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A NEW REARRANGEMENT IN THE REACTION OF HALOGENS WITH σ-(*o*-CARBORAN-3-YL)-π-CYCLOPENTADIENYLIRONDICARBONYL

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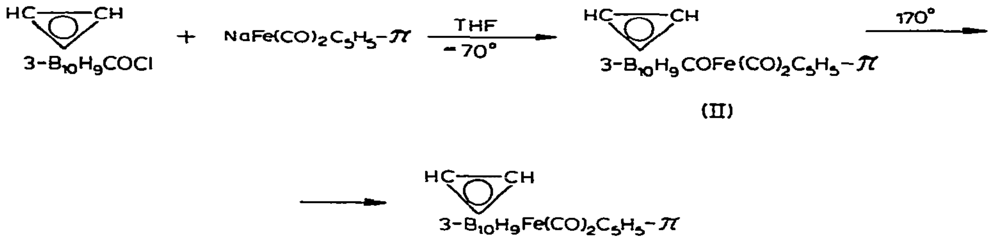
SUMMARY

A new rearrangement has been discovered in the reaction of chlorine and bromine with σ-(*o*-carboran-3-yl)-π-cyclopentadienylirondicarbonyl*. This involves a cleavage of the boron–iron σ-bond and a migration of 3-*o*-carboranyl group to the cyclopentadienyl ring giving π-[(*o*-carboran-3-yl)cyclopentadienyl]dicarbonyliron chloride or bromide. Under similar conditions the action of chlorine and bromine on σ-(1,2-dimethyl-*o*-carboran-3-yl)-π-cyclopentadienylirondicarbonyl results in a migration of the 3-*o*-carboranyl group to the CO group instead of the cyclopentadienyl ring. However, the reactions of both carborane complexes with PPh_3 and $HgCl_2$ are similar, giving rise to exchange products of one carbonyl ligand with PPh_3 and mercury carborane compounds with the boron–mercury bond.

We reported briefly earlier[1] on a synthesis of the first stable *o*-carborane compound containing a boron–iron σ-bond: σ-(*o*-carboran-3-yl)-π-cyclopentadienylirondicarbonyl (I)*. The proposed structure and numbering system of compound (I) is shown in Fig. 1. The compound was obtained from the readily available 3-*o*-carborane carboxylic acid chloride[2]:



(II)

(I)

In the same manner 1,2-dimethyl-3-*o*-carborane carboxylic acid chloride led to σ-(1,2-dimethyl-*o*-carboran-3-yl)-π-cyclopentadienylirondicarbonyl (III):

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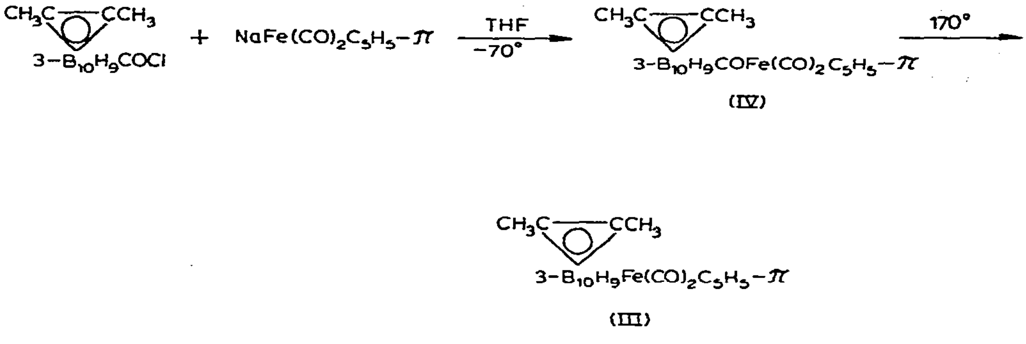
* *o*-Carborane = 1,2-dicarbaclosododecaborane(12).



Compounds (II) and (III) are light-yellow crystalline solids stable in air. In solution or in the absence of solvent they are not noticeably decomposed on heating to 180°. Table 1 shows the PMR data of compounds (I) and (III) and of the acyl complexes (II) and (IV). The PMR spectra of compounds (I)–(IV) display a narrow single signal with relative intensity 5 (δ 4.88–4.97) corresponding to the π-Cp-ligand protons. This chemical shift occurs in the spectral region characteristic of many similar compounds[3,4]. In addition, compounds (I) and (II) exhibit a broad signal from the carborane protons (relative intensity 2) and the compounds (III) and (IV) show the methyl group singlet (relative intensity 6). The IR spectra also confirm structures (I)–(IV).

Other workers[5,6] have found that in compounds of the type σ-RFe$(CO)_2$-C_5H_5-π cleavage of the R–Fe σ-bond occurs under action of halogens according to the scheme:

$$\sigma\text{-RFe(CO)}_2\text{C}_5\text{H}_5\text{-}\pi + \text{X}_2 \rightarrow \text{RX} + \text{XFe(CO)}_2\text{C}_5\text{H}_5\text{-}\pi \quad \text{where X} = \text{halogen.}$$

