ORGANOMETALLIC COMPLEXES

XVI[*]. FERRAINDENEIRON AND INDENONEIRON CARBONYL COMPLEXES

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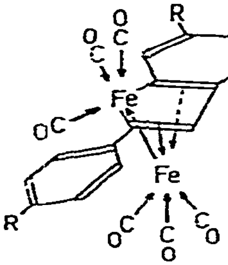
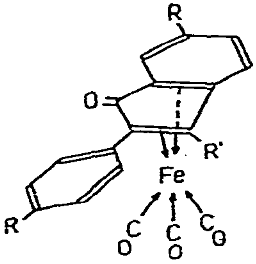
A compound of formula $PhC_2PhFe_2(CO)_6$, (I), formed from diphenylacetylene and dodecacarbonyltriiron together with other complexes has been described in a previous publication[1]. Bis(*p*-chlorophenyl)acetylene gives the same types of complex including $ClC_6H_4C_2C_6H_4ClFe_2(CO)_6$, (II), and in addition a compound of composition $ClC_6H_4C_2C_6H_4ClCOFe(CO)_3$, (III). A recent X-ray analysis[2,3] of (I) has shown it to be a (1,1,1-tricarbonylferraindene)-π-tricarbonyliron complex. Thus, (I) and (II) belong formally to the class of (1,1,1-tricarbonylferracyclopentadiene)-π-tricarbonylirons[1,4]. The migration of an aromatic hydrogen, involved in the formation of the ferraindene system, is surprising in view of the mild reaction conditions[1].



(I) R = H
(II) R = Cl



(III) R = Cl; R' = H
(IV) R = H; R' = Ph

The infrared spectrum of (III) has two bands for terminal carbonyl ligands; the strong band at 1623 cm^{-1}, which is also observed in the case of tricarbonylcyclopentadienoneiron complexes[5] is ascribed to a polarized ketonic group. Elemental analysis and infrared data thus both point to an indenone-π-tricarbonyliron structure for (III). In order to prove the existence of this new type of complex, 2,3-diphenylindenone was reacted with $Fe_3(CO)_{12}$ to give the expected tricarbonyl(2,3-diphenylindenone)iron, (IV). The stretching frequency of the ketonic group is shifted from 1700 cm^{-1} to 1631 cm^{-1} by complex formation, a shift which is approximately of the same magnitude as with cyclopentadienones[5]. Comparable values have also been found for 6-chloro-2-(*p*-chlorophenyl)indenone (1698 cm^{-1}) and (III) (1623 cm^{-1}).

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The formation of (III) most probably proceeds by replacement of the ring-bonded Fe(CO)$_3$ group in (II) by carbon monoxide as was found for (1,1,1-tricarbonyl-ferracyclopentadiene)-π-tricarbonyliron complexes; such conversions can be achieved under various conditions: action of air, light, bromine[4] or CO under pressure[1,4,6]. In an attempted preparation of (III) from (II), the latter was heated at 250° under CO pressure, but led directly to the free 6-chloro-2-(*p*-chlorophenyl)indenone; at lower temperatures no reaction took place.

The existence of tricarbonylindenoneiron complexes is of interest because only diolefins have so far been shown to form tricarbonyliron π-complexes (*cf.* ref. 7). It is a characteristic feature of the indenone as well as of the (tricarbonylferraindene)-π-Fe(CO)$_3$ complexes that the Fe(CO)$_3$ residue is π-bonded to only one true olefinic bond and to a part of an aromatic system. The question arises, of how far the aromatic character of the condensed benzene ring is affected in these types of complex.

The possibility that the π-bonded Fe(CO)$_3$ group induces a localization of the double bonds, thus stabilizing a Kekulé structure has been found in diindenyliron[8] and in cyclopentadienylindenyliron[9]. The olefinic nature of part of the condensed benzene ring is demonstrated by the ease of hydrogenation of both compounds[9,10].

