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SYNTHESIS AND SOME REACTIONS OF 1-SUBSTITUTED DERIVATIVES OF π-CYCLOPENTADIENYL-π-(3)-1,2-DICARBOLLYLIRON(III). STRUCTURE OF π-$C_5H_5Fe^{III}$—π-1,2-$C_2B_9H_{10}$-1-$CH(OEt)_2$

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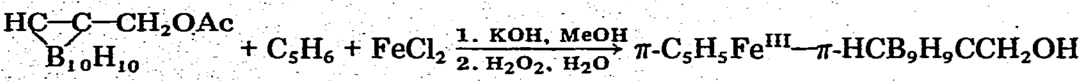
Summary

The synthesis of several 1-substituted functional derivatives 3-π-$C_5H_5Fe^{III}$—π-1,2-$C_2B_9H_{10}$-1-R (R = CH_2OH, CHO, COOH, $COCH_3$, CH_2COOH, etc.) is reported. Reactions of these compounds have been investigated. The 3-π-$C_5H_5Fe^{III}$—π-1,2-$C_2B_9H_{10}$-1-group was found to show pronounced electron-withdrawing properties (σ_i = +0.31). The crystal and molecular structure of 3-π-$C_5H_5Fe^{III}$—π-1,2-$C_2B_9H_{10}$-1-$CH(OEt)_2$ has been established.

Results and discussion

Our previous papers [1,2] have dealt with the properties of π-cyclopentadienyl-π-(3)-1,2-dicarbollyliron, π-$C_5H_5Fe^{III}$—π-HCB_9H_9CH (I) *, one of the most important higher ferracarboranes. In the present study some of its 1-substituted functional derivatives were obtained for the first time and their reactions were investigated.

The easiest substance to obtain in this series is the 1-hydroxymethyl derivative of complex I, π-$C_5H_5Fe^{III}$—π-$HCB_9H_9CCH_2OH$ (II). The synthesis involves a reaction between 1-acetoxymethyl-*o*-carborane **, cyclopentadiene and iron chloride in a methanol solution of KOH. The intermediate Fe^{II} complex is then oxidized by H_2O_2 using the modified method for obtaining complex I [3]:



$$\underset{B_{10}H_{10}}{HC{-}C{-}CH_2OAc} + C_5H_6 + FeCl_2 \xrightarrow[2.\ H_2O_2,\ H_2O]{1.\ KOH,\ MeOH} \pi\text{-}C_5H_5Fe^{III}\text{—}\pi\text{-}HCB_9H_9CCH_2OH$$

(II)

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* π-$C_5H_5Fe^{III}$—π-HCB_9H_9CH = 3-π-$C_5H_5Fe^{III}$—π-1,2-$C_2B_9H_{11}$.

** *o*-carborane = 1,2-dicarbo-closo-dodecaborane(12).

Compound II forms air-stable paramagnetic purple crystals and can be smoothly reduced by $NaBH_4$ in ethanol:

$$\mathrm{II} \xrightarrow[\text{2. CsCl, } H_2O]{\text{1. NaBH}_4\text{, EtOH}} [\pi\text{-}C_5H_5Fe^{II}\text{—}\pi\text{-}HCB_9H_9CCH_2OH]^-Cs^+$$

Complex III was isolated in the form of its cesium salt as red diamagnetic crystals. In the solid state III is stable in air, while in solutions it undergoes slow oxidation. The structure of III was confirmed by PMR spectroscopy (Table 1). Alcohol II was found to possess properties somewhat differing from those of its cobalt analog $\pi\text{-}C_5H_5Co^{III}\text{—}\pi\text{-}HCB_9H_9CCH_2OH$ (IV) [4]. Under the action of acetylating mixture alcohol II, as well as alcohol IV, gives rise to an acetoxymethyl derivative $\pi\text{-}C_5H_5Fe^{III}\text{—}\pi\text{-}HCB_9H_9CCH_2OAc$ (V); pyridinium chlorochromate readily oxidizes II to an aldehyde, VI:

$$\mathrm{II} \xrightarrow[CH_2Cl_2]{C_5H_5N \cdot HCrO_3Cl} \pi\text{-}C_5H_5Fe^{III}\text{—}\pi\text{-}HCB_9H_9CCHO$$

(VI)

Treatment of aldehyde VI with 2,4-dinitrophenylhydrazine gives a corresponding hydrazone, the formation of which at 20°C takes 24 hours.

In contrast to the cobalt complex IV, alcohol II, when heated in ethanol in the presence of a catalytic amount of H_2SO_4, gives an ethyl ether derivative VII:

$$\mathrm{II} + \mathrm{EtOH} \xrightarrow{H^+} \pi\text{-}C_5H_5Fe^{III}\text{—}\pi\text{-}HCB_9H_9CCH_2OEt$$

(VII)

TABLE 1

PMR SPECTRA OF III, X AND XIV

Compound	Chemical shift [a] (ppm) (J(HH) (Hz))	Assignment
III [b]	d. 2.62 (8)	CH_2
	s. 3.68	carborane CH
	t. 4.09 (8)	OH
	s. 4.32	C_5H_5
X [c]	t. 0.68 (8)	CH_3CH_2
	s. 1.94	CH_2
	s. 3.38	carborane CH
	q. 3.78 (8)	CH_3CH_2
	s. 3.96	C_5H_5
XIV [d]	d. 1.78 (6)	CH_3
	c. 3.25	$(CH_3)_4N$
	s. 4.29	carborane CH
	s. 4.76	C_5H_5
	m. 4.87	$CHCH_3$ OH
	d. 5.49 (5)	OH

[a] Relative to TMS with HMDSO as internal reference. [b] In CD_3CN. [c] In C_6H_6, internal reference C_6H_6. [d] In C_5H_5N.

and on interaction with dry HCl in the presence of $ZnCl_2$ in CH_2Cl_2 alcohol II smoothly substitutes a chlorine atom for its OH group, with the formation of a chloromethyl derivative VIII:

$$\mathrm{II} + \mathrm{HCl} \xrightarrow[CH_2Cl_2]{ZnCl_2} \pi\text{-}C_5H_5Fe^{III}\text{—}\pi\text{-}HCB_9H_9CCH_2Cl$$

(VIII)

It was found that the chlorine atom in VIII, unlike that in 1-chloromethyl-*o*-carborane and in the cobalt analog $\pi\text{-}C_5H_5Co^{III}\text{—}\pi\text{-}HCB_9H_9CH_2Cl$, is readily alcoholyzed in ethanol solution at 20°C to form the ether VII in a quantitative yield. It should be noted that the alcoholysis apparently involves the S_{N1} mechanism, since the reaction between the chloromethyl derivative VIII and KCN in aqueous methyl ether of ethylene glycol leads to products of interaction with the solvents rather than to a cyanomethyl derivative:

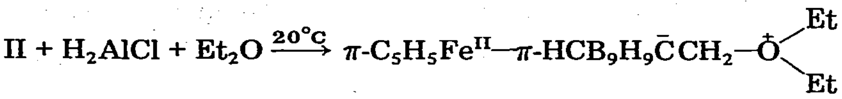
$$\mathrm{VIII} + KCN + CH_3OCH_2CH_2OH + H_2O \rightarrow$$

$$\pi\text{-}C_5H_5Fe^{III}\text{—}\pi\text{-}HCB_9H_9CCH_2OCH_2CH_2OCH_3 + \mathrm{II}$$

(IX)

Earlier it was suggested [5] that cobaltocarboranes are somewhat similar to closocarboranes because the $\pi\text{-}C_5H_5Co^{III}$ group of the former is to a certain extent similar to the {BH} group in the latter. The differences in the reactivity of the hydroxymethyl (II) and chloromethyl (VIII) derivatives of ferrocarborane I indicate, however, that the similarity between the $\{\pi\text{-}C_5H_5Co^{III}\}$ group and the {BH} fragment was rather overestimated. Hence the chemical properties of derivatives of I resemble those of ferrocene-ferricinium derivatives rather than closo- and cobaltocarboranes.