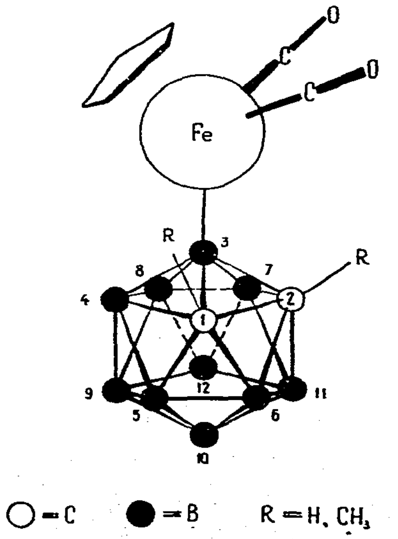
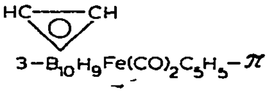
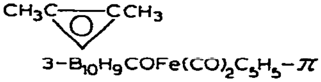
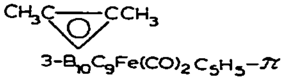
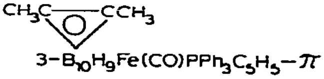
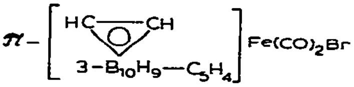
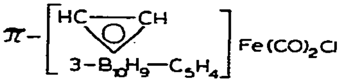
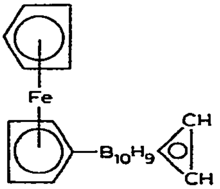
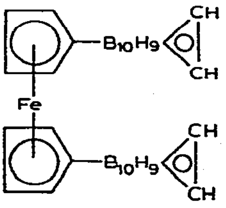


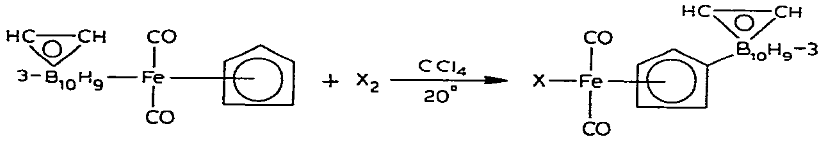
Fig. 1. The proposed structure and numbering system for 3-[π-$C_5H_5Fe(CO)_2$]-σ-$B_{10}C_2H_{11}$ and its 1,2-dimethyl derivative.

TABLE 1

THE ^{1}H NMR SPECTRA OF 3-o-CARBORANE COMPOUNDS CONTAINING A B–Fe BOND AND OF 3-o-SUBSTITUTED Cp DERIVATIVES OF Fe

	Compound	*Solvent*	*δ(Cp)*	*δ(CH)*	*δ(CH$_3$)*
(II)	 $\overset{HC\text{—}CH}{3\text{-}B_{10}H_9COFe(CO)_2C_5H_5\text{-}\pi}$	CCl_4	4.91	3.38	
(I)	 $\overset{HC\text{—}CH}{3\text{-}B_{10}H_9Fe(CO)_2C_5H_5\text{-}\pi}$	CCl_4	4.96	3.36	
(IX)	 $\overset{HC\text{—}CH}{3\text{-}B_{10}H_9Fe(CO)PPh_3C_5H_5\text{-}\pi}$	$CHCl_3$ C_6H_6	4.44 4.28	2.25; 2.80 2.38; 2.98	
(IV)	 $\overset{CH_3C\text{—}CCH_3}{3\text{-}B_{10}H_9COFe(CO)_2C_5H_5\text{-}\pi}$	CCl_4	4.88		1.87
(III)	 $\overset{CH_3C\text{—}CCH_3}{3\text{-}B_{10}C_9Fe(CO)_2C_5H_5\text{-}\pi}$	CCl_4	4.97		2.03
(X)	 $\overset{CH_3C\text{—}CCH_3}{3\text{-}B_{10}H_9Fe(CO)PPh_3C_5H_5\text{-}\pi}$	$CHCl_3$ C_6H_6	4.33 4.17		0.86; 2.03 0.94; 1.98
(V)	 $\pi\text{-}\left[\overset{HC\text{—}CH}{3\text{-}B_{10}H_9\text{—}C_5H_4}\right]Fe(CO)_2Br$	$CDCl_3$	4.73; 5.33	4.33	
(VI)	 $\pi\text{-}\left[\overset{HC\text{—}CH}{3\text{-}B_{10}H_9\text{—}C_5H_4}\right]Fe(CO)_2Cl$	Acetone	5.07; 5.66	4.83	
(VIII)		$CHCl_3$	4.28 broad	3.52	
(VII)			4.34; 4.44	3.56	

We have attempted to use this reaction for determining the position of the iron atom in the *o*-carborane nucleus in compounds (I) and (III); in this case *B*-monohalide-*o*-carboranes were expected in which the position of the halogen could be easily verified as described elsewhere[7,8]. It was found, however, that halogens react with (I) and (II) in a somewhat different manner. On investigating this reaction we have observed two novel rearrangements. The reaction of (I) with bromine and chlorine in CCl_4 is fast at room temperature, but instead of yielding *B*-bromo(chloro)-*o*-carborane as expected[7] the reaction led to an almost quantitative yield of π-[(*o*-carboran-3-yl)cyclopentadienyl]dicarbonyliron bromide (V) and π-[(*o*-carboran-3-yl)-cyclopentadienyl]dicarbonyliron chloride (VI). Unlike bromine and chlorine, iodine does not react under the same conditions even upon refluxing in CCl_4.



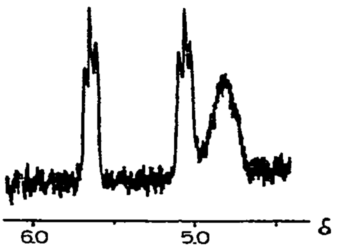
(I)

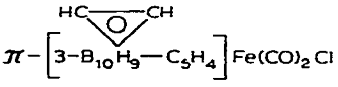
(V) X = Br
(VI) X = Cl

Thus, the reactions of Br_2 and Cl_2 with (I) occur through the cleavage of a B–Fe σ-bond with the migration of the 3-*o*-carboranyl group from iron to the cyclopentadienyl group. In this case the 3-*o*-carboranyl group replaces a hydrogen atom of the cyclopentadienyl ring which is eliminated as the halide HX (X=Cl, Br). It is quite surprising that the rearrangement occurs so easily and so rapidly. The structures of compounds (V) and (VI) were established from IR and PMR data. In addition, the NQR spectrum and polarographic reduction of (V) were investigated. The PMR spectra of (V) and (VI) (Table 1) exhibit, in addition to a broad single signal from the CH carborane protons (relative intensity 2), two triplets of the AA′BB′ system (intensity ratio 2/2) (Fig. 2). Such a spectral pattern is specific to transition metal compounds mono-substituted at the π-Cp cycle.

