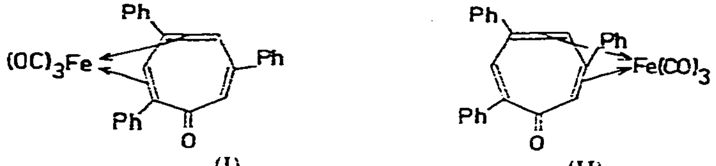
* Part XIV: W. HÜBEL AND R. MERÉNYI, *J. Organometal. Chem.*, 2 (1964) 213.



(I) (II)

Fig. 1. Tricarbonyl(2,4,6-triphenyltropone)iron isomers.

α-double bonds can be ruled out since complexes involving unconjugated double bonds would certainly be less stable and the complexes (I) and (II) would have a greater difference in their energy content than is actually observed (~ 0.5 kcal; see below).

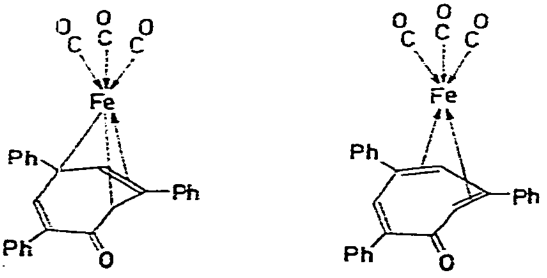
TABLE I

COMPLEXES FROM $PhC{\equiv}CH$ AND $Fe_3(CO)_{12}$[a]

	Formula	*Colour*	*M.p.*	*Wavenumber (cm^{-1}) of IR absorption bands (in KBr)*	
				CO ligands	*ketonic CO*
(I)	(2,4,6-Triphenyltropone)-$Fe(CO)_3$[2]	orange red	156–158° (dec.)	2062, 2000	1623
(II)	(2,4,6-Triphenyltropone)-$Fe(CO)_3$[2]	red	148–150° (dec.) or 162–165° (dec.)	2062, 1996	1629
(III)	(3,4-Diphenylcyclopentadienone)-$Fe(CO)_3$	brown yellow	142–146° (dec.)	2083, 2024, 2008	1647, 1637[b]
(IV)	(1,1,1-Tricarbonyl-3,4-diphenyl-ferracyclopentadiene)-$Fe(CO)_3$	orange	125–127°	2062, 2024 1972, 1934	—
(V)	$(PhC_2H)_3Fe_2(CO)_6$	red violet	160–180° (dec.)	2075, 2020 1988, 1934	—

[a] Other complexes from this reaction have been described previously[2]. [b] In CCl_4: 2083, 2024, 2008, 1669.

An X-ray investigation of (II) (isomer of m.p. 162–165°, dec.) has been carried out by Smith and Dahl[5] leading to the structure as depicted in Fig. 2 which fully agrees with the chemical evidence presented above. The organic ligand in (II) is bent



(IIa) (IIb)

Fig. 2. Detailed structures of (II).

as in tricarbonyltroponeiron[10], in tricarbonylcyclooctatetraeneiron[11] and in π-cyclopentadienylhexakis(trifluoromethyl)benzenerhodium[12]. It is clear from the X-ray structural analysis of (II) that indeed only a planar *syn*-butadiene group of the tropone ligand is bonded to the Fe(CO)$_3$ fragment as a four-electron donor. The detailed electronic structure can generally be explained in two ways: (*a*) a structure involving two π-bonds and in which the conjugated system remains essentially unaltered as was first formulated by Hallam and Pauson[13] [Fig. 2; (IIb)] or (*b*) a Diels-Alder type addition to the diene system as proposed by Wilkinson and co-workers[14] [Fig. 2; (IIa)]. The X-ray results strongly favour a three-point attachment[9] of the Fe(CO)$_3$ group, (IIa). However, the ultraviolet spectra of (I) and (II) (Fig. 3) are similar and resemble that of 2,4,6-triphenyltropone suggesting less change of the electronic configuration than one would expect for the Diels-Alder type structure (IIa). An intermediate status between (IIa) and (IIb) could explain both the X-ray results and the ultraviolet spectra.

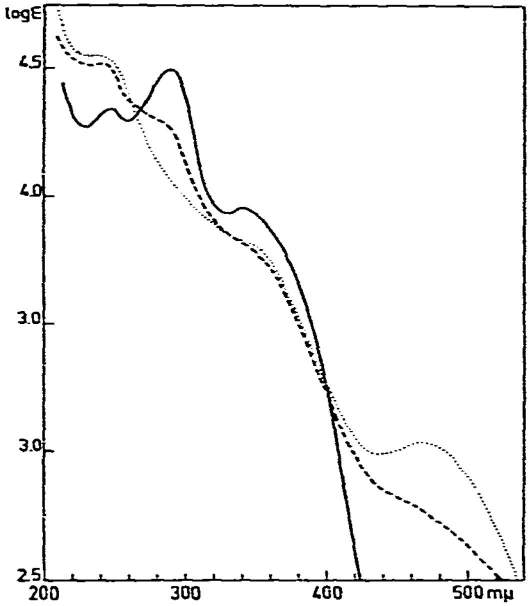


Fig. 3. Ultraviolet spectra of: —— 2,4,6-triphenyltropone; – – – (2,4,6-triphenyltropone)-Fe(CO)$_3$, (I); ···· (2,4,6-triphenyltropone)-Fe(CO)$_3$, (II).

