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Iron Cyclopentadienylcarbonyl Complexes with Azoles. I. Complexes of Imidazoles and Vicinal Triazoles

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The reactions of halides, π-$C_5H_5Fe(CO)_2X$ (X = Cl, Br, I), with sodium salts of some triazoles and imidazoles yield compounds of the composition π-$C_5H_5Fe(CO)_2L$ (L = heterocycle moiety). These complexes react with acids and complex anions in water to form the salts $[\pi\text{-}C_5H_5Fe(CO)_2LH]^+ A^-$ (A^- = anion). Stabilization of these salts is ensured by the formation of a hydrogen bond between the cation and anion parts (H-bonding contact ion pair) or between the cation and molecules of the solvent in the outer coordination sphere. The hydrogen bond is realized via the NH group of the heterocyclic ligands and the acceptor fragment of the outer sphere ligands. X-ray analysis of the benzimidazole complex $[\pi\text{-}C_5H_5Fe(CO)_2\text{-}1\text{-}N(C_7H_6N_2)]^+ B(C_6H_5)_4^- \cdot (CH_3)_2O$ showed that it has monoclinic crystals, a = 13.626(1), b = 25.410(7), c = 10.088(1)Å, β = 92.65(1)°, d_{exp} = 1.28, d_{calc} = 1.285 g/cm³, Z = 4, spatial group $P2_1/n$.

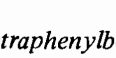
The compounds π-$C_5H_5Fe(CO)_2L$-$B(C_6H_5)_3$ have been isolated by decomposition of the salts $[\pi\text{-}C_5H_5Fe(CO)_2LH]^+A^-$, where $A^- = B(C_6H_5)_4^-$, and LH = some triazoles and imidazoles.

Introduction

The metal coordination compounds with azoles have been widely discussed [1–3]. Literature data show that the coordination possibilities of a polynitrogen heterocycle do not concern only the bonding with metal. Thus, such compounds may display an outer sphere coordination via the hydrogen bonds [4, 5]. There were yet no systematic studies of such phenomenon. Meanwhile, elucidation of the coordinative reserves in the combined polynitrogen heterocycles is an important problem in biochemistry concerned with protein–nucleic interaction. On the other hand, the nucleic bases with numerous acid–base groups are themselves rather complicate objects in the study of elementary outer sphere coordination mechanisms. Azoles and their complexes with univalent organometallic groups are more simple and similar to the nucleic bases. In our opinion they are good models for elucidating the specificities of unexhausted coordination in polynitrogen heterocyclic bases, specifically participation of the coordinated azoles in the H-bond formation and proton transfer reactions.

It is known that iron cyclopentadienyldicarbonyl iodide and the salts of some azoles (imidazole, pyrazole and 1,2,4-triazole) produce the complexes, $C_5H_5Fe(CO)_2L$, with an organometallic group, $C_5H_5Fe(CO)_2$–(Fp), joined to one of the nitrogens in heterocyclic ring [6]. Moreover, earlier we have obtained similar complexes with benzotriazole [7]. Fp fragment is a univalent group with a central iron atom having one vacant coordination site. This group forms sufficiently stable derivatives with heterocycles. On the other hand, the Fp derivatives with aliphatic ligands could be protonated into the organometallic cations [8]. Usually unlabile, the Fp group may in some cases undergo intramolecular metallotropic transformations [9]. All these properties qualify the Fp fragment as a convenient substituent in azole nucleus.

At the same time the coordinated diazoles are the most simple objects in revealing unexhausted coordinations in the azoles: they retain only one main center upon coordination with metallic group Fp.



This paper is concerned with reactions of Fp-X halides and sodium salts of various imidazoles. Analogous complexes of some vicinal triazoles were also prepared.

Results and Discussion

Tetraphenylborates

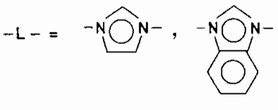
Reaction of iron cyclopentadienyldicarbonyl halides with sodium salts of some imidazoles (imidazole, benzimidazole, 5,6-dimethylbenzimidazole) and vicinal triazoles (1,2,3-triazole, 4-phenyl-1,2,3-

TABLE I. ^{1}H NMR Spectra (σ scale)^a.

Formula	Cp	2H	Other Signals of Heterocycle^b	Signals of Phenyl Groups in the Anions or BPh$_3$	N–H Signals	Solvent and Conditions of measurement^c
I	5.50(s)	8.11(s)		7.01(m), 7.43(m)	undetec.	Acetone
II	5.49(s)	8.50(s)		6.93(m), 7.34(m)	"	"
III	5.56(s)	8.51(s)	2.36(s), 2.47(s)	7.05(m), 7.52(m)	"	Acetone-D$_6$
IV	5.70(s)			7.40(m), 7.95(m)	"	"
V	5.64(s)		8.26(s), 7.71(m)	7.10(m), 7.33(m)	"	Acetone
VI	5.30(s)			7.10(m)	12.15	CH$_2$Cl$_2$ –88 ℃
VII	5.29(s)	8.02(s)		7.01(m), 7.57(m)		THF
VIII	5.20(s)	8.25(s)	2.31(s), 2.42(s)	6.99(m), 7.48(m)	13.34	THF –100 ℃
IX	5.38(s)		8.61(s), 7.91(m)	7.35(m), 7.60(m)	16.09	THF –70 ℃
IX	5.22(s)		8.29(s), 7.78(m)	6.95(m), 7.40(m)	undetec.	THF
X	5.33(s)	6.71(s)		7.11(m)		THF
XI	5.45(s)	6.87(s)	723(m)	7.11(m)		
XII	5.55(s)	6.68(s)	2.01(s), 2.34(s) 7.55(s), 7.62(s)	7.12(m)		Acetone-D$_6$ Acetone-D$_6$
XIII	5.43(s)		7.34(s), 7.72(s)	7.15(m)		Acetone-D$_6$
XIV	5.61(s)			7.20(m)		Acetone-D$_6$