The IR spectroscopic data also support the proposed structure for (V).

The CO stretching region of the IR spectrum of $CpFe(CO)_2R$ should exhibit two bands corresponding to the symmetric (high-frequency band) and antisymmetric





$$\pi\text{-}\left[3\text{-}\overset{HC\text{—}CH}{B_{10}H_9}\text{—}C_5H_4\right]Fe(CO)_2Cl$$

Fig. 2. The ^{1}H NMR spectrum (60 MHz) of π-[3-$B_{10}H_9$(HC—CH)—C_5H_4]$Fe(CO)_2Cl$ (in acetone).

(low-frequency band) CO modes. The positions of these bands are essentially determined by the nature of the substituent R. As reported previously[9] a linear correlation was observed between the frequencies of these bands and the inductive constant σ_I for the R substituent at the Fe atom. The frequencies increase as the electron-withdrawing nature of R increases from a value of 1946 and 2006 cm^{-1} for R=Me to 2004 and 2052 cm^{-1} for R=CN (in THF).

For compound (I) the respective bands were observed at 1960 and 2020 cm^{-1} indicating that the 3-o-carboranyl group is a moderate acceptor and comparable to p-Cl–C_6H_4 (1963 and 2016 cm^{-1} respectively).

An explanation can be provided for the specific pattern observed in the spectrum of (V). Firstly, the IR spectrum of this compound indicates that the carborane nucleus is retained in the molecule. Secondly, introduction of a bromine atom directly attached to the iron atom mainly increases the value of ν(CO) (1996 and 2041 cm^{-1} for CpFe$(CO)_2$Br). The presence of an electron-attracting carborane substituent in the Cp-ring however increases the frequencies still further to 2020 and 2060 cm^{-1}.

The IR spectrum (400–700 cm^{-1}) suggests that bromine atom insertion occurs directly at the iron atom. The carborane nucleus has no absorption in this region and this suggests that over this spectral region compound (V) should be similar to Cp$(CO)_2$FeBr; this is observed experimentally: (frequencies, cm^{-1}) compound (V): 440 m, 482 m, 535 vs, 565 vs, 605 vs; Cp$(CO)_2$FeBr: 440 m, 485 m, 540 vs, 570 vs, 605 vs. With the starting material, compound (I), where the carborane substituent is directly attached to the Fe atom, a slightly different spectrum is observed: 450 m, 470 m, 524 m, 555 w, 590 m, 610 vs, 645 vs, 667 w, 682 m.

The presence of a substituent in the Cp-ring is usually apparent from the absence of absorption in the IR spectrum at 1000 and 1100 cm^{-1} in comparison with that of the unsubstituted ligand. In this study such a comparison was not possible due to the strong absorption of the carborane nucleus in this region. However, the presence of the carborane substituent in the Cp-ring was indicated in this case by the presence of an intense band in the spectral region 1270–1280 cm^{-1}, such a band being also present in the spectrum of (VII) but absent from the spectra of both ferrocene, C_5H_5-$(CO)_2$FeBr and o-carborane. This band is apparently due to C–B vibrations.

Thus, the IR spectral data are in good agreement with the structure assumed for compound (V).

Similar conclusions supporting the structure of (VI) were also obtained on the basis of IR data for compound (VI) and CpFe$(CO)_2$Cl.

In the NQR spectrum of (V) the ^{81}Br frequency observed at −117.72 MHz is close to that of unsubstituted π-cyclopentadienyldicarbonyliron bromide (−123.80 MHz). The low-frequency shift is probably due to an electron-attractive effect of the carborane substituent, and since for a C–B bond in the Cp-ring the ^{81}Br NQR frequency should be about 250–260 MHz[11], the NQR data unequivocally support B–Fe bond formation.

The presence of an Fe–B bond is also supported by polarographic reduction studies of compound (V). It is known[12] that π-C_5H_5Fe$(CO)_2$Br is reduced at the dropping mercury electrode with cleavage of the Fe–Br σ-bond. In this case two waves corresponding to the following processes are observed: the first wave ($E_{\frac{1}{2}} = -0.66$ V; $i_d = 2.60$ μA) corresponds to

$$\begin{tikzcd}
\pi\text{-}C_5H_5Fe(CO)_2Br \arrow[r, "+e"] & {[\pi\text{-}C_5H_5Fe(CO)_2]^{\cdot}} + Br^- \arrow[d] \arrow[dr] & \\
 & \frac{1}{2}[\pi\text{-}C_5H_5Fe(CO)_2]_2Hg & \frac{1}{2}[\pi\text{-}C_5H_5Fe(CO)_2]_2
\end{tikzcd}$$

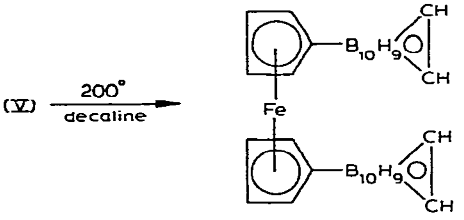
while the second wave ($E_{\frac{1}{2}} = -1.6$ V; $i_d = 2.3$ μA) corresponds to

$$[\pi\text{-}C_5H_5Fe(CO)_2]_2 \xrightarrow{+2e} [\pi\text{-}C_5H_5Fe(CO)_2]^-$$

In addition, the maximum observed at the potential ≈ -1.2 V indicates that a partial reaction occurs between the radical $[C_5H_5Fe(CO)_2]^{\cdot}$ and the mercury of the electrode. With similar experimental conditions the polarogram of (V) is found to be very similar to that of π-$C_5H_5Fe(CO)_2Br$, possessing two waves: the first wave $E_{\frac{1}{2}} = -0.45$ V, $i_d = 2.0$ μA, and the second wave: $E_{\frac{1}{2}} = -1.44$ V, $i_d = 1.6$ μA, and also a maximum at -1.2 V. The polarogram of (I) exhibits only one wave when reduction is effected under the same conditions ($E_{\frac{1}{2}} = -200$ V, $i_d = 3.10$ μA).