A surprising result was obtained in a reaction between alcohol II and monochloralane in ether solution. It had been found [6] that cobaltocarborane alcohol (IV) with H_2AlCl in ether shows smooth hydrogenolysis of the C—O bond leading to a methyl derivative, $\pi\text{-}C_5H_5Co^{III}\text{—}\pi\text{-}HCB_9H_9CCH_3$. On the contrary, alcohol II primarily gives an internal salt of diethyloxonium and ferrocarborane X, in which the iron atom is divalent (d^6 configuration):

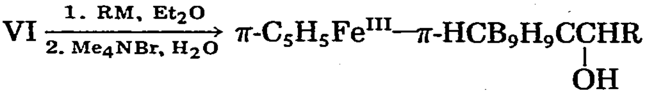


$$\mathrm{II} + H_2AlCl + Et_2O \xrightarrow{20°C} \pi\text{-}C_5H_5Fe^{II}\text{—}\pi\text{-}HCB_9H_9\bar{C}CH_2\text{—}\overset{+}{O}(Et)_2$$

(X)

Compound X forms yellow-orange diamagnetic crystals. It is stable to air, moisture and diluted mineral acids and bases. This high stability (as compared, e.g. to that of $Et_3O^+BF_4^-$) is probably due to the partial compensation of the positive charge at the oxygen atom by electron density supplied from the donor $\pi\text{-}C_5H_5Fe^{II}\text{—}\pi\text{-}HCB_9H_9C$-group. The structure of the oxonium zwitterion X was confirmed by PMR spectroscopy (Table 1). Even under the action of a great excess of H_2AlCl the reaction with the alcohol II led to 1-methylferrocarborane $\pi\text{-}C_5H_5Fe^{III}\text{—}\pi\text{-}HCB_9H_9CCH_3$ (XI) in an extremely small amount (<1%).

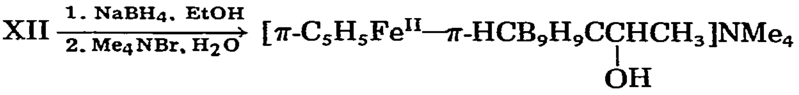
The action of organolithium and -magnesium compounds on aldehyde VI results in the formation of the corresponding secondary carbinols, while the iron atom is reduced to the divalent state. In view of the latter a two-fold excess of the organometallic reagent is used for the reaction. Oxidation by H_2O_2 transforms Fe^{II} to Fe^{III} to form neutral secondary carbinols:



$$\mathrm{VI} \xrightarrow[\text{2. } Me_4NBr,\ H_2O]{\text{1. } RM,\ Et_2O} \pi\text{-}C_5H_5Fe^{III}\text{—}\pi\text{-}HCB_9H_9C\underset{\displaystyle OH}{\underset{|}{C}}HR$$

(XII, R = Me, M = MgCl;
XIII, R = Ph, M = Li)

Phenylcarbinol XIII was formed as a mixture of diastereomers subsequently isolated by preparative TLC. Reduction of methylcarbinol XII by $NaBH_4$ in ethanol leads to a complex XIV isolated in the form of a tetramethylammonium salt:



$$\mathrm{XII} \xrightarrow[\text{2. } Me_4NBr,\ H_2O]{\text{1. } NaBH_4,\ EtOH} [\pi\text{-}C_5H_5Fe^{II}\text{—}\pi\text{-}HCB_9H_9C\underset{\displaystyle OH}{\underset{|}{C}}HCH_3]NMe_4$$

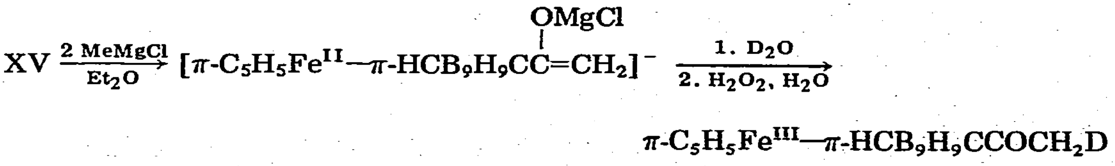
(XIV)

Complex XIV is a diamagnetic red crystalline substance, stable in air. The structure of XIV was confirmed by PMR spectroscopy (Table 1). Under the action of pyridinium chlorochromate in CH_2Cl_2 methylcarbinol XII is readily oxidized to the ketone XV:

$$\mathrm{XII} \xrightarrow[CH_2Cl_2]{C_5H_5N \cdot HCrO_3Cl} \pi\text{-}C_5H_5Fe^{III}\text{—}\pi\text{-}HCB_9H_9CCOCH_3$$

(XV)

An attempt to obtain the corresponding tertiary alcohol by the action of CH_3MgCl on ketone XV failed, since the reaction resulted in complete enolization of the acetyl group. Treatment of the reaction mixture with D_2O with subsequent oxidation by H_2O_2 resulted in a ketone XVa containing a D label:



$$\mathrm{XV} \xrightarrow[Et_2O]{2\ MeMgCl} [\pi\text{-}C_5H_5Fe^{II}\text{—}\pi\text{-}HCB_9H_9C\overset{\displaystyle OMgCl}{\overset{|}{C}}{=}CH_2]^- \xrightarrow[\text{2. } H_2O_2,\ H_2O]{\text{1. } D_2O} \pi\text{-}C_5H_5Fe^{III}\text{—}\pi\text{-}HCB_9H_9CCOCH_2D$$

(XVa)

The presence of the label in XVa was confirmed mass spectrometrically.