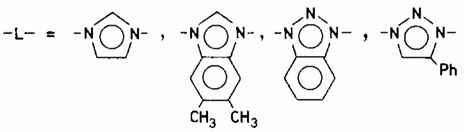
^{a}Chemical shift with respect to TMS. ^{b}Heterocycle signals nonoverlapping with Ph groups of the anions or BPh$_3$ group. ^{c}Measured at 34 ℃ beside the cases with indicated temperature: for I–V solv = acetone.

triazole, benzotriazole) produces the complexes with heterocycles which could be isolated by alumina chromatography. Action of sodium tetraphenylborate on aqueous acetonic solutions of the complexes precipitated the salts [Fp–L–H ··· solv]$^+$BPh$_4^-$*, where



Ia II

and solv = acetone;



Ib III IV V

and solv = water.

Solvent molecule (water or acetone) is retained in an outer coordination sphere by hydrogen bond with the heterocycle amino group. These salts are yellow crystalline solids, soluble in some polar solvents (THF, acetone, methanol).

The ^{1}H NMR spectra of compounds I–V (Table I) were measured in acetone. Thus the amino group of heterocycle coordinated with acetone molecule in solution.

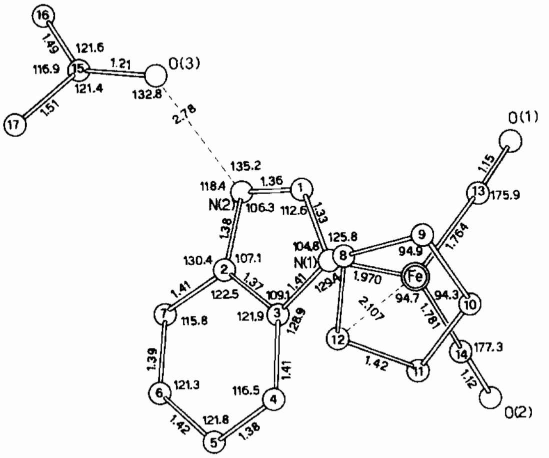


Figure 1. Structure of cation $(C_5H_5)Fe(CO)_2(C_7H_6N_2)^+$.

IR spectra

Some characteristic bands of various groups in compounds I–V are listed in Table II. Unlike acetone complexes, aqua-complexes show an intense broad OH band at 3310–3230 cm^{-1} due to coordinated water.

X-ray analysis

Benzimidazole salt (II) was subjected to X-ray study. Its crystal is composed of discrete complex cations, $(C_5H_5)Fe(CO)_2(C_7H_6N_2)^+$, anions, $B(C_6H_5)_4^-$ and acetone molecules combined with N(2) atom of the complex cation imidazole ligand *via* the O(3)···H–N(2) hydrogen bonds. Structure of the cation and its associated acetone molecule is shown

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*In the case of triazoles such salts were obtained only from 1–N–Fp derivatives.

TABLE II. Frequencies (ν cm^{-1}) of Some Groups in the IR Spectra (KBr Pellets).

Groups	Ib	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	XIII	XIV
CO	2059	2050	2050	2061	2062	2064	2060	2058	2072	2056	2055	2053	2055	2062
	2013	2009	2002	2007	2009	2015	2002	2012	2028	2004	2008	2003	2009	2006
CN						2192	2176	2181	2196					
N–H bond	3311	3300	3296	3240	3233	3210–2590	3140–2670	3150–2660	2980–2370					

TABLE III. Bond Lengths d (Å).