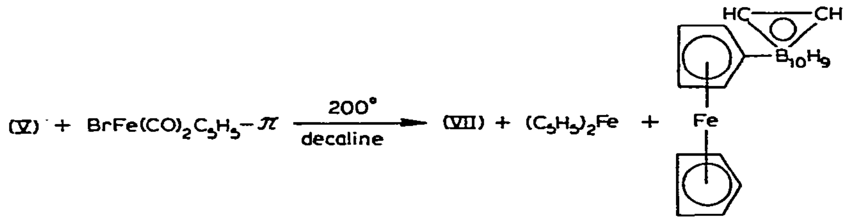
From this is follows that the data for the polarographic reduction of compound (V) are also in agreement with the suggestion that its structure contains a Fe–B bond. The shift of $E_{\frac{1}{2}}$ for the first and second waves towards lower negative potentials in comparison with those of the model compound $CpFe(CO)_2Br$ may be related to the electron attractive effect of the 3-*o*-carboranyl substituent in the Cp-ring.

A number of chemical reactions were also studied in order to confirm the structure of (V). Thus it is known that compounds of the type X–$Fe(CO)_2C_5H_5$-π (X = Cl, Br)[13,14] transform to ferrocene on heating. When compound (V) was heated in decaline at 200° a satisfactory yield of 1,1′-bis(*o*-carboran-3-yl)ferrocene (VII) was obtained:



(VII)

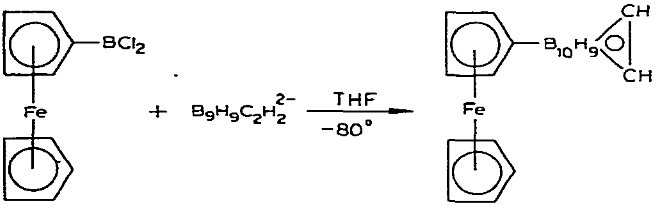
When the reaction was carried out in the presence of $BrFe(CO)_2C_5H_5$-π, (*o*-carboran-3-yl)ferrocene (VIII) was also produced in addition to compound (VII) and ferrocene.



(VIII)

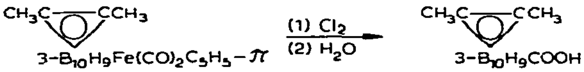
The structures of compounds (VII) and (VIII) were confirmed by means of IR and PMR spectroscopic data. The NMR spectrum of (VII) exhibits two poorly resolved triplets (intensity ratio 2/2) in the region of π-CpFe protons, and also a broad signal from the CH-protons of the carborane nucleus (relative intensity 4). The spectrum of (VIII) has a broad single asymmetric signal at δ 4.28 corresponding to the protons of the unsubstituted and substituted π-Cp ring and a signal from the C–H carborane protons at δ 3.52 (Table 1). The spectrum of diferrocenylboric acid has chemical shift and signal pattern[15] practically identical to that of (VIII).

The structure of (VIII) has also been confirmed by its independent synthesis from ferrocenylboron dichloride[16] and $B_9H_9C_2H_2^{2-}$ using a previously reported method[17].

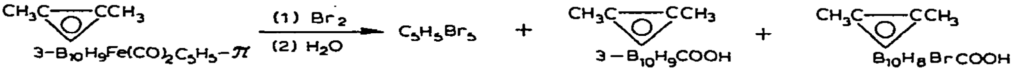


(VIII)

Unlike (I), compound (III) reacts with chlorine and bromine in a somewhat different manner. The action of 2 moles of chlorine upon 1 mole of (III) in CCl_4 over the temperature range −10 to +5° results in cleavage of the carborane–iron complex to 1,2-dimethyl-3-o-carborane carboxylic acid:



Reaction of (III) with excess Br_2 in CCl_4 at 20°, however, gives pentabromocyclopentane and two acids: 1,2-dimethyl-3-o-carborane and 1,2-dimethyl-*B*-bromo-3-o-carborane carboxylic acids.

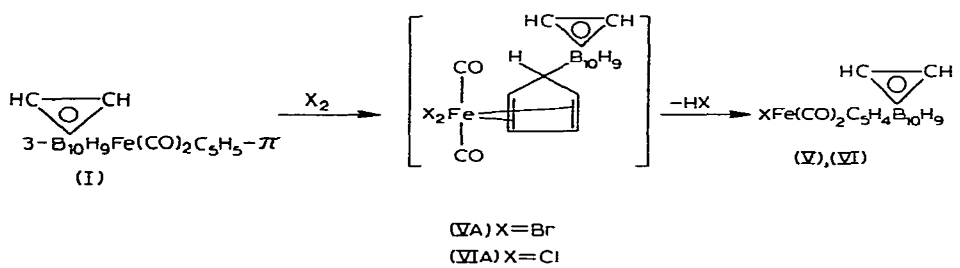


From the structures and compositions of the chlorination and bromination products of compound (III), it may be deduced that this reaction involves the cleavage of the B–Fe bond, migration of the 3-o-carboranyl group to the CO group with the formation of a B–C bond through the carbonyl ligand of complex (III), and the splitting off of a π-C_5H_5Fe fragment.