TABLE 2

ISOMERIZATION OF (I) AND (II)

Complex	*Temp. °C*	*Time in h*	*(I) %*	*(II) %*
(I)	25	138	80	8
(II)	25	138	6	91
(I)	80	4	29	63
(II)	80	4	31	62

The compounds (I) and (II) isomerize to each other in solution even at room temperature (Table 2) although isomerization is then slow. Equilibrium is attained after four hours boiling in benzene, giving for (I):(II) a ratio of 1:2; this indicates that (II) is energetically favoured by only about 0.5 kcal/mole at 80°.

As in the case of tropone and its iron tricarbonyl complex[6], the stretching frequency of the ketonic group in 2,4,6-triphenyltropone (1587 cm^{-1}) is also shifted to higher values in the complexes (I) and (II) (Table 1) indicating a decrease of its polarity, due to the loss of the "tropylium oxide" mesomeric structure[15,16]. In contrast to tricarbonyltroponeiron, complex (II) fails to give characteristic reactions of ketonic groups[6] such as the formation of a 2,4-dinitrophenylhydrazone or an oxime.

Hydrogenation of (I) or (II) on Pd at 50° gives only an extremely air- and light-sensitive compound, which according to its infrared spectrum, is most probably tricarbonyl(2,4,6-triphenyl-3,5-cycloheptadien-1-one)iron. When (II) is heated with PPh_3 in an open system, substitution of one CO ligand is achieved with formation of (2,4,6-triphenyltropone)-$Fe(CO)_2PPh_3$.

Since neither (I) nor (II) has an element of symmetry both complexes should exist in two optical antipodes. If the space group of (II) is $P2_12_12_1$, the crystal used in the X-ray analysis consisted only of one enantiomorph. However, no suitable single crystals of (II) could be obtained for sorting the optical isomers by hand.

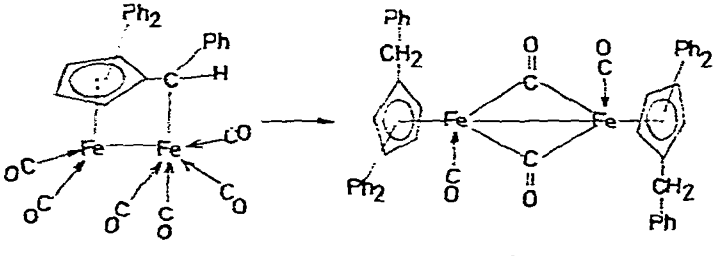
NEW "PHENYLACETYLENEIRON CARBONYLS"

A reinvestigation of the reaction of $Fe_3(CO)_{12}$ with phenylacetylene in light petroleum at various temperatures led to the isolation of new isomers of complexes described in an earlier paper[2] [(III), (IV) and (V), Table 1].

The infrared spectrum identifies (III) as of the tricarbonylcyclopentadienoneiron type. According to its NMR spectrum, (III) has two equivalent hydrogens on the cyclopentadienone ring ($\tau \approx 4.2$) and two equivalent phenyl groups ($\tau \approx 2.9$). Since the corresponding complex of 2,5-diphenylcyclopentadienone has been characterized[2,17], (III) is tricarbonyl(3,4-diphenylcyclopentadienone)iron.

Analysis and infrared spectrum show (IV) to be a (1,1,1-tricarbonyldiphenylferracyclopentadiene)-π-tricarbonyliron. Its reaction with sulphur gives 3,4-diphenylthiophene whereas its isomer[2] yields 2,5-diphenylthiophene. These reactions indicate that the phenyl groups on the ferracyclopentadiene ring are in the 3,4- (IV) and 2,5-position respectively.

The existence of complexes (III) and (IV) in addition to their isomers[2] show the complex formation not to be as stereospecific as had been thought. This has also been



(V) (Va)

found in the case of "1-phenylpropyne iron carbonyls" where all three possible isomers of the type $(MeC_2Ph)_2COFe_2(CO)_6$ have been isolated[18].

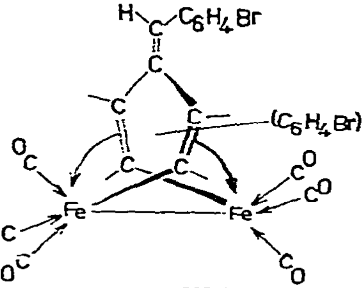
The infrared spectrum of (V) in the 2000 cm⁻¹ region strongly resembles that of the dark red acetylene complex $(HC_2H)_3Fe_2(CO)_6$ (m.p. 140°, dec.)[19] for which a hexacarbonyl(methylenecyclopentadienyl)diiron structure has been deduced from its chemistry[19]; the proposed structure has been confirmed by X-ray analysis[20]. (V) also gives a tetracarbonyldicyclopentadienyldiiron derivative when heated with CO under pressure[19], *viz.* the benzyldiphenylcyclopentadienyl complex (Va). For these reasons (V) is suggested to be hexacarbonyl(benzylidenediphenylcyclopentadienyl)-diiron. Complexes of this type are readily obtained from fulvenes and iron carbonyls[21].