Bond	d(Å)	Bond	d(Å)	Bond	d(Å)	Bond	d(Å)
Fe–N(1)	1.970(7)	C(8)–C(9)	1.42(1)	C(15)–C(16)	1.49(1)	C(32)–C(33)	1.34(1)
		C(9)–C(10)	1.42(1)	C(15)–C(17)	1.51(1)	C(33)–C(34)	1.40(1)
Fe–C(13)	1.764(8)	C(10)–C(11)	1.45(1)	mean	1.50	C(34)–C(35)	1.38(1)
Fe–C(14)	1.781(9)	C(11)–C(12)	1.44(1)			C(35)–C(30)	1.42(1)
mean	1.773	C(12)–C(8)	1.42(1)	C(18)–C(19)	1.43(1)	C(36)–C(37)	1.36(1)
		mean	1.43	C(19)–C(20)	1.42(1)	C(37)–C(38)	1.44(1)
Fe–C(8)	2.099(9)	N(1)–C(1)	1.33(1)	C(20)–C(21)	1.37(2)	C(38)–C(39)	1.41(1)
Fe–C(9)	2.105(9)	N(1)–C(3)	1.41(1)	C(21)–C(22)	1.39(1)	C(39)–C(40)	1.34(1)
Fe–C(10)	2.102(9)	N(2)–C(1)	1.36(1)	C(22)–C(23)	1.42(1)	C(40)–C(41)	1.42(1)
Fe–C(11)	2.111(9)	N(2)–C(2)	1.38(1)	C(23)–C(18)	1.40(1)	C(41)–C(36)	1.40(1)
Fe–C(12)	2.118(10)			C(24)–C(25)	1.37(1)	mean	1.40
mean	2.107	C(2)–C(3)	1.37(1)	C(25)–C(26)	1.40(1)		
		C(3)–C(4)	1.41(1)	C(26)–C(27)	1.37(1)	B–C(18)	1.65(1)
C(13)–O(1)	1.15(1)	C(4)–C(5)	1.38(1)	C(27)–C(28)	1.38(1)	B–C(24)	1.63(1)
C(14)–O(2)	1.12(1)	C(5)–C(6)	1.42(1)	C(28)–C(29)	1.42(1)	B–C(30)	1.63(1)
mean	1.14	C(6)–C(7)	1.39(1)	C(29)–C(24)	1.41(1)	B–C(36)	1.67(1)
		C(7)–C(2)	1.41(1)	C(30)–C(31)	1.39(1)	mean	1.65
C(15)–O(3)	1.21(1)	mean	1.40	C(31)–C(32)	1.43(1)		

TABLE IV. Bond Angles (°).

Angle	ω°	Angle	ω°	Angle	ω°
Fe N(1) C(1)	125.8(5)	C(11) C(12) C(8)	107.2(8)	C(18) C(19) C(20)	120.5(9)
Fe N(1) C(3)	129.4(5)	C(12) C(8) C(9)	107.3(8)	C(19) C(20) C(21)	122,0(9)
Fe C(13) O(1)	175.9(5)	mean	107.7	C(20) C(21) C(22)	118.6(9)
Fe C(14) O(2)	177.3(5)			C(21) C(22) C(23)	120.6(9)
N(1) Fe C(13)	94.9(3)	C(16) C(15) O(3)	121,6(8)	C(22) C(23) C(18)	121.9(9)
N(1) Fe C(14)	94.7(3)	C(17) C(15) O(3)	121.4(8)	C(23) C(18) C(19)	116.4(9)
C(13) Fe C(14)	94.3(3)	C(16) C(15) C(17)	116.9(8)	C(24) C(25) C(26)	121,9(8)
N(1) C(1) N(2)	112.6(8)			C(25) C(26) C(27)	119.7(9)
C(1) N(2) C(2)	106.3(8)	C(18) B C(24)	113.2(9)	C(26) C(27) C(28)	119.0(8)
N(2) C(2) C(3)	107.1(7)	C(18) B C(30)	112.2(9)	C(27) C(28) C(29)	120.4(9)
C(2) C(3) N(1)	109.1(7)	C(18) B C(36)	103.7(9)	C(28) C(29) C(24)	123.2(8)
C(3) N(1) C(1)	104.8(7)	C(24) B C(30)	102.6(9)	C(29) C(24) C(25)	115.7(9)
N(1) C(3) C(4)	128.9(7)	C(24) B C(36)	113.1(9)	C(30) C(31) C(32)	120.0(9)
N(2) C(2) C(7)	130.4(8)	C(30) B C(36)	113.3(9)	C(31) C(32) C(33)	122.0(8)
C(2) C(3) C(4)	121.9(8)			C(32) C(33) C(34)	119.8(8)
C(3) C(4) C(5)	116.5(8)	B C(18) C(19)	119.0(8)	C(33) C(34) C(35)	118.6(9)
C(4) C(5) C(6)	121.8(8)	B C(18) C(23)	124.6(8)	C(34) C(35) C(30)	123,3(9)
C(5) C(6) C(7)	121,3(8)	B C(24) C(25)	121,3(8)	C(35) C(30) C(31)	116.2(9)
C(6) C(7) C(2)	115.8(8)	B C(24) C(29)	122.5(8)	C(37) C(38) C(39)	117.8(9)
C(7) C(2) C(3)	122.5(8)	B C(30) C(31)	123.6(8)	C(38) C(39) C(40)	120.4(9)
		B C(30) C(35)	120.2(8)	C(39) C(40) C(41)	120.4(9)
C(8) C(9) C(10)	109.0(8)	B C(36) C(37)	124.6(8)	C(40) C(41) C(36)	121.4(8)
C(9) C(10) C(11)	107.0(8)	B C(36) C(41)	118.1(8)	C(41) C(36) C(37)	117.2(8)
C(10) C(11) C(12)	107.8(8)	mean	121.9	C(36) C(37) C(38)	122.6(9)
				mean	120.1

TABLE V. Equations of Planes Ax + By + Cz = D of Some Structural Fragments and Atomic Deviations from Them (Å).