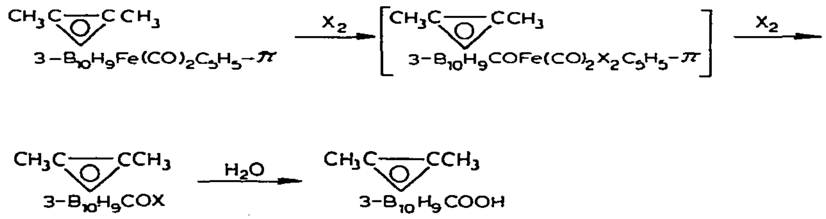
The cleavage of C–M bonds and the formation of a new C–C bond with the migration of the organic moiety to the carbonyl ligand of a transition metal has been reported elsewhere[18,19]. Thus, the complex $CH_3Fe(CO)_2C_5H_5$-π under the action of PPh_3 rearranges to the acyl complex $CH_3COFe(CO)PPh_3C_5H_5$-π[18]. Rearrangement of the acyl complex of manganese occurs in the presence of the iodide ion[19].

$$CH_3Mn(CO)_5 + LiI \rightarrow Li[CH_3COMnI(CO)_4]$$

In compounds of the type $RM(CO)_2C_5H_5$-π, migration of the organic group to the Cp-ring occurs on heating the ethyl molybdenum complex[20], and on arylation of the respective sodium derivatives of Mo and W with onium salts, ring-substituted binuclear complexes of the type $[RC_5H_4M(CO)_3]_2$ are formed. These rearrangements have been shown to occur via radical mechanisms[20,21]. The rearrangement of compound (I) to (V) and (VI) under the action of halogens is however probably non-radical. It may be assumed that reaction of (I) and (III) with chlorine and bromine involves coordination of the halogen molecule to the iron, followed by cleavage of the B–Fe bond and a migration of the 3-*o*-carborane group to the Cp-ring in the case of (I) and to the CO group in the case of (III). The rearrangement of (I) can therefore be described by the following scheme:



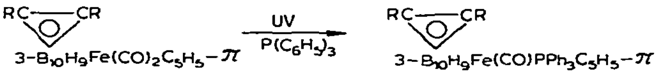
The intermediate dienic complex ((VA), (VIA)) which is generated is stabilized by the evolution of HX and by its transformation into (V) and (VI) respectively. The rearrangement of (III) can be described by the scheme:



The action of excess bromine on compound (III) results in the formation of 1,2-dimethyl-*B*-bromo-3-*o*-carborane carboxylic acid together with 1,2-dimethyl-3-*o*-carboxylic acid apparently as a result of a partial bromination of the initial compound (III) at the *o*-carborane nucleus prior to its rearrangement.

The reason for the different behaviour of (I) and (III) is as yet not known.

In addition to the reactions of (I) and (III) with halogens we have also studied their reactions with PPh_3 and $HgCl_2$. In the case of π-cyclopentadienylirondicarbonyl compounds, $C_5H_5Fe(CO)_2R$, the course of the reaction with PPh_3 depends upon the structure of the resulting radical and on the reaction conditions[22]. Heating $CpFe(CO)_2R$ with PPh_3 in benzene, THF and ether usually leads to the formation of the respective acyl compounds $CpFe(CO)PPh_3COR$. The use of UV-irradiation without heating results in carbonyl ligand exchange with PPh_3. Compounds (I) and (III) do not react with PPh_3 under prolonged heating in benzene and decane (at 170°). UV-irradiation of (I) and (III) with PPh_3 in benzene at 25–30° on the other hand results in the exchange of a carbonyl group with triphenylphosphine



(IX) R = H;
(X) R = CH_3

Compounds (IX) and (X) are red crystalline substances completely stable as solids but only for a short time in solution. The structures of (IX) and (X) have been established on the basis of IR and PMR spectra.

The IR spectra of (IX) and (X) show no absorption at 1640 cm^{-1} specific to the acyl carbonyl. The presence of one CO group is evident from the presence of a $\nu(C{\equiv}O)$ band at 1910 cm^{-1}. Its frequency is somewhat lower relative to those of the starting compounds ((I) 1960, 2020 cm^{-1}, (III) 1955, 2010 cm^{-1}) due to the insertion of the more electron-releasing PPh_3 ligand in place of CO. The presence of PPh_3 in the molecule is characterised by the presence of a group of bands in the IR spectrum, of which the most pronounced are those of the non-planar CH modes of the phenyl ring at 710 and 760 cm^{-1}. The presence of the carborane nucleus is clearly indicated by B–H stretching modes at 2600 cm^{-1}.

Replacement of one CO group for PPh_3 in compounds (I) and (III) leads to the presence of an asymmetric iron atom and to the loss of a symmetry plane in compounds (IX) and (X) (Fig. 3). Thus in each possible rotation isomer, the radicals R_a and R_b (= H, CH_3) may appear within a diastereomeric environment.

Due to the averaging of the shielding of each R_a and R_b group and due to internal rotation about the Fe–B bond they also remain diastereotopic[23]. As a result, in addition to the doublet from the π-Cp-proton ($J(^{31}P–C_5H_5) \approx 1.5$ Hz and relative intensity 5) two signals (instead of one, as in compounds (I) and (III)) are observed in the ^1H NMR spectra of both (IX) and (X) (Figs. 4 and 5). The spectrum of (X) exhibits two narrow singlets from CH_3(a) and CH_3(b) protons (intensity ratio 3/3), whereas the spectrum of (IX) has two broad single signals (intensity ratio 1/1) corresponding to the diastereotopic carborane CH protons H_a and H_b.