("*p*-BROMOPHENYL)ACETYLENEIRON CARBONYLS"

The reaction of p-$BrC_6H_4C{\equiv}CH$ with $Fe_3(CO)_{12}$ gave almost the same types of complexes as did phenylacetylene; they are listed in Table 3. The assignment of the structures is based on their infrared spectra and the similarity of other physical properties. No attempts were made to locate the positions of the *p*-bromophenyl groups.

Complexes (VI) and (VII) are both of the tricarbonylcyclopentadienoneiron type having the substituents in different positions. (VI) is also formed in the reaction of *p*-bromophenylacetylene with a mixture of $Fe(CO)_5$ and $Ni(CO)_4$ according to Jones *et al.*[22]. Since in the case of phenylacetylene this reaction gives only (2,5-diphenylcyclopentadienone)-$Fe(CO)_3$, (VI) is assumed to be the 2,5-isomer; this assignment is further supported by the physical properties of these compounds (m.p., ketonic carbonyl absorption band and adsorption strength on alumina).

The complexes (VIII) and (IX) are tricarbonyltroponeiron derivatives; their isomerism is believed to be of the same nature as that of the phenylacetylene analogues (I) and (II). Complex (XI) is a [tricarbonylbis(*p*-bromophenyl)ferracyclopentadiene]-π-tricarbonyliron complex. The structure adopted for (XII) is that of the complex $(HC_2H)_3Fe_2(CO)_6$ of m.p. 62° (ref. 19) on the basis of the similarity of the infrared CO absorption pattern. The structure of the acetylene complex has recently been established by X-ray analysis[23].



(XII)

EXPERIMENTAL*

The melting and decomposition temperatures have been determined by means of a hot stage microscope and are not corrected.

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* The analyses were carried out in this laboratory by F. GOES, D. GRAF and R. HOUQUET.

TABLE 3

COMPLEXES FROM (p-BROMOPHENYL)ACETYLENE AND $Fe_3(CO)_{12}$

	Formula	*Colour*	*M.p.*	*Wave number (cm^{-1}) of IR absorption bands (in KBr)*	
				CO ligands	*ketonic CO*
(VI)	[2,5-Bis(p-bromophenyl)cyclopentadienone]-$Fe(CO)_3$	pale yellow	247–253° (dec.)	2079, 2008	1618
(VII)	[3,4-Bis(p-bromophenyl)cyclopentadienone]-$Fe(CO)_3$	yellow	185–200° (dec.)	2075, 2008	1645, 1634
(VIII)	[Tris(p-bromophenyl)tropone]-$Fe(CO)_3$	dark red	199–205° (dec.)	2058, 2000, 1992	1623
(IX)	[Tris(p-bromophenyl)tropone]-$Fe(CO)_3$	yellow or red brown	166–175° (dec.) 154–165° (dec.)	2066, 2008	1618
(X)	$(BrC_6H_4C_2H)_6Fe(CO)_4$	brown	240–260° (dec.)	2024, 1972	1704, 1658
(XI)	[1,1,1-Tricarbonylbis(p-bromophenyl)ferracyclopentadiene]-π-$Fe(CO)_3$	yellow	208–215° (dec.)	2075, 2041, 2016, 1992, 1927	—
(XII)	$(p\text{-}BrC_6H_4C_2H)_3Fe_2(CO)_6$	red violet	*ca.* 200° [a]	2075, 2049, 2012	—

[a] Dec. without melting.

Preparation of the tricarbonyl(2,4,6-triphenyltropone)iron complexes, (I) and (II)

a) From PhC≡CH and $Fe_3(CO)_{12}$. See ref. 2.

b) From $(PhC_2H)_3COFe_2(CO)_5$ (refs. 2 and 7). $(PhC_2H)_3COFe_2(CO)_5$ (1 g) was refluxed in 25 ml of benzene for 15–30 min. Chromatography of the filtered solution on silica gel* yielded 0.21 g of (II) and 0.16 g of (I) (total yield 46 %). Longer reaction times decreased the yield; at 55° no decomposition was observed.

Decomposition on Al_2O_3: A solution of 1 g of $(PhC_2H)_3COFe_2(CO)_5$ was passed through an alumina column (25 × 2 cm). Benzene–ether and ethyl acetate eluted a mixture of (I) and (II) which were separated on a silica gel column. Yields: 0.25 g of (II) and 0.134 g of (I); total yields: 57 %.

c) From 2,4,6-triphenyltropone and $Fe_3(CO)_{12}$. 2,4,6-Triphenyltropone (0.14 g, 0.42 mmole) and $Fe_3(CO)_{12}$ (0.51 g, 1 mmole) were refluxed for 5 h in 20 ml of benzene. The filtered solution was chromatographed on silica gel and yielded in the order of elution 0.065 g (33 %) of (II), 0.035 g (17.5 %) of (I) and 0.035 g (25 %) of unreacted triphenyltropone. The complexes (I) and (II) were identified by their m.p. and IR spectra.