Atoms									A	B	C	D
N(1)	N(2)	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	10.42	16.10	8.23	11.22
0.01	0.00	0.02	−0.01	−0.02	−0.01	0.02	0.02	−0.01				
C(8)	C(9)	C(10)	C(11)	C(12)					13.22	4.97	−1.91	3.90
0.00	0.01	−0.01	0.00	0.00								
C(15)	C(16)	C(17)	O(3)						9.39	0.54	6.98	3.73
0.02	−0.01	0.00	−0.01									
C(18)	C(19)	C(20)	C(21)	C(22)	C(23)				3.77	−2.07	9.52	6.79
0.01	0.00	−0.01	0.01	0.00	0.01							
C(24)	C(25)	C(26)	C(27)	C(28)	C(29)				12.01	6.49	3.60	6.93
0.00	0.01	0.00	−0.01	0.01	−0.01							
C(30)	C(31)	C(32)	C(33)	C(34)	C(35)				−6.57	15.56	6.54	9.39
−0.01	−0.01	0.02	−0.01	0.00	0.01							
C(36)	C(37)	C(38)	C(39)	C(40)	C(41)				1.88	25.02	1.01	9.82
0.01	−0.01	0.00	0.01	−0.01	0.00							

in Fig. 1, the bond lengths and bond angles are given in Tables III and IV respectively.

As usually the iron atom coordination sphere includes h^5-cyclopentadienyl ligand, two carbonyl groups and N(1) atom of benzimidazole ligand. The iron atom coordination is pseudo-octahedral and, thus, the angles between monodentate carbonyl ligands and Fe–N(1) bond are about 90° (mean 94.6°). The Fe–N(1) bond length, 1.970(7)Å, is close to that in the iron imidazole complex with dimethylglyoxime, $(Im)_2Fe(DMG)_2 \cdot 2CH_3OH$ [10] (Im = imidazole, DMG = dimethylglyoxime, Fe–N(Im) = 1.985(5) Å). Benzimidazole ligand (Table V) is planar (the table shows equations of its mean planes and atomic deviations from them, in Å). Its imidazole geometry is similar to that of a coordinated imidazole in the above mentioned dimethylglyoxime complex [10] and other metal imidazole complexes [11] and slightly different from the geometry of the non-coordinated imidazole [12].

The bond lengths Fe–CO (mean 1.77(1)Å), C–O (mean 1.14(1)Å), Fe–C(C_5H_5) (mean 2.107(9)Å) and C–C in h^5-C_5H_5 (mean 1.43(1)Å) are common for Fp-derivatives [13]. Dihedral angle between the mean planes of cyclopentadienyl and benzimidazole ligands is equal to 32.0°.

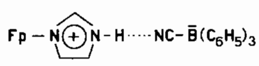
The hydrogen bond retaining an acetone molecule in the outer coordination sphere, (O(3)···N(2)) has a length of 2.78Å, specific of such interactions (2.7–2.8Å [14]). Dihedral angle between benzimidazole and acetone is 51.3°. The geometry of acetone coordinated via the hydrogen bond varies negligibly. The bond lengths, C(15)–C(16) 1.49(1)Å, C(15)–C(17) 1.51(1)Å and C(15)=O(3) 1.21(1)Å are close to the standard values [15]. Thus, localization of the H-bond proton at N(2) may be assumed.

The mean B–C distance (1.65(1)Å) in tetraphenylborate-anion is comparable to the values found in $[Cu_2(tren)_2L_2]^+B(C_6H_5)_4^-$ [16] (1.63(3), L = Cl; 1.643(5), L = NCO and 1.645(9)Å, L = NCS). The phenyl rings are planar with mean C–C distance equal to 1.39Å. As in $[Cu_2(tren)_2L_2]^+B(C_6H_5)_4^-$ the boron tetrahedron is essentially distorted: its C(18)BC(36) and C(24)BC(30) angles are 103.7(9) and 102.6(9)°, being somewhat smaller than the other four C–B–C angles (111.2(9)–113.3(9)°).

Thus the crystals of tetraphenylborate anion salts are composed of ion pairs separated by a solvent molecule. The anions are retained via nonspecific electrostatic interactions, while the solvent (water or acetone) is held by hydrogen bonding with ligand amino-group.

Triphenylcyanoborates

When the anion is able to produce hydrogen bonds, it may react directly with the heterocyclic ligand amino group affording the contact hydrogen bonded ion pairs. Such salts were isolated from aqueous solutions by addition of $NaB(C_6H_5)_3CN$ to a heterocyclic derivative of iron cyclopentadienyldicarbonyl. These compounds contain no outer sphere solvent ligands held by the H-bonds. The azole amino group is blocked by hydrogen bond with nitrilic group of an outer sphere anion



VI

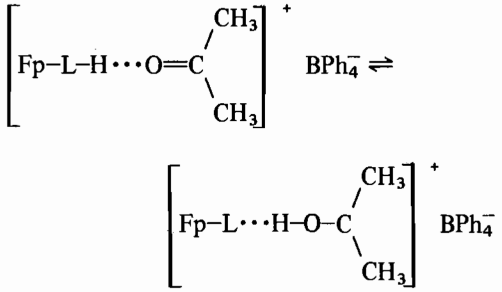
Analogous salts were prepared for the complexes with benzimidazole (VII), 5,6-dimethylbenzimidazole-(VIII) and 1-N-Fp substituted 1,2,3-triazole-4-phenyl (IX).