Unexpectedly, the main product of the reaction between aldehyde VI and anhydrous ethanol in the presence of a catalytic amount of EtONa was the diethylacetal of the aldehyde XVI. The reaction was accompanied by formation of minor amounts of complex I (caused by loss of a CHO group), methyl-substituted complex XI and the product of Ponndorf-Meerwein reaction (alcohol II):

$$\mathrm{VI} \xrightarrow[\mathrm{EtONa}]{\mathrm{EtOH,\ 20^\circ C}} \pi\text{-}\mathrm{C_5H_5Fe^{III}}\text{—}\pi\text{-}\mathrm{HCB_9H_9CCH(OEt)_2} + \mathrm{I} + \mathrm{XI} + \mathrm{II}$$

The mechanism of this reaction so far seems obscure. It should be noted that 1-formyl-*o*-carborane under these conditions readily loses a CHO group [7], whereas the cobalt analog π-$C_5H_5Co^{III}$—π-HCB_9H_9CHO shows a Kannizzaro-Tishchenko and a Ponndorf-Meerwein reaction pattern and also loses a CHO group but only to a minor extent [6]. The structure of XVI was proved by its independent synthesis from aldehyde VI and ethanol in the presence of H_2SO_4:

$$\mathrm{VI} + \mathrm{EtOH} \xrightarrow[2.\ \mathrm{Na_2CO_3}]{1.\ \mathrm{H^+}} \mathrm{XVI}$$

The same product XVI was obtained in a lower yield from aldehyde VI and orthoformic ester. Its structure was finally proved by X-ray diffraction analysis. The crystals of XVI are monoclinic, $a = 14.088(1)$, $b = 14.925(1)$, $c = 9.236(1)$ Å, $\beta = 104.943(9)°$, $V = 1876.1(5)$ Å^3, $Z = 4$, $d_{\text{calc.}} = 1.265$ g/cm^3. Space group $P2_1/a$. The structure of XVI is shown in Fig. 1.

X-ray diffraction evidence indicates unambiguously that XVI is indeed an acetal. The iron atom is η^5-coordinated by the "open" C_2B_3 face of the π-di-

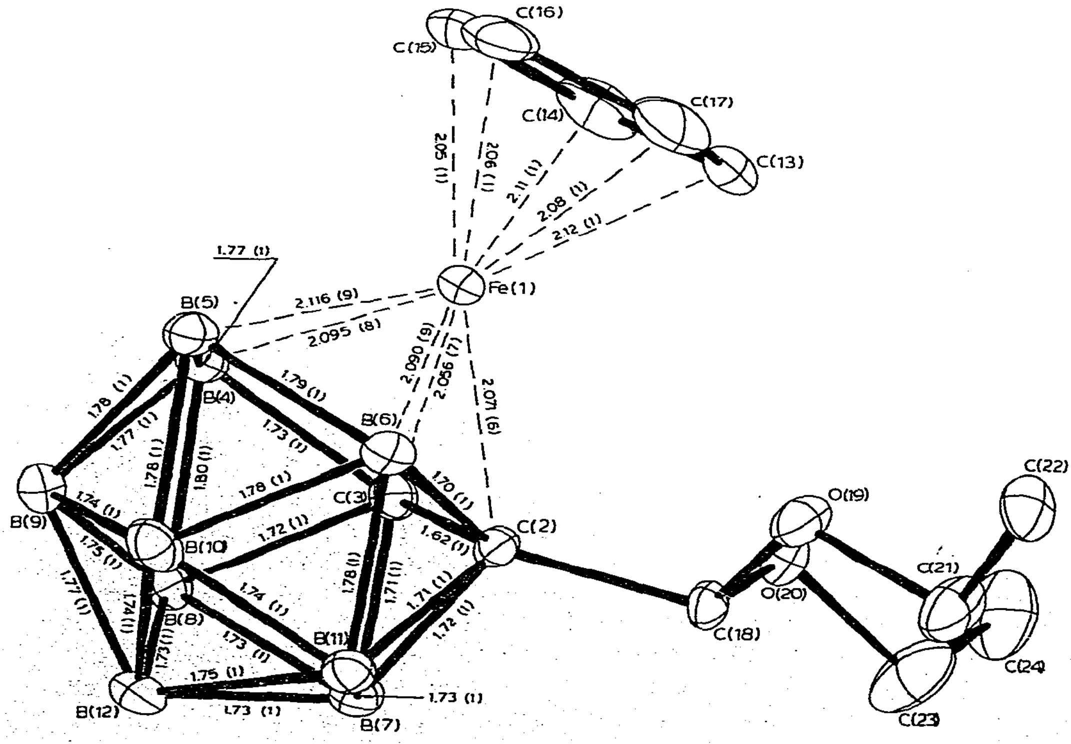


Fig. 1. Molecular structure of XVI (hydrogen atoms not shown).

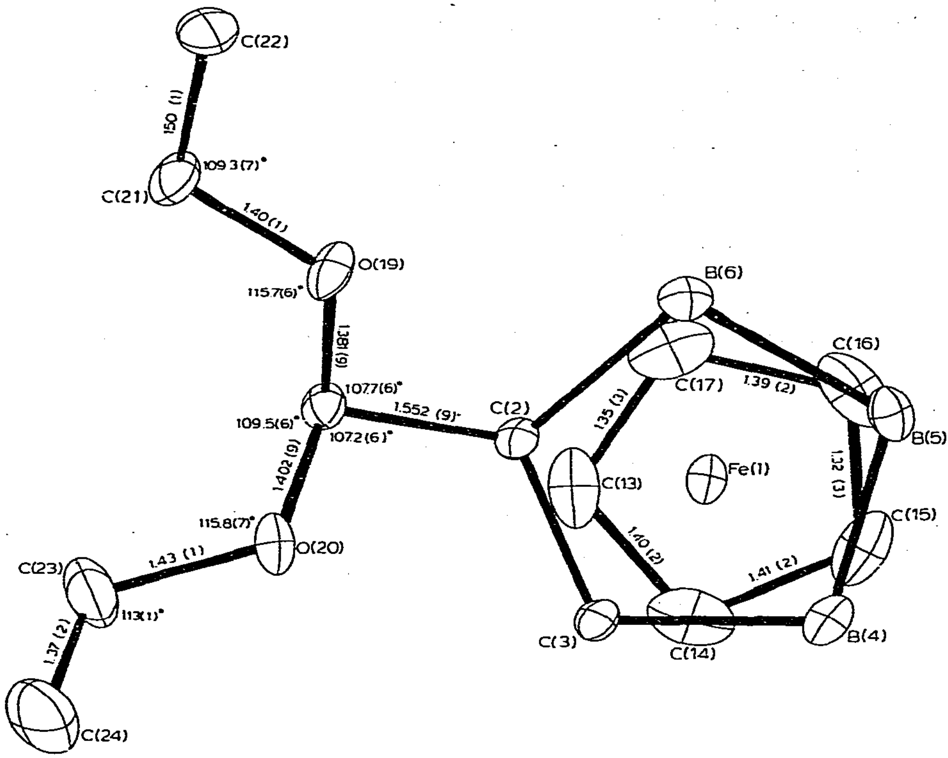


Fig. 2. Projection of molecule XVI on the plane of the π-C_5H_5 ligand (hydrogen atoms not shown).

carbollyl ligand and the π-C_5H_5 ligand; its distance from these planes is 1.486 and 1.725 Å, respectively.