In order to investigate the nature of the benzene ring in these ferraindene- and indenoneiron carbonyls a number of chemical reactions has been carried out. Since hydrogenation failed because of the poisoning of the catalyst, (I) and (IV) were treated with the powerful dienophile 4-phenyl-1,2,4-triazoline-3,5-dione[11] but no Diels-Alder addition took place. Neither did any reaction occur between (IV) and tetracyanoethylene. Attempted complex formation of the "butadiene part" of (II) by treating this complex with Fe$_2$(CO)$_9$ at room temperature for 3 days or by ultraviolet irradiation of a solution of (II) mixed with Fe(CO)$_5$ was also unsuccessful. From these reactions it must be concluded that the aromaticity of the benzene ring in the ferraindene and indenone systems is not appreciably disturbed by complex formation and that the two π-electrons donating to the iron atom still participate in an aromatic sextet. Further support for this interesting result derives from the NMR spectrum of (I) which has all proton signals located in the aromatic region (τ = 2.3–3.0).

The X-ray measurements[3] of (I) favour a butadiene structure of the condensed benzene ring. An alternate deviation from the standard C–C distances in benzene rings, however, does not necessarily imply a loss of aromaticity as has been shown in 2,2'-dichlorobenzidine[12] or in *m*-toluidine hydrochloride[13], where the alternate long and short distances were found to differ more than in (I).

EXPERIMENTAL*

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

Preparation of bis(p-chlorophenyl)acetylene via 4,4'-dichlorobenzil dihydrazone

p,p'-Dichlorobenzil was prepared by oxidation of the corresponding benzoin by means of NH$_4$NO$_3$/Cu(OAc)$_2$[14] in yields of 91 %. Hydrazine hydrate (14.5 ml ,0.3 mole) was slowly added to 27.9 g (0.1 mole) of *p,p'*-dichlorobenzil dissolved in 110 ml of

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

boiling dioxane, and the mixture refluxed for 65–70 h. After addition of 300 ml water the reaction mixture was extracted with ether and the ethereal layer worked up to a syrupy residue. Recrystallization from benzene–light petroleum gave 28.2 g (92%) of 4,4'-dichlorobenzil dihydrazone, colourless needles of m.p. 100–101°. (Found: N, 18.05. $C_{14}H_{12}Cl_2N_4$ calcd.: N, 18.24%.)

Oxidation of 4,4'-dichlorobenzil dihydrazone with HgO[15] led to bis(*p*-chlorophenyl)acetylene in yields of 77%, m.p. 178° (lit.[16] 175–176°).

Reaction of bis(p-chlorophenyl)acetylene with dodecacarbonyltriiron

A suspension of 25 g (0.05 mole) of $Fe_3(CO)_{12}$ and 30 g (0.12 mole) of bis(*p*-chlorophenyl)acetylene in 4 l light petroleum (b.p. 80°) was refluxed until the green colour of $Fe_3(CO)_{12}$ had disappeared (about 3 h). The reaction mixture was worked up by chromatography as described previously[1] leading to tetrakis(*p*-chlorophenyl)cyclopentadienone[17] and the organoiron carbonyls listed in Table 1 in the order of elution from Al_2O_3; they have the same properties as the corresponding compounds deriving from diphenylacetylene[1].

Tricarbonyl(2,3-diphenylindenone)iron, (IV)

2,3-Diphenylindenone[18] (3.5 g) and $Fe_3(CO)_{12}$ (8.7 g) were refluxed in a benzene–toluene mixture of b.p. 85° for 2 h. A brown powder was filtered off and the solution chromatographed on silica gel. Unreacted indenone (1.0 g) was eluted with benzene–methylene chloride and (IV) (red band) taken off with ether; this fraction was evaporated *in vacuo* and the residue recrystallized from ethanol–light petroleum yielding 1.5 g (40%) (IV) as brownish-red crystals of m.p. 128–132° (dec.). (Found: C, 68.60; H, 3.40; Fe, 12.90. $C_{24}H_{14}FeO_4$ calcd.: C, 68.27; H, 3.34; Fe, 13.23%.) IR spectrum (KBr): C≡O: 2066, 2016 and 1984 cm^{-1}; C=O: 1631 cm^{-1}.

Reaction of [1,1,1-tricarbonyl-2-(p-chlorophenyl)-6-chloroferraindene]-π-tricarbonyliron, (II), with CO: 2-(p-chlorophenyl)-6-chloroindenone

A 50 ml rotating autoclave was charged with a solution of 0.2 g of (II) in 5 ml benzene and 85 atm of carbon monoxide and was heated at 250° for 15 h. The filtered reaction mixture was chromatographed on silica gel. No complex was recovered. Benzene eluted a yellow band which gave a yellow solid on concentration; recrystallization from ether–light petroleum led to 0.04 g of strongly fluorescent orange crystals of m.p. 219–221°; according to the infrared spectrum and analysis it was the expected 2-(*p*-chlorophenyl)-6-chloroindenone. (C=O at 1698 cm^{-1}; found: C, 65.18; H, 3.07. $C_{15}H_8Cl_2O$ calcd.: C, 65.47; H, 2.93%.)