The ^1H NMR spectra confirm the hydrogen bond formation. As seen from Table I, the ^1H NMR spectra of these salts (unlike the salts of $B(C_6H_5)_4^-$ anion which showed no N–H resonance) exhibit broad N–H signals in a downfield region below –70 °C. In complex IX (see Table I) an abnormally great downfield shift of NH absorption may be due to the effect of neighbouring planarly located phenyl group in the heterocycle. Such downfield signals are characteristic of the N–H protons participating in the hydrogen bond formation with long life-time (*e.g.* intramolecular bonds [17]). These signals disappear at higher temperatures probably owing to quadrupole relaxation. The bond between the Fp group and the heterocycle is nonlabile in the compounds investigated (for both $B(C_6H_5)_4^-$ and $B(C_6H_5)_3CN^-$) and no ligand exchange was detected from +34 to 100 °C.

The IR spectra are shown in Table II. In the region of 2900–2500 cm^{-1} the N–H vibrations have complex pattern specific of the hydrogen bond producing systems. The anion nitrile group absorbs at 2196–2170 cm^{-1}.

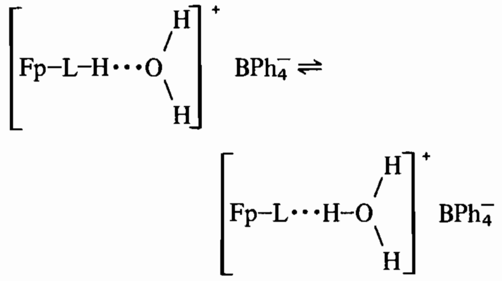
Triphenylboron Derivatives

The N–H proton is blocked by hydrogen bond with a solvent molecule proton transfer within the H-bridge, however, creates a possibility for direct attack by one of the anion phenyl rings, which results in salt decay. For example, the following reactions take place for acetone compounds:



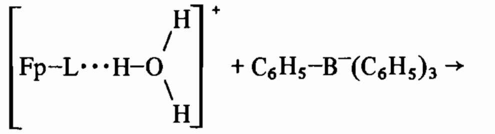
$$\left[\mathrm{Fp{-}L{-}H\cdots O{=}C}\begin{matrix}\mathrm{CH_3}\\ \mathrm{CH_3}\end{matrix}\right]^+ \mathrm{BPh_4^-} \rightleftharpoons \left[\mathrm{Fp{-}L\cdots H{-}O{-}C}\begin{matrix}\mathrm{CH_3}\\ \mathrm{CH_3}\end{matrix}\right]^+ \mathrm{BPh_4^-} \qquad (1)$$

or aquacomplexes:



$$\left[\mathrm{Fp{-}L{-}H\cdots O}\begin{matrix}\mathrm{H}\\ \mathrm{H}\end{matrix}\right]^+ \mathrm{BPh_4^-} \rightleftharpoons \left[\mathrm{Fp{-}L\cdots H{-}O}\begin{matrix}\mathrm{H}\\ \mathrm{H}\end{matrix}\right]^+ \mathrm{BPh_4^-} \qquad (2)$$

and further



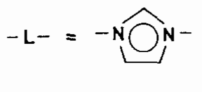
$$\left[\mathrm{Fp{-}L\cdots H{-}O}\begin{matrix}\mathrm{H}\\ \mathrm{H}\end{matrix}\right]^+ + \mathrm{C_6H_5{-}B^-(C_6H_5)_3} \rightarrow$$

$$\mathrm{Fp{-}L{:}} + \mathrm{H_2O} + \mathrm{C_6H_6} + \mathrm{BPh_3} \qquad (3)$$

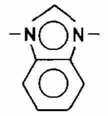
In this case the generated triphenylboron (Lewis acid) reacts with a liberated electron pair of the coordinated heterocycle imino group, now acting as a Lewis base [18]:

$$Fp{-}L{:} + BPh_3 \rightarrow Fp{-}L{-}BPh_3 \tag{4}$$

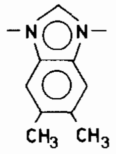
where



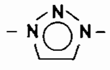
X



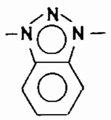
XI



XII



XIII



XIV

By comparing the acid properties of coordinated heterocycle

$$[Fp{-}L{-}H]^+ \rightleftharpoons Fp{-}L{:} + H^+ \tag{5}$$

and the properties of heterocycle conjugate acid

$$[H{-}L{-}H]^+ \rightleftharpoons H{-}L{:} + H^+ \tag{6}$$

one may easily understand that imidazole, benzimidazole and 5,6-dimethylbenzimidazole produce stable tetraphenylborate salts (the pK_a's of heterocycle conjugate acids are 6.95, 5.53 and 5.98 respectively [19]), while no such analytically pure salts were isolated for 1,2,3-triazole (pK_a = 1.17 [19]) and benzotriazole (pK_a = 1.6 [19]).