2,4,6-Triphenyltropone from (I) and (II)

a) A solution of 0.72 g (1.52 mmoles) of (I) and 0.82 g (3.13 mmoles) of triphenylphosphine in 10 ml of benzene was heated in a sealed tube for 6 h at 100°. By chromatrography on silica gel 0.98 g (98 %) of $Fe(CO)_3(PPh_3)_2$ was isolated, eluted with benzene and 0.41 g (82 %) of 2,4,6-triphenyltropone, eluted with methylene chloride. The tropone was crystallized from ethanol and yielded yellow crystals of m.p. 127–129°. IR spectrum (in KBr): very strong band at 1587 cm^{-1} ascribed to C=O. (Found: C, 89.89; H, 5.33; O, 5.01. $C_{25}H_{28}O$ calcd.: C, 89.76; H, 5.42; O, 4.79 %.)

The 2,4-dinitrophenylhydrazone of 2,4,6-triphenyltropone was prepared in 80 % yield by using the phosphoric acid–2,4-dinitrophenylhydrazine reagent[24] and was obtained as violet crystals of m.p. 237–238° from dioxane–ethanol. (Found: C, 72.20; H, 4.37; N, 10.33. $C_{31}H_{22}N_4O_4$ calcd.: C, 72.35; H, 4.31; N, 10.89 %.)

b) A solution of 0.95 g (2 mmoles) of (II) and 1.1 g (4.2 mmoles) of PPh_3 in 15 ml of benzene was heated in a sealed tube for 9 h at 100°. After cooling, 1.32 g (quant. yield) of $Fe(CO)_3(PPh_3)_2$ was filtered off. A 72 % yield of 2,4,6-triphenyltropone, partly isolated as its 2,4-dinitrophenylhydrazone, was obtained from the mother liquor. IR spectrum and m.p. were identical with those of the triphenyltropone obtained from (I).

Isomerization of tricarbonyl(2,4,6-triphenyltropone)iron compounds, (I) and (II)

In each experiment (see Table 2) 1 g of pure (I) or (II) was dissolved in 40 ml of benzene and the solution kept in a thermostat. At the indicated time, the solution was chromatographed on silica gel. At room temperature the rate of isomerization is slow enough to enable the separation of (I) and (II) without appreciable error.

Attempted reactions on the ketonic group of (II)

The 2,4-dinitrophenylhydrazone of (II) could not be prepared in EtOH–HCl or by using the phosphoric acid–2,4-dinitrophenylhydrazine reagent[24], even at elevated temperature (5 h at 80°): (II) was partly recovered.

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* Purchased from Gebr. HERMAN, Cologne, Germany and used without any previous treatment; when dried, the separation was less efficient.

Attempts to obtain an oxime of (II) by treating it with $NH_2OH \cdot HCl$ in the presence of NaOH at 80° also failed; the complex was decomposed completely into oily products.

Hydrogenation of (I) and (II)

(I) (1 g), dissolved in 15 ml of benzene, and 0.3 g of a Pd catalyst (10% on charcoal) were heated under a 150 atm pressure of H_2 in a 50 ml rotating autoclave at 50° for 12 h. The filtrate yielded by chromatography on silica gel, besides oily products, *ca.* 0.11 g of a complex (yellow needles of m.p. 141–144°, dec.) which was eluted with benzene. It was extremely sensitive to air and light and could not be obtained analytically pure. According to its IR spectrum, which showed the ketonic group to absorb at 1706 cm^{-1} corresponding to a non-conjugated C=O group, the hydrogenation product of (I) is probably tricarbonyl(2,4,6-triphenyl-3,5-cycloheptadien-1-one)iron; the terminal carbonyl groups absorb at 2036 and 1968 cm^{-1}. In an identical reaction with pure (II) the same hydrogenation product was observed.

Attempted hydrogenation of a mixture of (I) and (II) with zinc in acetic acid–ethyl acetate containing small amounts of HCl led only to decomposition products. The same occurred in an attempted reduction of (II) with $LiAlH_4$ or $NaBH_4$.

(2,4,6-Triphenyltropone)-Fe(CO)$_2$PPh$_3$

A solution of 0.8 g (1.7 mmoles) (II) and 1.55 g (6 mmoles) PPh_3 in 75 ml benzene was refluxed for $2^1/_4$ h. The reaction mixture was chromatographed on silica gel and yielded (in the order of elution): 1.4 g unreacted PPh_3, 0.36 g unreacted (II) (with benzene), 0.21 g (I) (with benzene) formed by isomerization of (II) and 0.21 g (2,4,6-triphenyltropone)-Fe(CO)$_2$PPh$_3$ (with benzene containing some ether). The latter formed dark violet crystals of m.p. 172–177°, dec. and showed infrared absorption bands at 1996 and 1938 cm^{-1} due to the CO ligands; the strong band at 1602 cm^{-1} is ascribed to the ketonic group. From the IR spectrum it was impossible to decide whether this complex derived from (I) or (II); no further attempts have been made in this respect. (Found: C, 76.33; H, 4.71. $C_{45}H_{32}FeO_3P$ calcd.: C, 76.27; H, 4.70%.)

New "phenylacetylene iron carbonyl complexes" from PhC≡CH and Fe$_3$(CO)$_{12}$

Repetition of the reaction between phenylacetylene and dodecacarbonyltriiron under somewhat different conditions and in greater amounts allowed the separation of three new complexes in addition to those described previously[2].