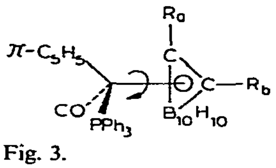


Fig. 3.

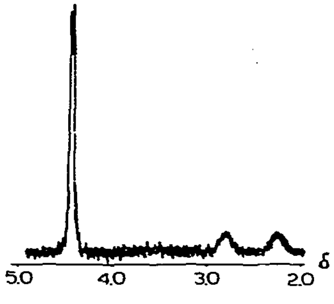
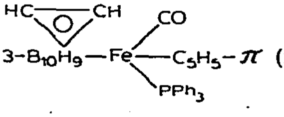
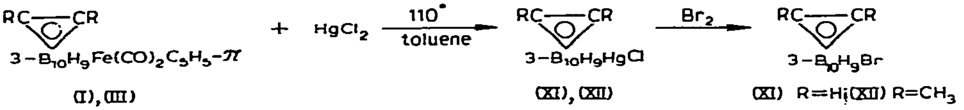


Fig. 4. The ^1H NMR spectrum (60 MHz) of  (in chloroform).



The reactions of (I) and (III) with $HgCl_2$ proceed in a similar manner and lead to the previously unknown carboranes with a B–Hg bond. Compound (I) reacts with $HgCl_2$ much more readily than compound (III), producing compound (XI) in 80–85% yield, while the yield of (XII) does not exceed 25%.

On treatment of compound (XI) with bromine, cleavage of the B–Hg bond occurs, yielding the known compound 3-bromo-*o*-carborane which provides evidence for the position of iron in compound (I) and of mercury in compound (XI).

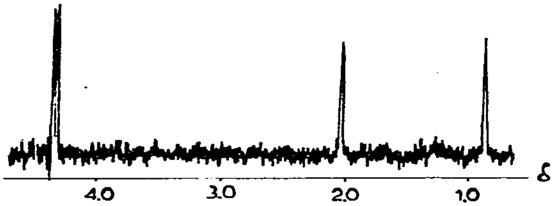
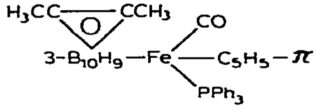


Fig. 5. The ^{1}H NMR spectrum (60 MHz) of  (in chloroform).

Compounds (XI) and (XII) are white crystalline substances stable in air and in solution, readily soluble in benzene and $CHCl_3$, less soluble in ether and practically insoluble in hydrocarbons. They undergo no symmetrization on heating to 150–170°. Compound (XI) readily exchanges its chlorine with iodine.

EXPERIMENTAL

^{1}H NMR spectra were measured on a Perkin–Elmer R-12 and on a Hitachi–Perkin–Elmer R-20 spectrometer at 60 MHz. Tetramethylsilane was used as an internal standard. Chemical shifts are quoted in the δ scale. The IR spectra were measured on a UR-20 spectrometer using KBr pellets or CCl_4 solutions. The NQR spectrum was recorded on an IC III-I pulsive spectrometer. Polarograms were obtained on an LP-60 polarograph in CH_3CN and with 0.1 *N* $(C_2H_5)NClO_4$ as the supporting electrolyte with a dropping mercury electrode (the electrode was supplied with a spade for forced dropping). The concentrations of the polarographed substances were $1 \cdot 10^{-3}$ mole/l. The half-wave potentials ($E_{\frac{1}{2}}$) were measured with reference to an aqueous saturated calomel electrode. Measurement error was within ±0.01 V.

All reactions were carried out under a stream of dry argon. THF was purified by distillation over $LiAlH_4$ in argon.

Synthesis of acyl-o-carboranes containing a B–Fe σ bond

A 0.02 mole solution of 3-*o*-carborane carboxylic acid chloride was added dropwise with stirring to 0.02 mole of $NaFe(CO)_2C_5H_5$-π in 75 ml of THF at −70°.

The temperature of the mixture was allowed to rise slowly to room temperature and the mixture was then allowed to stand overnight. THF was removed *in vacuo* and the residue chromatographed on an alumina column (activity grade II), using benzene as a solvent. The compounds obtained were recrystallized from hexane.

σ-(o-carborane-3-carbonyl)-π-cyclopentadienylirondicarbonyl (II). M.p. 158–159°. Found: C, 34.80; H, 4.55; Fe, 16.63%. $C_{10}H_{20}B_{10}FeO_3$ calcd.: C, 34.49; H, 4.62; Fe, 16.03%.

σ-(1,2-Dimethyl-o-carborane-3-carbonyl)-π-cyclopentadienylirondicarbonyl (IV). M.p. 155–156° (decomp.), yield 65%. Found: C, 38.11; H, 5.52; B, 28.33; Fe, 14.63%. $C_{12}H_{20}B_{10}FeO_3$ calcd.: C, 38.27; H, 5.36; B, 28.72; Fe, 14.84%. Yield 60%.

Synthesis of 1,2-dimethyl-3-o-carborane carboxylic acid

The acid was prepared by the method previously described[2]. Heating 1,2-dimethyl-3-amine-*o*-carborane[7] with an excess of formic acid gave 1,2-dimethyl-3-*N*-formylamine-*o*-carborane. M.p. 252–253° (petroleum ether/$CHCl_3$, 1/1), yield 95%. Found: N, 6.75%. $C_5H_{17}B_{10}NO$ calcd.: N, 6.94%. Treatment of 1,2-dimethyl-3-*N*-formylamine-*o*-carborane with $POCl_3$ in pyridine at −10° gave 1,2-dimethyl-3-*o*-isonitrile carborane in 60% yield. M.p. 252–253° (hexane). Found: C, 30.22; H, 7.65%. $C_5H_{15}B_{10}N$ calcd.: C, 30.43; H, 7.67%.