The Fe—C and Fe—B distances to the C_2B_3 face are on average equal to 2.063(7) Å and 2.100(9) Å, respectively; the Fe—C distance to the atoms of the π-C_5H_5 ligand averages to 2.08(1) Å. These distances virtually coincide with those found earlier for ferrocarboranes π-$C_5H_5Fe^{III}$—π-$C_2H_2B_9H_8$-8-$OCOCF_3$ (average Fe—C 2.069 Å, Fe—B 2.094 Å, Fe—C (π-C_5H_5) 2.07 Å) [8]. The C_2B_3 face is practically planar, the largest deviation from its mean plane being 0.02 Å for B(5). The dihedral angle between the C_2B_3 and the C_5H_5 planes is 7°. The diethoxymethyl substituent has quite usual geometry. The C(2)—C(18) bond is bent towards the iron atom and forms a 19° angle with the C_2B_3 plane. The length of the C(23)—C(24) bond is 1.37(2) Å, much less than the standard value of 1.54 Å. This may be due to a certain disorder of the terminal ethyl group or its intense thermal motion. Atomic coordinates and the anisotropic thermal parameters are presented in Table 2.

An attempt to oxidize aldehyde VI to the corresponding acid π-$C_5H_5Fe^{III}$—π-HCB_9H_9CCOOH (XVII) proved unsuccessful, since the oxidation of the CHO group was accompanied by that of the π-dicarbollyl ligand.

It was found that the C—H bonds of the π-dicarbollyl ligand in complex I may be metallated by n-BuLi in ether at —20°C, though the yield was not high.

The main process under these conditions is the reduction of Fe to the divalent (d^6) state:

$$\text{I} + \text{n-BuLi} \xrightarrow[\text{Et}_2\text{O}]{-20^\circ\text{C}} \pi\text{-}C_5H_5Fe^{III}\text{—}\pi\text{-}HCB_9H_9CLi + [\pi\text{-}C_5H_5Fe^{II}\text{—}\pi\text{-}HCB_9H_9CH]Li$$

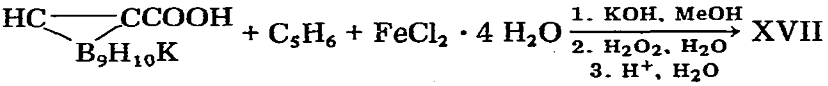
(XVIII) (XIX)

Treatment of the reaction mixture with CO_2, hydrochloric acid, diazomethane and, finally, H_2O_2 leads to a mixture of methyl ester of ferrocarboranecarboxylic acid XX and complex I.

$$\text{XVIII} + \text{XIX} \xrightarrow[\substack{2.\ CH_2N_2 \\ 3.\ H_2O_2,\ H_2O}]{1.\ CO_2,\ H^+} \pi\text{-}C_5H_5Fe^{III}\text{—}\pi\text{-}HCB_9H_9CCOOCH_3 + \text{I}$$

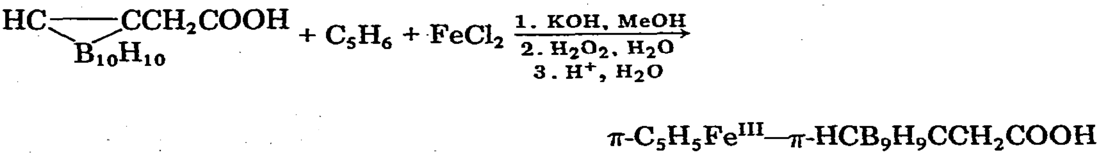
(XX)

It is more convenient to obtain acid XVII directly from potassium 1-carboxy-*o*-dicarbaundecaborate, cyclopentadiene and ferric chloride in methanol solution of KOH:



$$HC\text{—}CCOOH\ (B_9H_{10}K) + C_5H_6 + FeCl_2 \cdot 4\ H_2O \xrightarrow[\substack{2.\ H_2O_2,\ H_2O \\ 3.\ H^+,\ H_2O}]{1.\ KOH,\ MeOH} \text{XVII}$$

The ionization constant of XVII as measured in 50% ethanol is $pK_a = 3.49$. Acid XVII is therefore weaker than 1-*o*-carboranecarboxylic acid [9] ($pK_a = 2.50$) but about as strong as $\pi\text{-}C_5H_5Co^{III}\text{—}\pi\text{-}HCB_9H_9CCOOH$[4] ($pK_a = 3.54$). These data suggest that the $\pi\text{-}C_5H_5Fe^{III}\text{—}\pi\text{-}HCB_9H_9C$ group exerts a pronounced electron-withdrawing effect which we have estimated using Charton's method [10]. To this end we obtained ferrocarboranylacetic acid XXI from 1-*o*-carboranylacetic acid, cyclopentadiene and ferric chloride:



$$HC\text{—}CCH_2COOH\ (B_{10}H_{10}) + C_5H_6 + FeCl_2 \xrightarrow[\substack{2.\ H_2O_2,\ H_2O \\ 3.\ H^+,\ H_2O}]{1.\ KOH,\ MeOH} \pi\text{-}C_5H_5Fe^{III}\text{—}\pi\text{-}HCB_9H_9CCH_2COOH$$

(XXI)

The ionization constant of XXI was measured in 80% methyl Cellosolve solution ($pK_a = 5.70$) and, according to ref. 10, the induction constant of the $\pi\text{-}C_5H_5Fe^{III}\text{-}\pi\text{-}HCB_9H_9C$ group was then calculated ($\sigma_i = 0.31$). Thus, this group is a strong electron acceptor with an electron-withdrawing effect stronger than that of the $\pi\text{-}C_5H_5Co^{III}\text{—}\pi\text{-}HCB_9H_9C$ group [11] ($\sigma_i = 0.206$), although weaker than that of the 1-*o*-carboranyl group [9] ($\sigma_i = 0.42$). The pronounced electron-accepting properties of the $\pi\text{-}C_5H_5Fe^{III}\text{—}\pi\text{-}HCB_9H_9C$ group make it difficult at present to explain the distinct capacity for S_N1 reactions exhibited by alcohol II and chloromethyl derivative VIII.

TABLE 2

ATOMIC COORDINATES (X 10^4) AND ANISOTROPIC THERMAL PARAMETERS IN THE FORM OF $T = \exp[-1/4(B_{11}h^2a^{*2} + ... + 2B_{23}klb^*c^*)]$ FOR COMPLEX XVI