The salts decay on heating in THF solution. Subsequent chromatography revealed the triphenylboron derivatives. They are yellow crystalline solids, stable in air, soluble in THF and acetone.

The IR spectra are shown in Table II. Unlike the salts I–IX, in complexes X–XIV no vibrations specific of the N–H protons are observed in the high-frequency part of IR spectrum. In most other groups the characteristic frequencies are shifted slightly.

The ^1H NMR spectra show the difference in phenyl group absorption for $B(C_6H_5)_3$ and $B(C_6H_5)_4^-$ In the salts I–V two multiplets are observed while one multiplet shifted upfield was detected in the triphenyl derivatives X–XIV. Moreover, in imidazoles X–XII the protons in position 2 of the heterocycle were shifted upfield owing to a decrease of ring charge upon conversion of cation into the neutral triphenylboron complex.

Experimental

All the syntheses and sample preparations for spectral investigations were carried out under argon atmosphere.

The ^1H NMR spectra were taken on R–12 Perkin Elmer, R–20 Perkin Elmer–Hitachi, PR-2310 (USSR) instruments. IR spectra were measured on a UR-10 Carl Zeiss spectrometer.

X-ray study of benzimidazole complex II (Fig. 1) was performed on an automatic 4-fold X-ray diffractometer (Hilger–Watts) using Cu-source and graphite monochromator. 2580 reflections with $F^2 \geqslant 36$ were measured in the region of $2\nu \leqslant 114°$ under $\nu/2\nu$ scanning using the method of ordinate analysis. The elementary cell parameters, intensity measurements and reduction to F^2 scale were calculated with no account for absorption using the programs and methods described [20].

The structure was decoded by means of the heavy atom approach and corrected by least squares method within anisotropic block-diagonal approximation to R = 0.079. Atomic coordinates and temperature factors are listed in Table VI. Anisotropic correction was performed using DMIKSA program [21], other computations were made with Rentgen-70 program [22].

The complex II crystals are monoclinic, a = 13.626(1), b = 25.410(7), c = 10.088(1)Å, β = 92.65(1)°, d_{exp} = 1.28, d_{calc} = 1.285 g/cm³, Z = 4, spatial group $P2_1/n$.

Synthesis of Salts

0.02 mol of iron cyclopentadienyldicarbonyl halide and 0.02 mol of heterocyclic sodium derivative were stirred in acetonitrile at 45–55 °C for two hours. The solvent was evaporated. The residue was extracted with THF and chromatographed with THF on alumina (Brokman's IV activity grade). The eluate was concentrated and chromatographed repeatedly on the alumina using THF/water or acetone/water mixture. Addition of $NaB(C_6H_5)_4$ or $NaB(C_6H_5)_3$-CN aqueous solution to the eluate resulted in yellow salt precipitation. It was washed with distilled water on the filter and dried *in vacuo*. The salts could be reprecipitated from acetone/ether, acetone/heptane and THF/water mixtures, recrystallized from THF or acetone.

Synthesis of ironcyclopentadienyldicarbonylbenzimidazole tetraphenylborate(II)

6.08 g (0.02 mol) of FpI and 2.80 g (0.02 mol) of sodium benzimidazolide afforded 3.74 g (28%) of salt II. Recrystallization from acetone gave yellow needles of II (see X-ray analysis). *Anal.* Calcd. $C_{41}H_{37}N_2O_3BFe$: C 73.21, H 5.51, N. 4.17. Found: C 73.30, H 5.74, N 4.05%.

Synthesis of ironcyclopentadienyldicarbonylimidazole tetraphenylborate (I)

4.25 g (0.02 mol) of FpCl and 1.80 g (0.02 mol) of sodium imidazolide gave 3.79 g (32.5%) of salt I-b. *Anal.* Calcd. $C_{34}H_{31}N_2O_3BFe$: C 70.10, H 5.33,

TABLE VI. Atomic Coordinates and Temperature Factors in the Form T = exp $-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}\,hk + b_{13}\,hl + b_{23}kl)$ (Multiplied by 10^4).