Tricarbonyl(3,4-diphenylcyclopentadienone)iron, (III) was obtained under the following conditions: 45 g (0.09 mole) of $Fe_3(CO)_{12}$ and 56.5 g (0.535 mole) of PhC≡CH were heated in 1 l of light petroleum of b.p. 85°. When after 10 min the green colour of $Fe_3(CO)_{12}$ had disappeared, the warm reaction mixture was filtered and the precipitate extracted with hot benzene. The light petroleum solution was passed over a neutral alumina column (5 × 110 cm) and followed immediately by the benzene extracts. The last fraction, eluted with methanol containing 20% water, gave a yellow brownish fraction which was rechromatographed on silica gel yielding 0.15 g of benzaldehyde*, isolated as its 2,4-dinitrophenylhydrazone, and 1.15 g [3%

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* Benzaldehyde may have been formed from phenylcyclobutenedione, which according to Skattebøl and Roberts[25] readily hydrolyzes to benzaldehyde. Phenylcyclobutenedione has been obtained in this laboratory from $NaHFe(CO)_4$ and PhC≡CH[19].

calcd. on $Fe_3(CO)_{12}$] of (III). The latter was obtained as brownish yellow crystals of m.p. 142–146° dec., from benzene–ether, which are very soluble in benzene and only slightly in light petroleum, ether or methanol. (Found: C, 64.34; H, 3.17; Fe, 15.41; O, 17.28. $C_{20}H_{12}FeO_4$ calcd.: C, 64.55; H, 3.25; Fe, 15.00; O, 17.20%.)

(1,1,1-Tricarbonyl-3,4-diphenylferracyclopentadiene)-π-tricarbonyliron, (IV). Complex (IV) was isolated in small yields [0.4% calculated on $Fe_3(CO)_{12}$] from the combined products of several runs carried out mainly between 50° and 65° in light petroleum–benzene mixtures (ratio 3:1 to 7:1) using about six moles of PhC≡CH for one $Fe_3(CO)_{12}$. The reaction products were chromatographed on silica gel. From the first fraction, eluted with light petroleum–benzene, the solvent and the excess of PhC≡CH were distilled off *in vacuo* and the residue was crystallized from benzene–light petroleum yielding $(PhC_2H)_3Fe_2(CO)_6$ (V). By means of repeated chromatography on alumina and fractional crystallization of the mother liquor 1,2,4-triphenylbenzene[2], 1,3,5-triphenylbenzene and the isomer $(PhC_2H)_2Fe_2(CO)_6$ of m.p. 180° (dec.)[2] are eliminated. From the combined remaining mother liquors, a red oil was distilled off *in vacuo* (b.p. 180–190°) which after addition of light petroleum, yielded (IV) as orange needles of m.p. 125–127°. Complex (IV) is readily soluble in common organic solvents. (Found: C, 54.43; H, 2.33; O, 20.04. $C_{22}H_{12}Fe_2O_6$ calcd.: C, 54.59; H, 2.50; O, 19.83%.)

Reaction of complex (IV) with sulphur. Complex (IV) (0.38 g) and sulphur (0.8 g) were heated together in a test tube for 15 min at 200°. The excess of sulphur was removed by heating the reaction mixture with a concentrated aqueous solution of Na_2S. Chromatography of the benzene extracts on alumina yielded 0.03 g of 3,4-diphenylthiophene, characterized by comparison of its m.p. and IR spectrum with that of an authentic sample[26].

Reaction of (1,1,1-tricarbonyl-2,5-diphenylferracyclopentadiene)-π-tricarbonyliron [$(PhC_2H)_2Fe_2(CO)_6$[2] of m.p. 180°] with sulphur. An intimate mixture of 1 g of complex $(PhC_2H)_2Fe_2(CO)_6$ of m.p. 180° (dec.) and 2 g of sulphur was heated for 5 min at 200°. It was then taken up in dioxane, refluxed for one hour with $Na_2S \cdot 9H_2O$, diluted with water and extracted with benzene. Purification by chromatography yielded 0.35 g (65%) of 2,5-diphenylthiophene (m.p. 153–153.5°) identified by comparison of the IR spectrum with that of a sample prepared according to Melles *et al.*[27] (m.p.[27]: 153–154°).

$(PhC_2H)_3Fe_2(CO)_6$, (V). The highest yield of (V) (6.4%) was obtained by heating 25 g of $Fe_3(CO)_{13}$ with 25 ml of PhC≡CH in a mixture of 650 ml of light petroleum and 200 ml of benzene at 55° for 17 h. Complex (V) was eluted with benzene from silica gel or with benzene–ether from neutral alumina and crystallized from benzene in red violet needles which are only slightly soluble in the common organic solvents. (Found: C, 61.13; H, 3.19; Fe, 19.27; O, 16.38. $C_{30}H_{18}Fe_2O_6$ calcd.: C, 61.47; H, 3.09; Fe, 19.06; O, 16.38%.)