On heating in dodecane, 1,2-dimethyl-3-*o*-isonitrile carborane was converted to 1,2-dimethyl-3-*o*-nitrile carborane. M.p. 249–250° (hexane), yield 80%. Found: C, 30.18; H, 7.72%. $C_5H_{15}B_{10}N$ calcd.: C, 30.43; H, 7.67%.

1,2-Dimethyl-3-*o*-carborane carboxylic acid was obtained by hydrolysis of the respective nitrile. M.p. 239–240° (heptane/$CHCl_3$ 2/1), yield 80%. Found: C, 27.92; H, 7.56%. $C_5H_{16}B_{10}O_2$ calcd.: C, 27.76; H, 7.47%.

Synthesis of 1,2-dimethyl-3-o-carborane carboxylic acid chloride

3 g of the acid in 50 ml of benzene was heated with 5 g of PCl_5 for 1 h, the benzene evaporated, the residue dissolved in heptane and filtered, and the solvent evaporated to give 0.24 g of the chloride. M.p. 170–175° (heptane). The chloride readily hydrolyzes to the acid.

Decarbonylation of the acyl derivatives of (II) and (IV)

Heating the acyl derivatives of (II) and (IV) in decane at 170° for 4 h resulted in quantitative yields of the respective alkyl compounds.

σ-(o-Carboran-3-yl)-π-cyclopentadienylirondicarbonyl (I) M.p. 124–125° (hexane). Found: C, 33.95; H, 5.01; Fe, 17.65%. $C_9H_{16}B_{10}FeO_2$ calcd.: C, 33.75; H, 5.05; Fe, 17.44%.

σ-(1,2-Dimethyl-o-carboran-3-yl)-π-cyclopentadienylirondicarbonyl (III). M.p. 156–157° (hexane). Found: C, 37.95; H, 5.68; B, 31.12; Fe, 16.07. $C_{11}H_{20}B_{10}FeO_2$ calcd.: C, 37.93; H, 5.79; B, 31.04; Fe, 16.03%.

Synthesis of π-[(o-carboran-3-yl)cyclopentadienyl]dicarbonyliron bromide

0.7 g of Br_2 in CCl_4 was added dropwise with stirring at 20° to 0.64 g of (I) in 30 ml of CCl_4. A red solid precipitated after several minutes. After stirring for 1 h, the solid was filtered off, washed with CCl_4 and dried *in vacuo*. The yield of product was 0.79 g (90%). The π-[(*o*-carboran-3-yl)cyclopentadienyl]dicarbonyliron bromide

(V) obtained decomposed at 150° without melting. The product was crystallized from benzene. Found: C, 27.01; H, 3.83; B, 27.13; Br, 19.95; Fe, 14.49%. $C_9H_{15}B_{10}BrFeO_2$ calcd.: C, 27.08; H, 3.79; B, 27.08; Br, 20.02; Fe, 14.74%.

Synthesis of π-[(o-carboran-3-yl)cyclopentadienyl] dicarbonyliron chloride (VI)

0.002 mole (0.14 g) of Cl_2 in 20 ml of CCl_4 was added dropwise to 0.001 mole (0.32 g) of (I) in 30 ml of CCl_4. After 30 min the red solid precipitated was filtered off, washed with CCl_4 and dried *in vacuo*. Compound (VI) was obtained, 0.32 g (94%). It decomposed at 150° without melting. The product was crystallized from benzene. Found: C, 30.69; H, 4.35; Cl, 9.98; Fe, 15.67%. $C_9H_{15}B_{10}FeClO_2$ calcd.: C, 31.36; H, 4.39; Cl, 10.28; Fe, 16.25%.

Synthesis of 1,1-bis(o-carboran-3-yl)ferrocene (VII)

0.8 g of (V) was heated at 180° for 3 h in 50 ml of decaline. Then decaline was evaporated *in vacuo* and the residue chromatographed on an alumina column (solvent: petroleum ether/benzene, 1/1). 0.3 g of (VII) was obtained. M.p. 253–254° (benzene/hexane, 1/1). Found: C, 36.07; H, 6.51; Fe, 11.90%. $C_{14}H_{30}B_{20}Fe$ calcd.: C, 35.73; H, 6.44; Fe, 11.87%.

Synthesis of (o-carboran-3-yl)ferrocene (VIII)

Method A. 0.4 g of (V) was heated for 3 h at 180° in 50 ml of decaline with $C_5H_5Fe(CO)_2Br$. Decaline was evaporated in vacuum and the residue chromatographed on an alumina column. The first fraction (petroleum ether 40–60°) was ferrocene, the second fraction (petroleum ether 40–60°) was monosubstituted ferrocene (VIII), while the third fraction (benzene/petroleum ether, 1/1) consisted of disubstituted ferrocene (VII).

The yield of monosubstituted ferrocene (VIII) was 0.15 g. M.p. 154–155° (hexane). Found: C, 43.58; H, 6.17; Fe, 17.67%. $C_{12}H_{20}B_{10}Fe$ calcd.: C, 43.90; H, 6.15; Fe, 17.01%.

Method B. A solution of ferrocenylboron dichloride in 50 ml of hexane (prepared from 2 g of ferrocenylmercury chloride[16]) was added with stirring at −80° to a solution of $Na_2B_9H_9C_2H_2$ in 75 ml of THF (prepared from 2 g of $(CH_3)_3NHB_9C_2H_{12}$). The reaction mixture was slowly heated to room temperature and allowed to stand overnight. THF was removed in vacuum and the residue chromatographed on an alumina column. The first fraction was ferrocene (petroleum ether) while the second fraction was (o-carboran-3-yl)ferrocene (VIII) (petroleum ether), 0.15 g. M.p. 154–155° (hexane). Ferrocenes prepared by the methods A and B were identified by means of their IR spectra after chromatography. Mixed m.p. determinations gave no depression.