Atom	x	y	z	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Fe	2591.7(9)	5168.5(4)	1972.8(11)	52(1)	11(1)	87(1)	0(1)	19(1)	6(1)
O(1)	3109(6)	5953(3)	13(7)	128(6)	20(1)	166(9)	12(4)	40(11)	−35(5)
O(2)	3883(6)	5565(3)	4115(6)	129(6)	28(2)	136(8)	49(5)	−57(11)	8(6)
O(3)	5286(5)	3640(2)	−2041(6)	103(5)	17(1)	157(8)	14(4)	70(10)	11(5)
N(1)	3509(5)	4626(3)	1385(6)	22(4)	6(1)	15(7)	6(3)	7(8)	−3(4)
N(2)	4382(5)	4134(3)	39(7)	24(5)	10(1)	42(8)	11(4)	14(9)	−7(5)
C(1)	3734(6)	4535(3)	141(8)	59(6)	18(2)	136(11)	4(5)	41(12)	−19(7)
C(2)	4573(6)	3949(3)	1306(8)	52(5)	15(1)	107(9)	5(4)	11(11)	−18(4)
C(3)	4053(5)	4255(3)	2137(7)	51(5)	14(1)	96(9)	−2(4)	3(10)	−3(5)
C(4)	4072(6)	4166(3)	3513(8)	65(6)	16(2)	96(10)	3(5)	−2(11)	4(6)
C(5)	4640(6)	3753(4)	3981(8)	67(6)	23(2)	101(9)	4(5)	−13(12)	−3(7)
C(6)	5193(7)	3440(4)	3128(10)	85(7)	22(2)	147(12)	20(6)	−6(15)	19(8)
C(7)	5185(6)	3536(3)	6770(9)	67(6)	18(2)	131(10)	−15(5)	38(12)	7(7)
C(8)	1375(7)	4713(4)	1337(9)	65(6)	23(2)	149(12)	−22(5)	33(13)	−17(7)
C(9)	1139(7)	5253(4)	1198(10)	63(6)	21(2)	174(13)	−7(5)	30(14)	13(8)
C(10)	1242(6)	5499(4)	2464(10)	66(6)	20(2)	185(14)	−19(5)	57(15)	19(8)
C(11)	1524(7)	5093(4)	3412(9)	72(6)	25(2)	134(11)	20(6)	56(13)	20(8)
C(12)	1604(6)	4605(4)	2696(10)	65(6)	21(2)	158(13)	−22(5)	63(14)	−3(8)
C(13)	2938(6)	5644(3)	809(8)	67(6)	15(2)	126(11)	1(5)	9(13)	6(6)
C(14)	3402(6)	5411(3)	3267(9)	71(6)	14(2)	145(11)	19(5)	−4(13)	4(6)
C(15)	5463(6)	3183(4)	−2277(9)	61(6)	22(2)	111(11)	−16(5)	−4(12)	14(7)
C(16)	6212(10)	3031(5)	−3243(12)	155(11)	24(2)	222(17)	−49(8)	233(23)	−33(10)
C(17)	4975(10)	2742(4)	−1555(14)	134(11)	20(2)	296(22)	−21(7)	169(24)	−9(11)
C(18)	2061(6)	4118(3)	7199(7)	56(5)	15(1)	80(8)	10(4)	19(10)	4(5)
C(20)	1974(8)	5081(4)	7469(9)	110(8)	16(2)	135(12)	−9(6)	−29(16)	−13(7)
C(19)	1529(7)	4580(3)	7530(9)	87(7)	16(2)	127(11)	11(5)	6(13)	14(7)
C(21)	2921(8)	5145(4)	7085(8)	124(9)	19(2)	86(10)	21(6)	−6(14)	−7(7)
C(22)	3460(7)	4702(4)	6789(8)	87(7)	25(2)	89(9)	−32(6)	28(13)	−1(7)
C(23)	3034(6)	4192(3)	6859(8)	62(6)	19(2)	93(9)	−18(5)	30(11)	−1(6)
C(24)	2129(5)	3065(3)	6636(7)	45(5)	14(1)	100(9)	0(4)	−7(10)	5(6)
C(25)	2474(6)	3112(3)	5383(8)	62(6)	17(2)	99(9)	8(5)	5(11)	3(6)
C(26)	2905(7)	2697(4)	4715(9)	92(6)	18(2)	115(10)	11(5)	51(13)	−17(7)
C(27)	2996(7)	2211(4)	5297(9)	91(7)	17(2)	147(12)	23(6)	−22(14)	−31(7)
C(28)	2647(7)	2137(4)	6548(9)	95(7)	16(2)	128(11)	14(3)	5(14)	2(6)
C(29)	2230(6)	2565(3)	7220(9)	71(6)	15(1)	134(11)	3(5)	23(13)	3(6)
C(30)	478(6)	3528(3)	6447(7)	55(5)	18(2)	88(9)	15(4)	16(11)	−15(6)
C(31)	251(7)	3870(8)	5408(8)	79(7)	29(2)	82(9)	45(6)	1(12)	2(7)
C(32)	−643(8)	3806(5)	4627(10)	99(8)	45(3)	107(11)	−59(8)	−34(15)	4(10)
C(33)	−1299(8)	3434(6)	4893(11)	84(8)	49(4)	173(16)	−31(9)	−13(18)	105(13)
C(34)	−1098(8)	3078(5)	5932(12)	67(8)	35(3)	212(16)	5(7)	−32(17)	71(11)
C(35)	−224(6)	3127(4)	6669(10)	40(5)	22(2)	181(13)	5(5)	0(13)	51(8)
C(36)	1395(5)	3458(3)	8926(8)	43(5)	12(1)	115(10)	−9(4)	−7(10)	1(5)
C(37)	532(6)	3506(3)	9545(8)	70(6)	13(2)	120(11)	−13(4)	47(12)	4(6)
C(38)	465(7)	3450(4)	10959(9)	100(7)	18(2)	121(11)	−23(5)	51(14)	−2(7)
C(39)	1339(7)	3348(3)	11720(8)	107(8)	14(1)	114(10)	−34(3)	3(14)	4(6)
C(40)	2206(7)	3318(3)	11133(8)	84(7)	16(2)	112(11)	−19(5)	−17(13)	16(6)
C(41)	2245(7)	3364(3)	9731(8)	80(7)	12(1)	127(10)	−11(5)	48(13)	4(6)
B	1518(6)	3538(3)	7303(8)	79(5)	22(2)	170(11)	−2(5)	34(12)	8(6)

N 4.81. Found: C 70.69, H 5.20, N 4.79%. Recrystallization in acetone led to compound 1-a. *Anal.* Calcd. $C_{37}H_{35}N_2O_3BFe$: C 71.38, H 5.63, N 4.50 Found: C 71.57, H 5.74, N. 4.76%.