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Fe(1)	1948(1)	1798(1)	1511(1)	5.86(6)	3.48(4)	3.32(4)	−0.15(5)	1.38(4)	0.19(4)
C(2)	2279(5)	3069(4)	884(6)	4.5(3)	3.3(3)	3.1(3)	0.1(2)	0.3(2)	0.1(2)
C(3)	1222(5)	2703(4)	−67(7)	4.8(3)	4.1(3)	3.3(3)	−0.5(3)	0.5(3)	−0.1(2)
B(4)	1309(7)	1646(6)	−790(9)	6.3(5)	4.6(4)	3.9(4)	−1.3(4)	1.2(3)	0.0(3)
B(5)	2577(7)	1379(6)	−225(10)	6.3(5)	3.8(4)	4.6(4)	0.7(4)	2.4(4)	0.6(3)
B(6)	3173(6)	2301(6)	894(10)	4.5(4)	4.8(4)	4.4(4)	−0.1(3)	1.0(3)	0.6(3)
B(7)	1777(7)	3515(6)	−867(9)	7.1(5)	3.8(4)	3.5(4)	−0.3(3)	0.2(4)	0.9(3)
B(8)	1178(7)	2632(6)	−1943(9)	6.1(5)	5.1(4)	2.7(3)	0.0(4)	0.0(3)	0.0(3)
B(9)	2050(7)	1813(7)	−2046(10)	7.7(5)	4.7(4)	4.1(4)	0.1(4)	2.4(4)	−0.3(4)
B(10)	3184(7)	2217(7)	−1030(10)	5.5(5)	5.9(5)	5.6(5)	−0.2(4)	2.6(4)	0.4(4)
B(11)	3018(6)	3261(6)	−288(9)	5.2(4)	4.9(4)	4.8(4)	−1.2(4)	1.3(3)	0.3(4)
B(12)	2329(7)	2965(6)	−2082(10)	7.2(5)	5.4(5)	3.9(4)	−0.8(4)	1.6(4)	0.6(3)
C(13)	1638(15)	1891(7)	3637(13)	15(1)	5.5(5)	5.0(5)	0.4(6)	5.4(6)	1.0(4)
C(14)	913(8)	1382(12)	2666(15)	6.8(6)	14(1)	7.4(7)	1.6(7)	3.7(6)	5.2(7)
C(15)	1410(14)	652(8)	2228(12)	14(1)	6.5(6)	5.5(6)	−4.7(7)	3.9(7)	0.2(4)
C(16)	2356(13)	702(9)	2887(16)	11.4(9)	7.1(6)	8.3(7)	3.0(7)	5.2(7)	4.1(6)
C(17)	2506(11)	1477(12)	3758(11)	9.2(8)	13(1)	4.2(5)	−2.8(8)	−0.3(5)	3.7(6)
C(18)	2339(5)	3803(5)	2095(7)	5.5(4)	4.4(3)	3.7(3)	0.3(3)	0.3(3)	−0.8(3)
O(19)	3049(4)	3544(3)	3357(5)	10.2(4)	4.4(2)	4.2(2)	0.0(3)	−1.9(2)	0.0(2)
O(20)	1422(4)	3831(3)	2423(6)	9.0(3)	4.4(3)	6.1(3)	0.6(2)	3.0(3)	−1.1(2)
C(21)	3545(7)	4241(6)	4252(10)	7.9(5)	6.0(4)	6.8(5)	0.1(4)	−2.1(4)	−1.8(4)
C(22)	4345(6)	3857(6)	5490(9)	6.2(4)	8.1(5)	5.3(4)	0.8(4)	−0.5(4)	−0.5(4)
C(23)	1073(9)	4707(7)	2669(16)	10.5(7)	7.1(6)	19(1)	1.5(6)	6.4(8)	−3.0(7)
C(24)	229(9)	4689(9)	3151(14)	11.0(8)	14.0(9)	13.5(9)	4.4(8)	4.6(7)	−4.0(8)

Experimental

Reagents and materials

The reactions forming ferrocarboranes from carboranes, ferric chloride and cyclopentadiene, as well as the reactions involving boron and aluminium hydrides and organolithium and -magnesium compounds, were carried out under dry argon. Cyclopentadiene was freshly distilled. Ether was distilled over $LiAlH_4 \cdot$ KOH tablets containing 85% of the alkali. Column and thin layer preparative chromatography were performed with the use of silica gel with the particle size 100—160 μ (Chemapol); TLC involved use of Silufol plates.

Apparatus

IR spectra were recorded on a two-beam UR-10 spectrometer. The samples were pressed into tablets with KBr. PMR spectra were measured with a RYa-2309 spectrometer with a 90 MHz working frequency, mass spectra were obtained using a MS spectrometer. A "pH-340" pH meter was employed in pK_a measurements. The unit cell parameters and the intensities of 1599 independent reflections with $F^2 \geqslant 2\sigma$ were measured at 20°C using a 4-circle Hilger-Watts diffractometer (Cu-K_α radiation, graphite monochromator, $\theta/2\theta$ scan, $\theta \leqslant 66°$). The diffraction experiment was carried out as reported [12] without absorption corrections. The structure was solved by the heavy atom method and refined using the least squares technique, at first in the isotropic and then in the anisotropic approximation. The hydrogen atoms of the C_5H_5 and $C_2B_9H_{10}$ ligands were placed geometrically and included into the final refinement of the structure with constants $B_{iso} = 6$ Å^2. The final R factor is 0.056. All calculations were performed on an Eclipse-S/200 computer with the use of modified EXTL programs.

π-$C_5H_5Fe^{III}$—π-$HCB_9H_9CCH_2OH$ (II)

70 g (1.05 mol) of KOH was added in small portions to 22.81 g (105.48 mmol) of 1-acetoxymethyl-*o*-carborane in 100 ml CH_3OH, and the mixture was stirred vigorously. When the strongly exothermic reaction was complete, the mixture was refluxed while stirring for 3 hours. Upon cooling to 20°C and addition of 13.94 g (210.93 mmol) of cyclopentadiene the mixture was stirred for 5 minutes, while the mixture was stirred vigorously, a solution of 20.05 g (158.2 mmol) of anhydrous $FeCl_2$ in 50 ml CH_3OH was added. After refluxing for 5 hours and cooling to 20°C the mixture was diluted with 200 ml of water and filtered. The precipitate was washed with water (5 × 50 ml). The combined dark red filtrates were concentrated in vacuo at 40—50°C to 300 ml, treated with CO_2 to pH 8—9 and filtered. 10 ml of 30% H_2O_2 was carefully added to the filtrate. The purple precipitate was filtered, washed with water and dried. Upon recrystallization from C_6H_6/heptane there were 20.37 g (71.88 mol, 68%) of needle-shaped purple crystals, m.p. 140—142°C. Found: C, 33.74; H, 6.27; B, 33.81; Fe, 19.85. $C_8H_{18}B_9FeO$ calcd.: C, 33.91; H, 6.40; B, 34.43; Fe, 19.71%. IR spectrum: 3580 (free OH), 3340 (associated OH), 3120 (C_5H_5), 3050 (carborane CH), 2960 (CH_2), 2500—2600 (BH) cm^{-1}.

$[\pi\text{-}C_5H_5Fe^{III}\text{—}\pi\text{-}HCB_9H_9CCH_2OH]Cs$ (III)

A solution of 1.63 g (5.75 mmol) of alcohol II in anhydrous ethanol (75 ml) was treated with the excess of $NaBH_4$, vividly stirred for 5 minutes and allowed to stand for 15 hours at 20°C. The mixture was filtered, the precipitate washed with anhydrous ethanol (20 ml). The combined filtrates were evaporated to dryness in vacuo. The residue was dissolved in 25 ml of water, and filtered. The filtrate was treated with aqueous CsCl. The precipitate was filtered, washed with ice-cold water (2 × 25 ml) and dried. Recrystallization from C_2H_5OH/C_6H_6 gave 2.20 g (5.29 mmol, 92%) of complex III in the form or orange-red needles. $T_{decomp.} = 212\text{—}214°C$. Found: C, 22.82; H, 4.36; B, 23.48; Fe, 13.48. $C_8H_{18}B_9CsFeO$ calcd.: C, 23.08; H, 4.36; B, 23.37; Fe, 13.42%. IR spectrum: 3400—3600 (associated OH), 3580 (free OH), 3580 (free OH in hexachlorobutadiene) cm^{-1}.