Attempted Diels-Alder reactions

4-Phenylurazole (0.1115 g, 0.65 mmole) was oxidized to 4-phenyl-1,2,4-triazoline-3,5-dione[11] by adding about 0.6 mmole of *tert*-butyl hypochlorite in acetone solution at −70°. Then 0.3 g (0.65 mmole) of (I) dissolved in 20 ml acetone was added under nitrogen and the mixture allowed to warm up slowly to 25°. Acetone was replaced by benzene and the reaction mixture worked up by chromatography on silica gel. The sole compound obtained was 0.19 g of (I). In a similar reaction using 1 g of (IV) 0.6 g of the unchanged complex was the only product recovered.

TABLE I

COMPLEXES FROM $ClC_6H_4C{\equiv}CC_6H_4Cl$ AND $Fe_3(CO)_{12}$

Formula[a]	*Yield* %	*Colour*	*M.p. °C*	*Wavenumber (cm⁻¹) of IR absorption bands (KBr)*		*Empirical formula*	*Analyses* *Found* *Calcd.*				
				CO ligand	*ketonic CO*		*C*	*H*	*Cl*	*Fe*	*O*
$RFe_2(CO)_6$, (II)	0.5–2	red	175	2075, 2037, 1988, 1923	—	$C_{20}H_8Cl_2Fe_2O_6$			13.89 13.46	21.12 21.20	
$R_2Fe_2(CO)_6$[b]	20–25	orange	133–135 or 185–188 (dec.)	2070, 2037, 1988, 1923	—	$C_{34}H_{16}Cl_4Fe_2O_6$	52.51 52.76	2.40 2.08	18.14 18.32	14.65 14.43	
$R_2Fe_3(CO)_8$[c]	15–20	black	215–220 (dec.)	2058, 2008, 1972, 1859[d], 1848[d]	—	$C_{36}H_{16}Cl_4Fe_3O_8$			15.97 16.01	19.17 18.92	
$R_2COFe_2(CO)_6$	5–10	red	200–220 (dec.)	2070, 2049, 2016	1667	$C_{35}H_{16}Cl_4Fe_2O_7$	52.55 52.41	2.11 2.02	17.74 17.68	13.89 13.93	14.14 13.96
$RCOFe(CO)_3$, (III)	[e]	red	189–200 (dec.)	2075, 2004	1623	$C_{18}H_8Cl_2FeO_4$	52.50 52.09	2.25 1.94			15.32 15.42
$R_2COFe(CO)_3$[f]	2–5	yellow	175–180 (dec.)	2070, 2016, 2000	1645						

[a] $R = ClC_6H_4C_2C_6H_4Cl$. [b] $\mu_D = 1.44 \pm 0.15$ D. [c] $\chi_{Mol}^{293°K} = (-7.44 \pm 25) \cdot 10^{-6}$ cm³/Mol; the complex crystallizes also with one mole of C_6H_6. [d] Ascribable to bridging carbonyl groups. [e] Was only found occasionally. [f] Has also been prepared from tetrakis(*p*-chlorophenyl)cyclopentadienone and $Fe_2(CO)_9$[5].

Under the same conditions butadiene gave the corresponding Diels-Alder adduct[11] of m.p. 160–162° in a 70% yield.

A sample of 0.5 g of (IV) was refluxed with 0.25 g tetracyanoethylene in 20 ml of benzene for 1 h. By chromatography on silica gel only the starting materials, 0.35 g (IV), were recovered together with some 2,3-diphenylindenone.

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SUMMARY

The formation of stable (1,1,1-tricarbonylferraindene)-π-tricarbonyliron complexes and tricarbonylindenoneirons is described. It appears from chemical reactions that the condensed benzene ring in these types of complex remains aromatic in character in spite of its donation of electrons to an Fe(CO)$_3$ group. Other complexes deriving from bis(*p*-chlorophenyl)acetylene and dodecacarbonyltriiron are also described.

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