Reaction of $(PhC_2H)_3Fe_2(CO)_6$ (V) with CO under pressure: (Va). Complex (V) (1 g, 1.7 mmole) and 5 ml of light petroleum were placed in a 50 ml rotating autoclave and heated under a pressure of 100 atm of CO for a period of 24 h at 150°. The reaction mixture was dissolved in benzene and chromatographed on silica gel. A deep red complex, (Va), (0.12 g) was eluted with benzene; (Va) crystallized as black crystals (dec. 195–210° without melting) from benzene–light petroleum. IR spectrum: two strong bands at 1988 and 1949 cm⁻¹ for terminal carbonyl, one strong band at 1767 cm⁻¹ ascribed to a bridging carbonyl. (Found: C, 74.35; H, 4.58; O, 7.61; C:H ratio*, $C_{50}:H_{37.94}$. $C_{50}H_{33}Fe_2O_4$ calcd.: C, 73.73; H, 4.70; O, 7.85%; C:H ratio, $C_{50}:H_{33}$.)

Reaction of p-bromophenylacetylene with $Fe_3(CO)_{12}$

a) In light petroleum. (*p*-Bromophenyl)acetylene[29] (36 g, 0.2 mole) and $Fe_3(CO)_{12}$ (20 g, 0.04 mole) were refluxed for 3 h in 2.5 l of light petroleum b.p. 65°. The insoluble products (10.4 g) were filtered off and dissolved in a minimum amount of CS_2. The filtrate of the reaction mixture was passed over an alumina column and was immediately followed by the filtered CS_2 solution. Complex (XI) (2% yield) formed a yellow band which was eluted with light petroleum. This and the next fractions also contained some 1,2,4-tris(*p*-bromophenyl)benzene[30]. Elution with CS_2 yielded about 3% of $(BrC_6H_4C_2H)_3Fe_2(CO)_6$, (XII), usually contaminated with 1,2,4-tris(*p*-bromophenyl)benzene; their separation, though difficult, was effected by fractional crystallization from benzene–methanol. Continued elution with CS_2 or CS_2–C_6H_6 yielded some 1,3,5-tris(*p*-bromophenyl)benzene, m.p. 262°, identified by comparison with an authentic sample[31]. A small amount of $(BrC_6H_4C_2H)_3Fe(CO)_4$, (X), was eluted next with benzene containing some ether. The main band (red brown) was eluted with benzene–ether; evaporation of the solvents yielded an oil which upon addition of ether gave deep red crystals of tricarbonyl[tris(*p*-bromophenyl)tropone]iron, (VIII), in about 20% yield. The presence of the isomeric complex (IX) has not been established with certainty. Small amounts (0.1 g) of a tris(*p*-bromophenyl)tropone were eluted next with benzene–ether. Tricarbonyl[2,5-bis(*p*-bromophenyl)cyclopentadienone]iron, (VI), (1–2% yield) was eluted with acetone or acetone–methanol.

b) In benzene. (*p*-Bromophenyl)acetylene (36 g, 0.2 mole) and $Fe_3(CO)_{12}$ (20 g, 0.04 mole) were stirred for 4½ h at 60° in 100 ml of benzene. The reaction mixture was evaporated to dryness (under reduced pressure) and the residue, dissolved in CS_2, chromatographed on acidic alumina (Woelm). Further working up was as described above with the following differences. The main band (red), eluted with benzene containing a small amount of ether, consisted this time not of (VIII) but of its isomer, (IX), contaminated with some $(BrC_6H_4C_2H)_3Fe(CO)_4$ (X); the separation of (X) from (IX) was achieved by a separate chromatography. The rest of (IX) was found in the next fraction eluted with benzene–ether (1:1) or pure ether; the total yield of (IX) was about 20%. In addition to (VI) minor quantities of its isomer tricarbonyl[3,4-bis(*p*-bromophenyl)cyclopentadienone]iron, (VII), were also isolated from the benzene–methanol fraction.

c) Without solvent. $Fe_3(CO)_{12}$ (10 g, 0.02 mole) was added to 60 g (0.33 mole) of molten *p*-$BrC_6H_4C{\equiv}CH$ and the mixture stirred for 45 min at 65–70°. The unreacted $Fe_3(CO)_{12}$ crystallized out overnight; the reaction mixture was taken up in a minimum amount of CS_2 and chromatographed on acid alumina as described under *a*). The unreacted *p*-$BrC_6H_4C{\equiv}CH$ present in the first fractions was distilled off in a high vacuum together with the solvent and the residue worked up by usual procedures (crystallization or chromatography). Under these conditions $(BrC_6H_4C_2H)_3Fe(CO)_4$, (X), was formed in a 15% yield. Complexes (VII), (VIII) and (XII) were not found in this reaction.

Reaction of p-$BrC_6H_4C{\equiv}CH$ with $Fe(CO)_5$–$Ni(CO)_4$

Tricarbonyl[2,5-bis(p-bromophenyl)cyclopentadienone]iron, (VI). According to the

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* This determination was made according the method published by Unterzaucher[23].

procedure of Jones *et al.*[22], a mixture of 1 ml (1.4 g, 8.2 mmoles) of $Ni(CO)_4$ and 3.8 ml (5.5 g, 28 mmoles) of $Fe(CO)_5$ in ethanol was added to a solution of 12.67 g (70 mmoles) of p-$BrC_6H_4C{\equiv}CH$ in 20 ml of ethanol, 1 ml of water and 4.2 ml of acetic acid and the reaction mixture stirred for 2 h at 60–65°. After cooling 0.54 g [4 % calcd. on $Fe(CO)_5$] of (VI) were filtered off; crystallization from ether–methanol or from acetone gave pale yellow needles of m.p. 247–253° dec. (Found: C, 45.48; H, 2.14; O, 12.35. $C_{20}H_{10}Br_2FeO_4$ calcd.: C, 45.32; H, 1.90; O, 12.08 %.)