$\pi\text{-}C_5H_5Fe^{III}\text{—}\pi\text{-}HCB_9H_9CCH_2OAc$ (V)

0.94 g (3.31 mmol) of II was dissolved in a mixture of 6 ml of Ac_2O, 8 ml of AcOH and 0.2 ml of H_2SO_4. On standing for 30 min the mixture was poured onto 30 g of crushed ice, neutralized with saturated $NaHCO_3$ solution to pH 7—8 and extracted with CH_2Cl_2 (3 × 100 ml). The organic layers were washed with $NaHCO_3$ solution and water and then dried over $CaCl_2$. Upon evaporation to dryness the residue was chromatographed on a 2.5 × 25 cm column packed with silica gel deactivated by water (10%). The eluent was benzene. After the eluent was evaporated, the dry residue was washed with hexane. The yield was 0.72 g (2.19 mmol, 66%) of complex VI (pruple crystals). M.p. 93—94°C. Found: C, 36.91; H, 6.19; B, 29.85; Fe, 17.03. $C_{10}H_{20}B_9FeO_2$ calcd.: C, 36.91; H, 6.91; B, 29.90; Fe, 17.16%. IR spectrum: 1750 (C=O), 2400—2600 (B—H), 3050 (carborane CH), 3100 (C_5H_5) cm^{-1}.

$\pi\text{-}C_5H_5Fe^{III}\text{—}\pi\text{-}HCB_9H_9CCHO$ (VI)

A solution of 2.5 g (8.82 mmol) of alcohol II in dry CH_2Cl_2 (50 ml) was added to a suspension of 5.71 g (26.46 mmol) of $C_5H_5NHCrO_3Cl$ in dry CH_2Cl_2 (50 ml). The mixture was allowed to stand for 15 hours upon stirring for 3 hours at 20°C and then filtered. The precipitate was washed by CH_2Cl_2 (2 × 25 ml). The combined filtrates were concentrated in vacuo to 30 ml and chromatographed on a silica gel column (3 × 20 cm) with CH_2Cl_2 as an eluent. Recrystallization from C_6H_6/heptane yielded 1.53 g (5.44 mmol, 62%) of aldehyde VI in the form of dark purple crystals. M.p. 153—154°C. Found: C, 34.26; H, 5.75; B, 34.32; Fe, 19.53. $C_8H_{16}B_9FeO$ calcd.: C, 34.15; H, 5.73; B, 34.58; Fe, 19.85. IR spectrum: 1710 (C=O), 2400—2600 (B—H), 2870 (C—H of the CHO group), 3050 (carborane C—H), 3120 (C_5H_5) cm^{-1}.

2,4-dinitrophenylhydrazine and aldehyde VI in C_2H_5OH gave a hydrazone which was recrystallized from AcOH. $T_{decomp.}$ 209°C (with explosion). Found: B, 21.22; Fe, 12.18. $C_{14}H_{20}B_9FeN_4O_4$ calcd.: B, 21.08; Fe, 12.10%. IR spectrum: 3310 (NH), 3120 (C_5H_5), 3040 (carborane CH), 2400—2600 (BH), 1620 (C=N), 1520, 1340 (NO_2) cm^{-1}.

π-$C_5H_5Fe^{III}$—π-$HCB_9H_9CCH_2OEt$ (VII)

0.74 g (2.61 mmol) of alcohol II was refluxed in C_2H_5OH (50 ml) in the presence of H_2SO_4 (1 ml) for 3 hours. Upon cooling, solid $NaHCO_3$ was carefully added until the evolution of CO_2 ceased. The mixture was filtered, evaporated to dryness in vacuo; the residue was chromatographed on a silica gel column (2.5 × 25 cm) with $CHCl_3$ as an eluent. Recyrstallization from $CHCl_3$/hexane gave 0.67 g (2.16 mmol, 33%) of purple crystals of ethyl ether VII. M.p. 124—125°C. Found: C, 38.74; H, 7.18; B, 31.73; Fe, 17.80. $C_{10}H_{22}B_9FeO$ calcd.: C, 38.57; H, 7.12; B, 31.24; Fe, 17.93%. IR spectrum: 2400—2600 (BH), 2870, 2900 (CH_2), 2990 (CH_3), 3050 (carborane CH), 3110 (C_5H_5) cm^{-1}.

π-$C_5H_5Fe^{III}$—π-$HCB_9H_9CCH_2Cl$ (VIII)

0.41 g (1.45 mmol) of alcohol II in dry CH_2Cl_2 (50 ml) was mixed with 0.2 g (1.45 mmol) of anhydrous $ZnCl_2$ and saturated with dry HCl at 0°C. The mixture was sealed and allowed to stand for 15 hours at 20°C. Upon evaporation of the solvent the dry residue was chromatographed on a silica gel volumn (1.5 × 30 cm), eluent C_6H_6. Recrystallization from $CHCl_3$/hexane gave 0.25 g (0.83 mmol, 57%) of dark purple crystals of chloromethyl derivative VIII. M.p. 122—123°C. Found: C, 31.65; H, 5.50; Cl, 11.01. $C_8H_{17}B_9FeCl$ calcd.: C, 31.84; H, 5.68; Cl, 11.75%. IR spectrum: 3120 (C_5H_5), 3045 (carborane CH), 3020, 2965 (CH_2), 2400—2600 (BH) cm^{-1}.

Ethanolysis of chloromethyl derivative VIII

0.15 g (0.51 mmol) of complex VIII was dissolved in 25 ml anhydrous ethanol and allowed to stand for 72 hours at 20°C. After evaporation of the solvent in vacuo, recrystallization from $CHCl_3$/hexane yielded 0.15 g (0.47 mmol, 93%) of purple crystals of ethyl ether derivative VII. M.p. 124—125°C.

Solvolysis of VIII by aqueous methyl Cellosolve in the presence of KCN

A solution of 0.34 g (5.06 mmol) of KCN in 30 ml of methyl Cellosolve/water mixture (5/1) was added dropwise to 1.45 g (4.82 mmol) of VIII in 60 ml of the same mixture while stirring. After 2 hours stirring the solvent was evaporated in vacuo at 40°C. A solution of the residue in 30 ml C_6H_6 was filtered from the KCl precipitate and chromatographed on a silica gel column (2.5 × 30 cm); eluent benzene. The yield was 1.20 g (3.52 mmol, 73%) of complex IX in the form of purple crystals. M.p. 95—97°C (from C_6H_6/heptane). Found: C, 38.90; H, 7.10; B, 28.59. $C_{11}H_{24}B_9FeO_2$ calcd.: C, 38.69; H, 7.08; B, 28.50%. IR spectrum: 3115 (C_5H_5), 3060 (carborane CH), 2990, 2870—2930, 2920 (CH_2CH_3), 2400—2600 (BH). 0.15 g (0.53 mmol, 11%) of alcohol II was also obtained. M.p. 140—142°C.