Synthesis of ironcyclopentadienyldicarbonylimidazole cyanoborate(VI)

5.14 g (0.02 mol) of FpBr and 1.80 g (0.02 mol) of sodium imidazolide gave 2.64 g (25.7%) of salt

VI recrystallized from acetone. *Anal.* Calcd. $C_{29}H_{24}O_2N_3BFe$: C 67.83, H 4.68, N 8.19. Found: C 67.91, H 4.54, N 8.14%.

Synthesis of iron cyclopentadienyldicarbonyl-5,6-dimethylbenzimidazole tetraphenylborate(III)

5.44 g (0.02 mol) of FpBr and 3.36 g (0.02 mol) of sodium 5,6-dimethylbenzimidazolide gave 4.03 g (30.5%) of salt III. *Anal.* Calcd. $C_{40}H_{37}N_2O_3BFe$: C 72.73, H 5.61, N 4.24. Found: C 72.72, H 5.76, N 4.25%.

Synthesis of iron cyclopentadienyldicarbonyl-5,6-dimemethylbenzimidazole cyanoborate (VIII)

5.14 g of FpBr and 3.36 g of heterocycle sodium salt gave 5.41 g (45.8%) of complex VIII. *Anal.* Calcd. $C_{35}H_{30}N_3O_2BFe$: C 71.07, H 5.08, N 7.11. Found: C 71.15, H 5.11, N 6.93%.

Synthesis of iron cyclopentadienyldicarbonyl-1-N-(4-phenyl-1,2,3-triazole) cyanoborate (IX)

Reaction of 5.14 g of FpBr and 3.34 g of heterocycle sodium salt gave after chromatography 2.1 g (32.7%) of ironcyclopentadienyldicarbonyl-1-N-(4-phenyl-1,2,3-triazolyl)*. Precipitation of this complex from aqueous acetonic solution with $NaB(C_6H_5)_3CN$ afforded 3.52 g (29.8%) of compound IX. *Anal.* Calcd. $C_{34}H_{27}N_4O_2BFe$: C 69.15, H 4.58, N 9.49. Found: C 69.04, H 4.56, N 9.45%.

Synthesis of Triphenylboron Derivatives

Synthesis of iron cyclopentadienyldicarbonyl-1-N-(3-N-triphenylborbenzimidazolyl) (XI)

Tetrahydrofurane solution of benzimidazole complex tetraphenylborate (II) (0.90 g) was refluxed for 1.5 hour, concentrated and chromatographed on alumina (Brokman's second activity grade) in THF. The eluate was evaporated, the residue crystallized from THF/ether mixture. 0.41 g (57.3%) of the yellow crystals of triphenyl boron complex XI** was isolated. *Anal.* Calcd. $C_{32}H_{25}O_2N_2BFe$: C 71.64, H 4.66, N 5.22. Found: C 71.79, H 5.00, N 5.21%.

Synthesis of iron cyclopentadienyldicarbonyl-1-N-(3-N-triphenylborimidazolyl) (X)

Analogously to the previous case 1.2 g of salt I-a yielded 0.58 g (54.9%) of complex X. *Anal.* Calcd. $C_{28}H_{23}N_2O_2BFe$: C 69.21, H 4.73, N 5.75. Found: C 69.05, H 5.14, N 5.75%.

Synthesis of iron cyclopentadienyldicarbonyl-1-N-(3-N-triphenyl-boron-5,6-dimethylbenzimidazolyl) (XII)

0.81 g of salt III gave 0.22 g of complex XII (31.8%) using the preceding procedure. *Anal.* Calcd. $C_{34}H_{29}N_2O_2BFe$: C 72.34, H 5.15, N 4.96. Found: C 72.54, H 5.45, N 5.15%.

Synthesis of iron cyclopentadienyldicarbonyl-1-N-(3-N-triphenylboronbenzotriazolyl) (XIV)

Aqueous solution of $NaBPh_4$ was added to an aqueous– acetonic solution of 1.42 g of iron cyclopentadienyldicarbonyl-1-N-benzotriazolyl obtained from FpI and sodium benzotriazolide. The precipitate was filtered off, washed and dried. Further operations were analogous to those described previously. 2.88 g of complex XIV (92.1% per initial benzotriazole) was isolated. *Anal.* Calcd. $C_{31}H_{24}N_3O_2BFe$: C 69.27, H 4.47, N 7.82. Found: C 69.56, H 4.72, N 7.37%.

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*See Part II.

**We failed to obtain melting points of the complexes X–XIV: they decompose without melting above 100–120 °C.