Other "(p-bromophenyl)acetylene iron carbonyl complexes"

Tricarbonyl[3,4-bis(p-bromophenyl)cyclopentadienone]iron, (VII), crystallized from CS_2 or ether in yellow needles of m.p. 185–200°, dec. This complex was more strongly absorbed on alumina than its isomer (VI). (Found: C, 45.16; H, 1.89; Fe, 10.79; O, 12.24. $C_{20}H_{10}Br_2FeO_4$ calcd.: C, 45.32; H, 1.90; Fe, 10.54; O, 12.08 %.)

Tricarbonyl[tris(p-bromophenyl)tropone]iron, (VIII). Complex (VIII) formed well-shaped dark red crystals from CS_2–light petroleum or from benzene–methanol. They melted at 199–205° with decomposition; from the melt, needles crystallized out which melted at 245° [probably tris(p-bromophenyl)tropone; see thermal decomposition of (VIII)]. (Found: C, 47.80; H, 2.29; Br, 34.00, 33.33; Fe, 7.82; O, 9.10. $C_{28}H_{15}Br_3FeO_4$ calcd.: C, 47.30; H, 2.12; Br, 33.72; Fe, 7.86; O, 9.00 %.)

Tris(p-bromophenyl)tropone. Complex VIII (1 g, 1.4 mmole) was heated with a 10 % excess of PPh_3 (0.825 g, 3.1 mmoles) in 20 ml of benzene at 110° for 9 h in a sealed tube. Yellow needles (0.33 g, m.p. 263–270°) of tris(p-bromophenyl)tropone crystallized out upon cooling. The filtrate was chromatographed on silica gel in order to separate $Fe(CO)_3(PPh_3)_2$ (0.43 g, eluted with benzene) from the remaining tropone (0.20 g, eluted with CH_2Cl_2); its total yield amounted to 0.53 g (65 %). The tropone was recrystallized from THF–EtOH or better from toluene giving thin needles of m.p. 268–274° (transition point at 60°); it is only slightly soluble in cold benzene or acetone and was eluted with ether or acetone from alumina. Sublimation occurred at 220° *in vacuo*. IR spectrum: strong band at 1582 cm^{-1} and medium band at 1623 cm^{-1} ascribed to the C=O and C=C groups respectively[6]. (Found: C, 52.97; H, 2.94; O, 3.08. $C_{25}H_{15}Br_3O$ calcd.: C, 52.57; H, 2.65; O, 2.80 %.)

Thermal decomposition of (VIII). Complex (VIII) (0.2 g) was refluxed for 3 h in xylene. The mixture was filtered with charcoal and the filtrate evaporated to dryness. Crystallization of the residue from a small amount of THF and ethanol gave also tris(p-bromophenyl)tropone.

Tricarbonyl[tris(p-bromophenyl)tropone]iron, (IX). When crystallized from ether, (IX) was obtained in thin yellow needles of m.p. 166–175° dec. whereas, in the presence of benzene, (IX) crystallized with half a mole of benzene in thick red brown crystals of m.p. 154–165° dec. The IR spectra of both crystal forms are identical and resemble closely that of the isomer (VIII). (Found: C, 47.15; H, 2.11; O, 9.26. $C_{28}H_{15}Br_3FeO_4$ calcd.: C, 47.30; H, 2.12; O, 9.00 %. Found: C, 49.61; H, 2.42; O, 8.59. $C_{31}H_{18}Br_3FeO_4$ calcd.: C, 49.64; H, 2.42; O, 8.53 %.)

$(BrC_6H_4C_2H)_5Fe(CO)_4$, (X). Compound (X) crystallized from benzene or ether in thin brown needles of m.p. 240–260°, dec.; it was eluted from acid alumina by means of benzene containing small amounts of ether. (Found: C, 49.76; H, 2.48; Fe, 5.18; O, 6.25. $C_{44}H_{25}Br_5FeO_4$ calcd.: C, 49.24; H, 2.35; Fe, 5.20; O, 5.96 %.)

[1,1,1-Tricarbonylbis(p-bromophenyl)ferracyclopentadiene]-π-tricarbonyliron, (XI).

Complex (XI) was obtained from acetone–methanol in orange yellow hexagonal plates of m.p. 208–215°, dec. which could be sublimed at 120–150° *in vacuo*. It is readily soluble in benzene, methylene chloride, chloroform, less in ether, alcohols and light petroleum. The infrared CO absorption pattern is similar to that of the other ferracyclopentadiene-π-tricarbonyliron complexes[1,2]. (Found: C, 41.46; H, 1.54; Br, 25.08; Fe, 17.38; O, 15.05. $C_{22}H_{10}Br_2Fe_2O_6$ calcd.: C, 41.17; H, 1.58; Br, 24.90; Fe, 17.39; O, 14.96%.)