Reaction of alcohol II with H_2AlCl in ether.

A solution of 35 mmol of H_2AlCl in ether (obtained by mixing equivalent amounts of $LiAlH_4$ and $AlCl_3$ in ether) was added dropwise, while stirring, to 3.1 g (10.93 mmol) of II in 100 ml ether at 20°C. The bulky precipitate dissolved as the addition of H_2AlCl proceeded. Upon stirring the mixture for 5 hours, 5 ml of anhydrous CH_3OH was added. The solvent was evaporated in vacuo, the dry residue dispersed in 2% aqueous NaOH, the mixture filtered, the precipitate washed with water and dried. Chromatography on a silica gel column (3 × 25 cm) with benzene as eluent gave 2.34 g (6.89 mmol, 63%) of complex X in the form of yellow-orange crystals. Recrystallization from C_6H_6/heptane was performed by slow evaporation in vacuo at 20°C. $T_{\text{decomp.}}$ 143—145°C. Found: C, 42.30; H, 7.52; B, 29.26. $C_{12}H_{27}B_9FeO$ calcd.: C, 42.33; H, 7.99; B, 28.58%. IR spectrum: 3110 (C_5H_5), 2850—2970 (CH_3, CH_2), 2500—2600 (BH) cm^{-1}. The filtrate was neutralized with CO_2 to pH 8—9 and treated with 30% H_2O_2 (2 ml) to yield 0.023 g (0.087 mmol, 0.8%) of methyl derivative XI in the form of purple crystals. M.p. 167—169°C (C_6H_6/heptane). Found: C, 36.48; H, 7.12; B, 36.41; Fe, 20.63. $C_8H_{18}B_9Fe$ calcd.: C, 35.94; H, 6.79; B, 36.39; Fe, 20.87%. Mass spectrum: $m/e = 269$ (M^+ — $^{12}C_8{}^1H_{18}{}^{11}B_9{}^{56}Fe^+$). IR spectrum: 3120 ($C_5H_5$), 3050 (carborane CH), 3000, 2945 (CH_3), 2400—2600 (BH) cm^{-1}.

π-$C_5H_5Fe^{III}$—π-$HCB_9H_9C(OH)HCH_3$ (XII)

A solution of 6.03 mmol of CH_3MgCl in 15 ml ether was added to 0.81 g (2.91 mmol) of aldehyde VI in 100 ml ether for 20 minutes under stirring. After stirring for 1.5 hours the solvent was evaporated in vacuo, the dry residue dissolved in water and filtered. The filtrate was treated with CO_2 to pH 8.0 and 2 ml of 30% H_2O_2 was carefully added. The precipitate was filtered, washed with water, dried and chromatographed on silica gel (3 × 25 cm column) deactivated by 15% water (by weight), eluent C_6H_6. Recrystallization from C_6H_6/heptane yielded 0.37 g (1.25 mmol, 43%) of purple crystals of methylcarbinol XII. M.p. 171—172°C (with decomposition). Found: C, 36.87; H, 6.91; B, 32.71; Fe, 18.80. $C_9H_{20}B_9FeO$ calcd.: C, 36.35; H, 6.78; B, 32.72; Fe, 18.78% IR spectrum (in hexachlorobutadiene): 3550 (free OH), 3490 (associated OH), 3130 (C_5H_5), 3050 (carborane CH), 2980, 2940 (CH_2CH_3) cm^{-1}.

π-$C_5H_5Fe^{III}$—π-$HCB_9H_9CC(OH)HC_6H_5$ (XIII)

As in the previous case, 0.96 g (2.66 mmol, 37%) of phenylcarbinol XIII was obtained as a mixture of diastereomers from 2.03 g (7.20 mmol) of aldehyde VI and 15.12 mmol of C_6H_5Li in 200 ml ether. The mixture was separated by preparative TLC on silica gel (18 × 24 cm plate, eluent C_6H_6, 4 runs per plate). The front diastereomer has m.p. 141—142°C (pentane). Found: B, 27.27; Fe, 15.35. $C_{14}H_{22}B_9FeO$ calcd.: B, 27.07; Fe, 15.54%. IR spectrum: 3130, 3110, 3090 (C_6H_5, C_5H_5), 3040 (carborane CH), 2400—2600 (BH), 3570 (free OH) cm^{-1} in hexachlorobutadiene. The second diastereomer has m.p. 163—165°C (with decomposition, from C_6H_6/heptane). Found: C, 46.99; H, 6.44; Fe, 15.68. $C_{14}H_{21}B_9FeO$ calcd.: C, 46.78; H, 6.17; Fe, 15.44%. IR spectrum: 3110 (C_6H_5, C_5H_5), 3050, 3040 (carborane CH), 2400—2600 (BH), 3580 (free OH) cm^{-1} (in hexachlorobutadiene).

[π-$C_5H_5Fe^{II}$—π-$HCB_9H_9CC(OH)HCH_3$]$N(CH_3)_4$ (XIV)

As in the synthesis of complex III, 0.78 g (2.09 mmol, 93%) of red crystals XIV were obtained from 0.67 g (2.25 mmol) of XII. M.p. 214—215°C (with decomp., from CH_3CN/toluene). Found: C, 42.43; H, 8.77; B, 26.34; $C_{13}H_{32}B_9FeNO$ calcd.: C, 42.03; H, 8.68; B, 26.18%. IR spectrum: 3100 (C_5H_5), 3030 (carborane CH), 2830—3000 (CH_2CH_3), 2400—2600 (BH), 3560 (free OH) cm^{-1} (in hexachlorobutadiene).

π-$C_5H_5Fe^{III}$—π-$HCB_9H_9CCOCH_3$ (XV)

As in the synthesis of aldehyde VI, 1.52 g (5.15 mmol, 72%) of ketone XV was obtained from 2.14 g (7.20 mmol) of methylcarbinol XXII and 5.43 g (25.19 mmol) of $C_5H_5N \cdot HCrO_3Cl$ in 100 ml of dry CH_2Cl_2. M.p. 177—178°C (from C_6H_6/heptane). Found: C, 36.81; H, 6.07; B, 32.99. $C_9H_{18}B_9FeO$ calcd.: C, 36.60; H, 6.14; B, 32.94%. IR spectrum: 3114 (C_5H_5), 3050 (carborane CH), 2400—2600 (BH), 1698 (C=O) cm^{-1}, Mass spectrum: $m/e = 297$ (M^+ — $^{12}C_9{}^1H_{18}{}^{11}B_9{}^{56}Fe^{16}O$).

Reaction of ketone XV with CH_3MgCl

A mixture of 0.16 g (0.54 mmol) of ketone XV and 1.19 mmol of CH_3MgCl in ether (100 ml) was treated with D_2O (25 ml) followed by 30% H_2O_2 (1 ml) to yield 0.14 g (0.47 mmol, 87%) of ketone XVa. The presence of the D-label follows from the shift of the basic isotopic peaks M^+ by unity.