Action of Br_2 on σ-(1,2-dimethyl-o-carborane-3-yl)-π-cyclopentadienyliron dicarbonyl (III)

A solution consisting of 1 g of Br_2 in CCl_4 was added with stirring to 0.35 g of (III) in CCl_4. The black solid precipitated was filtered off, the solvent evaporated *in vacuo* and the residue dissolved in ether and extracted three times with 20% KOH solution. The alkaline extracts were acidified with HCl and extracted with ether. After evaporation of the ether 0.1 g of a mixture of 1,2-dimethyl-3-o-carborane carboxylic (60%) and 1,2-dimethyl-*B*-bromo-3-*o*-carborane carboxylic (40%) acids was obtained. The ethereal extract was washed with water until neutral, dried over $CaCl_2$ and the ether evaporated. 0.27 g of $C_5H_5Br_5$ was obtained. M.p. 103–104° (heptane). Found: C, 13.21; H, 1.09; Br, 85.87%. $C_5H_5Br_5$ calcd.: C, 12.92; H, 1.08; Br, 85.97%.

Action of Cl_2 on σ-(1,2-dimethyl-o-carboran-3-yl)-π-cyclopentadienylirondicarbonyl (III)

0.14 g of Cl_2 in 20 ml of CCl_4 was added dropwise with stirring at −10° to a solution of 0.35 g (0.001 mole) of (III) in 30 ml of CCl_4. The mixture was slowly heated to 20°. The black solid precipitate was filtered off, CCl_4 evaporated in vacuum, the residue dissolved in ether and extracted three times with 20% KOH solution. The alkaline extracts were acidified with HCl and extracted with ether. After evaporation of the ether 0.15 g of 1,2-dimethyl-3-*o*-carborane carboxylic acid was obtained. M.p. 239–240° (heptane).

Reaction of (I) with PPh_3

A solution of 0.5 g of (I) and 0.55 g of PPh_3 in benzene was subjected to UV-irradiation for 10 h. The solvent was evaporated and the residue placed on an alumina column. The first fraction consisted of unchanged (I) and PPh_3 (petroleum ether) and the second fraction of σ-(*o*-carborane-3-yl)-π-cyclopentadienylironcarbonyl triphenylphosphine (benzene) 0.4 g (50%). M.p. 181–182° (decomp.) (benzene/heptane, 1/1). Found: C, 56.28; H, 5.68; B, 19.36; Fe, 10.00; P, 5.54%. $C_{20}H_{31}B_{10}FeOP$ calcd.: C, 56.31; H, 5.64; B, 19.49; Fe, 10.07; P, 5.58%.

Reaction of (III) with PPh_3

A solution of 0.5 g of (III) and 0.5 g of PPh_3 in benzene was subjected to UV-irradiation for 4 h. The solvent was evaporated and the residue placed on an alumina column. The first fraction consisted of unchanged (III) and PPh_3 (petroleum ether) and the second fraction of σ-(*o*-carboran-3-yl)-π-cyclopentadienylironcarbonyl triphenylphosphine (benzene), 0.2 g. M.p. 152–153° (decomp.) (Benzene/heptane, 1/1). Found: C, 58.41; H, 6.05; B, 18.15; Fe, 9.70; P, 5.20. $C_{28}H_{35}B_{10}FePO$ calcd.: C, 57.72; H, 6.06; B, 18.50; Fe, 9.56; P, 5.31%.

Synthesis of 3-o-carboranylmercury chloride (XI)

1 g of (I) was refluxed in toluene with 3 g of $HgCl_2$ for 10 h. The black solid precipitated was filtered off and washed repeatedly with hot benzene. The resulting benzene solution was washed three times with aqueous (1/1) HCl then with water (until neutral) and dried over $CaCl_2$. 3-*o*-Carboranylmercury chloride was isolated (yield 80–85%). M.p. 296–297° (benzene). Found: C, 6.59; H, 3.14; B, 28.76; Cl, 9.52; Hg, 51.72%. $C_2H_{11}B_{10}HgCl$ calcd.: C, 6.33; H, 2.92; B, 28.50; Cl, 9.34; Hg, 52.88%. 0.2 g of (XI) was heated for 20 h with 0.08 g of Br_2 in 20 ml of acetic acid. The mixture was poured into water and the solid precipitated was filtered off and dried. Yield 0.1 g. The product obtained had an IR spectrum and a GLC retention time[8] identical to that of 3-bromo-*o*-carborane[7].

3-*o*-Carboranylmercury iodide: m.p. 294–295°. Found: C, 5.23; H, 2.38; B, 23.00; I, 27.30; Hg, 41.88%. $C_2H_{11}B_{10}HgI$ calcd.: C, 5.07; H, 2.35; B, 22.96; I, 26.95; Hg, 42.61%.

Synthesis of 1,2-dimethyl-3-o-carboranylmercury chloride (XII)

1 g of (III) was refluxed for 30 h in toluene with 3 g of $HgCl_2$. The black solid precipitated was filtered off and washed repeatedly with benzene. The benzene solutions were washed three times with aqueous (1/1) HCl then with water until neutral and dried over $CaCl_2$. 0.3 g (25%) of (XII) was isolated. M.p. 271–272° (benzene). Found: C, 11.72; H, 3.75; B, 26.30; Cl, 9.53; Hg, 48.45. $C_4H_{15}B_{10}HgCl$ calcd.: C, 11.79; H, 3.72; B, 26.53; Cl, 8.73; Hg, 49.24%.

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