$(BrC_6H_4C_2H)_3Fe_2(CO)_6$, (XII). Crystallization of (XII) from benzene–methanol gave red violet crystals which decomposed without melting at *ca.* 200°, the habit of the crystals remaining unchanged up to 320°. Complex (XII) is readily soluble in conventional solvents, even in light petroleum. (Found: C, 44.21; H, 1.98; Br, 29.14; Fe, 13.56; O, 11.77. $C_{30}H_{15}Br_3Fe_2O_6$ calcd.: C, 43.78; H, 1.84; Br. 29.14; Fe, 13.57; O, 11.67%.)

ACKNOWLEDGEMENTS

The authors wish to express their thanks to Messrs. J. NIELSEN, J. VANDEWALLE and R. VANNIEUWENHOVEN for valuable technical assistance and to Dr. J. F. M. OTH for the NMR measurements.

SUMMARY

Preparation and structure of the two tricarbonyl(2,4,6-triphenyltropone)iron complexes are described and their isomerism discussed together with some of their reactions. Three new complexes deriving from the reaction of phenylacetylene and dodecacarbonyltriiron are reported as well as seven complexes obtained from *p*-bromophenylacetylene and $Fe_3(CO)_{12}$.

REFERENCES

1 W. HÜBEL, E. H. BRAYE, A. CLAUSS, E. WEISS, U. KRÜERKE, D. A. BROWN, G. S. D. KING AND C. HOOGZAND, *J. Inorg. Nucl. Chem.*, 9 (1959) 204.
2 W. HÜBEL AND E. H. BRAYE, *J. Inorg. Nucl. Chem.*, 10 (1959) 250.
3 G. N. SCHRAUZER, *J. Am. Chem. Soc.*, 81 (1959) 5307.
4 E. H. BRAYE, C. HOOGZAND, W. HÜBEL, U. KRÜERKE, R. MERÉNYI AND E. WEISS, in ST. KIRSCHNER, *Advances in the Chemistry of the Coordination Compounds*, Macmillan, New York, 1961, p. 190.
5 E. WEISS AND W. HÜBEL, *J. Inorg. Nucl. Chem.*, 11 (1959) 42.
6 E. WEISS AND W. HÜBEL, *Chem. Ber.*, 95 (1962) 1179.
7 G. S. D. KING, *Acta Cryst.*, 15 (1962) 243.
8 D. A. BROWN, *J. Inorg. Nucl. Chem.*, 13 (1960) 212.
9 D. L. SMITH AND L. F. DAHL, *J. Am. Chem. Soc.*, 84 (1962) 1743.
10 R. P. DODGE AND V. SCHOMAKER, private communication, 1961.
11 B. DICKENS AND W. N. LIPSCOMB, *J. Am. Chem. Soc.*, 83 (1961) 4862.
12 M. R. CHURCHILL AND R. MASON, *Proc. Chem. Soc.*, (1963) 365.
13 B. F. HALLAM AND P. L. PAUSON, *J. Chem. Soc.*, (1958) 642.
14 M. L. GREEN, L. PRATT AND G. WILKINSON, *J. Chem. Soc.*, (1959) 3753.
15 H. J. DAUBEN, JR. AND H. J. RINGOLD, *J. Am. Chem. Soc.*, 73 (1951) 876.
16 W. VON E. DOERING AND F. L. DETERT, *J. Am. Chem. Soc.*, 73 (1951) 876.
17 G. N. SCHRAUZER, *Chem. Ind. (London)*, (1958) 140.
18 E. H. BRAYE AND W. HÜBEL, unpublished results.
19 E. WEISS, W. HÜBEL AND R. MERÉNYI, *Chem. Ber.*, 95 (1962) 1155.
20 M. VAN MEERSSCHE, *Ind. Chim. Belge*, (1963) 507.

21 E. Weiss and H. Hübel, *Chem. Ber.*, 95 (1962) 1186.
22 E. R. H. Jones, P. C. Wailes and M. C. Whiting, *J. Chem. Soc.*, (1955) 4021.
23 M. van Meerssche, private communication.
24 Houben-Weyl, *Die Methoden der Organischen Chemie*, Vol. 2, Georg Thieme Verlag, Stuttgart, 1953, p. 449.
25 L. Skattebol and J. D. Roberts, *J. Am. Chem. Soc.*, 85 (1958) 4085.
26 H. J. Backer and W. Stevens, *Rec. Trav. Chim.*, 59 (1940) 423.
27 J. L. Melles and H. J. Backer, *Rec. Trav. Chim.*, 72 (1953) 314, 491.
28 J. Unterzaucher, *Microchim. Acta*, (1957) 448.
29 Ch. Dufraisse and A. Dequesnes, *Bull. Soc. Chim. France*, 49 (1931) 1880.
30 W. Hübel and C. Hoogzand, *Chem. Ber.*, 93 (1960) 103.
31 R. E. Lyle, E. J. DeWitt, N. M. Nichols and W. Cleland, *J. Am. Chem. Soc.*, 75 (1953) 5959.