π-$C_5H_5Fe^{III}$—π-$HCB_9H_9CCH(OC_2H_5)_2$ (XVI)

(a) A solution of 0.19 mmol of C_2H_5ONa in 1.1 ml of C_2H_5OH was added to 0.22 g (0.78 mmol) of aldehyde VI in anhydrous C_2H_5OH (20 ml). The mixture was allowed to stand for 96 hours at 20°C, treated with CO_2 and evaporated in vacuo. Chromatography on silica gel (3 × 30 cm column, eluent C_6H_6) yielded 0.06 g (0.17 mmol, 22%) of purple crystals XVI. M.p. 159—160°C ($CHCl_3$/hexane). Found: C, 40.73; H, 7.38; B, 27.12; Fe, 15.56; $C_{12}H_{28}B_9FeO_2$ calcd.: C, 40.32; H, 7.89; B, 27.22; Fe, 15.62%. IR spectrum: 3115 (C_5H_5), 3050 (carborane CH), 2890—2990 (CH, CH_2, CH_3). According to TLC and mass spectrometric evidence, the mixture contains also complex I, alcohol II and methyl derivative XI.

(b) 0.24 g (0.84 mmol) of aldehyde VI and 0.05 ml of H_2SO_4 in 30 ml of anhydrous C_2H_5OH was allowed to stand for 3 hours at 20°C, mixed with 1 g of Na_2CO_3, stirred and filtered. Recrystallization of the dry residue gave 0.26 g (0.73 mmol, 87%) of diethylacetal XVI. M.p. 159—160°C.

(c) 0.15 g (0.55 mmol) of aldehyde VI, 0.1 ml of orthoformic ester and a few NH_4NO_3 crystals were refluxed for 1 min in 30 ml of anhydrous C_2H_5OH and allowed to stand for 10 hours at 20°C. After evaporation to dryness in vacuo the residue was chromatographed on silica gel (2.5 × 20 cm column, eluent C_6H_6) to yield 0.1 g (0.27 mmol, 49%) of XVI, m.p. 159—160°C.

Reaction between complex I and n-BuLi

At —20°C 16.59 mmol of BuLi in benzene was added dropwise, while stirring, to 2 g (7.9 mmol) of complex I in ether (200 ml). After being stirred for an hour at 20°C the mixture was treated with dry CO_2 for 20 minutes. On addition of water (200 ml) the organic layer was separated. The aqueous layer was acidified with diluted hydrochloric acid to pH 2.0, mixed with 1 ml of 30% H_2O_2 and extracted by ether (3 × 100 ml). The combined organic phases were washed with water (4 × 150 ml), concentrated in vacuo to 100 ml and treated with an excess of CH_2N_2 in ether. The solvent was evaporated to dryness in vacuo, the residue chromatographed on silica gel (2.5 × 30 cm column, eluent benzene). The yield was 1.42 g (5.6 mmol, 71%) of complex I, m.p. 179—180 (benzene/heptane) and 0.54 g (1.73 mmol, 22%) of complex XX. $T_{\text{decomp.}}$ 192—194°C (benzene/heptane). Found: C, 34.79; H, 6.11; B, 31.40; Fe, 17.90. $C_9H_{18}B_9FeO_2$ calcd.: C, 34.72; H, 5.83; B, 31.25; Fe, 17.93%. IR spectrum: 1730 (C=O) 2400—2600 (BH), 2850, 2960 (CH_3), 3065 (carborane CH), 3120 (C_5H_5) cm^{-1}.

π-$C_5H_5Fe^{III}$—π-HCB_9H_9CCOOH (XVII)

To 60.03 mmol of potassium 1-carboxy-1,2-dicarbaundecaborate (from 11.3 g of 1-*o*-carborane-carboxylic acid and 20.45 g of piperidine in 100 ml of dry benzene) in 70 ml of CH_3OH were added 40 g (0.6 mmol) of KOH and the suspension was stirred until it became homogeneous. Then 7.95 g (120.1 mmol) of cyclopentadiene was added and, in 5 minutes, a solution of 17.9 g (90.05 mmol) of $FeCl_2 \cdot 4\ H_2O$ in 40 ml of CH_3OH. The mixture was boiled and stirred for 4 hours, diluted with 150 ml of water and filtered. The residue was washed with water (3 × 50 ml) and the combined dark red filtrates were concentrated in vacuo at 40—50°C to 200 ml. The solution was then treated with CO_2 to pH 8—9 and, upon careful addition of 20 ml of 30% H_2O_2 and the appearance of a dark purple colouring, slowly acidified with diluted hydrochloric acid to pH 2.0. The dark purple precipitate was filtered off and washed with water (3 × 100 ml), dissolved in 0.1 *N* aqueous NaOH, filtered again and carefully acidified with diluted HCl. The residue was filtered, washed with water and dried. Recrystallization from 1,2-dichloroethane and then from C_2H_5OH/H_2O gave 6.07 g (20.41 mmol, 34%) of acid XVII, m.p. 350°C. Found: C, 32.61; H, 5.12; B, 32.14; Fe, 18.56. $C_8H_{16}B_9FeO_2$ calcd.: C, 32.31; H, 5.42; B, 32.72; Fe, 18.78%. IR spectrum: 1700 (C=O), 2400—2600 (BH), 3040 (carborane CH), 3110 (C_5H_5), 2600—3200 (OH) cm^{-1}.

0.2 g (0.67 mmol) of acid XVII and CH_2N_2 in ether solution yielded 0.19 g (0.62 mmol, 92%) of methyl ester XX. $T_{\text{decomp.}}$ 192—194°C.

π-$C_5H_5Fe^{III}$—π-$HCB_9H_9CCH_2COOH$ (XXI)

23 g (0.34 mmol) of KOH was slowly added while stirring to a suspension of 6.87 g (33.97 mmol) of 1-*o*-carboranylacetic acid in 40 ml CH_3OH. As the vigorous reaction was complete, the mixture was boiled and stirred for 5 hours. After cooling to 20°C, 4.5 g (67.95 mmol) of cyclopentadiene and (in 5 minutes) 6.46 g (50.96 mmol) of anhydrous $FeCl_2$ in 30 ml of CH_3OH were added. The solution was refluxed and stirred for 4.5 hours and treated as described for acid XVII. Final purification was performed by chromatography on silica gel (3 × 20 cm column, eluent $CHCl_3/CH_3OH$ 23/2). Recrystallization from $CHCl_3$ gave 5.53 g (17.76 mmol, 52%) of acid XXI in the form of purple needles. $T_{\text{decomp.}}$ 148—150°C. Found: C, 34.85; H, 5.84; B, 30.32. $C_9H_{18}B_9FeO_2$ calcd.: C, 34.72; H, 5.83; B, 30.25%. IR spectrum: 1715, 1730 (C=O), 2400—2600 (BH), 3065 (carborane CH), 3125 (C_5H_5), 2800—3200 (OH) cm^{-1}.

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