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Iron Cyclopentadienyldicarbonyl Complexes with Azoles. II. Iron Cyclopentadienyl Complexes with Vicinal Triazoles

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The reaction of iron cyclopentadienyldicarbonyl halides with some vicinal triazole salts was investigated. It has been shown that these reactions yield isomeric complexes of triazoles. These complexes undergo isomeric rearrangement on heating in acid and neutral media. The coordinated triazoles contain two vacant basic centers. Therefore they participate in reactions with acids. H-bond formation and proton transfer reactions have been investigated for these complexes.

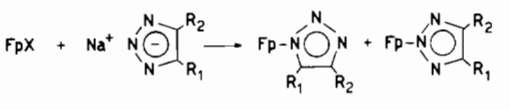
Introduction

The reaction of iron cyclopentadienyldicarbonyl halides with some vicinal triazole salts was investigated. Such reactions afford isomeric triazoles with localized σ–Fe–N– bond between heterocyclic ligand and metal. However, the coordinative capabilities of heterocyclic ligands do not include such bonding alone since vicinal triazoles are trifunctional.

The coordinated triazoles contain two vacant basic centers. Thus their reactions with acid–base compounds are more complicate with respect to the coordinated diazoles [1].

Results and Discussion

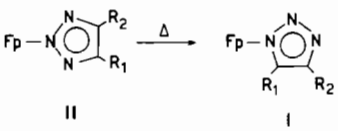
Reactions of iron cyclopentadienyldicarbonyl halides with triazolide, 4-phenyl-1,2,3-triazolide and benzotriazolide of sodium in acetonitrile or tetrahydrofuran (THF) generate two types of complexes. They are isomeric in the iron cyclopentadienyldicarbonyl fragment positions (Fp) with respect to heterocyclic ligands:



(1)

	R_1	R_2
a	H	H
b	C_2H_2–C_2	H_2
c	H	Ph

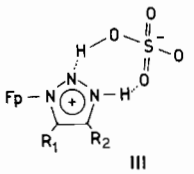
Symmetric 2-isomers (IIa, b) rearrange irreversibly into 1-isomers (Ia, b) (scheme 2) on heating in THF or benzene:



(2)

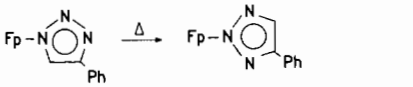
Reaction (1) with sodium benzotriazolide at 25 °C (for no more than an hour) affords the symmetric 2-isomer (IIb). Increase of temperature and time results almost exclusively in the asymmetric 1-isomer (I). Triazoles themselves undergo similar transformations. However, reaction (1) with sodium 4-phenyl-1,2,3-triazole under kinetic control conditions (minimal drastic conditions: temperature below 35 °C, time 1.5 h) produces compound (Ic) with terminal iron coordination. Isomer (Ic) rearranged into the 2-isomer (IIc) on heating.

We found that in protic media the heterocyclic ligands of compounds (Ia, Ib, Ic, IIa) may accept protons by their vacant imino groups [1, 2]. Thus the complexes (I)–(II) are easily protonated with mineral and organic acids and also with water. Bibasic acids react with compounds (Ia–c) specifically. Sulfuric and oxalic acids in THF solution produce salts insoluble in THF. Such effect is not observed for the 2-isomer, however. This may be explained by vicinal imino and amino groups of the triazole ligands complementary bound to acid fragments of the bibasic acids giving the salts (III):



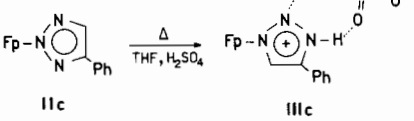
III

In acid media the triazole and benzotriazole complexes rearrange very easily analogously to reactions in neutral media (scheme (2)): the protonated complex (II) transforms into the more stable compound (III). However, 4-phenyl-1,2,3-triazole derivatives behave alternatively. Unlike reaction (3) in the neutral media, in sulfuric acid and THF the reaction follows equation (4).



(3)

Ic IIc



(4)

IIc IIIc

This may be due to complex (Ic) being less stable thermodynamically in the neutral media producing the more stable salt IIIc by means of chelate H-bonding.

It should be pointed out that the third possible isomer, cyclopentadienyldicarbonyl-1-N-(5-phenyl-1,2,3-triazolyl)iron is never formed, which may be explained by efficient repulsion between the bulky phenyl substituent and the Fp fragment. Similarly, only 1-N- and 2-N-isomers [3, 4] have been found in the alkylation products of 4-phenyl-1,2,3-triazole anion with ethylchloroacetate, β-chloropropionate and dimethylsulfate.

In 1-N-substituted 5-phenyl-1,2,3-triazoles (third isomer in our case) the phenyl ring plane may rotate with respect to heterocycle plane which is evident from the ^{1}H NMR spectra. In 5-phenyl-1-N-isomers the phenyl ring protons exhibit a singlet, while two multiplets are observed in 4-phenyl-1-N and 2-N-isomers [5–8].

Mass Spectra

Mass spectrometric fragmentation of triazole complexes (scheme 5) is specific for $CpFe(CO)_2L$ compounds [9]:

The molecule ion of mean abundance loses consecutively two carbonyl groups producing the fragment ion $[C_5H_5FeL]^+$. Then fragmentation involves elimination of the entire heterocyclic ligand or consecutive decay of the heterocyclic part of the $[C_5H_5FeL]^+$ ion. This ion may also lose its cyclopentadienyl ring. The mass spectra always show $[C_5H_5FeC_5H_5]^+$ ion on fragmentation of these compounds. All above described compounds $CpFe(CO)_2L$ follow such decay scheme. Table 1 lists the molecular, fragmental and metastable ions corresponding to elimination of the carbonyl groups.

Different heterocycle structure and metal group coordination with respect to triazolic triade should affect the mass spectrometric fragmentation of complexes at the step of consecutive elimination of heterocyclic part of $[C_5H_5FeL]$ fragment ion. The following example usually serves as a reliable test of substituent position with respect to the nitrogens in triazole ring: 1-N-derivatives eliminate N_2 molecules, while 2-N-compounds expel HCN [10]. This test was inconsistent in the present case, since various rearrangements may be assumed as well.

Special experiments on decay of the complexes revealed no difference in the fragmentation of 1-N and 2-N isomers in each pair of compounds. Thus the structures of $[C_5H_5FeL]^+$ ion are identical for each pair of 1-N isomers. This may be possible only when one isomer is generated by the molecular ion fragmentation or when σ-π rearrangement of CpFe fragment with respect to triazole ligand is taking place.

In elucidating the structure of fragment ion $[C_5H_5FeL]^+$ it is necessary to discuss its specific decay defined by the structure of heterocyclic ligand.

In benzotriazole complexes (Ib and IIb) the fragment $[C_5H_5FeL]^+$ loses nitrogen molecule:

$$\underset{239}{[C_5H_5FeC_6H_4N_3]^+} \xrightarrow[-28]{-N_2} \underset{211}{[C_5H_5FeC_6H_4N]^+} \quad (6)$$

Metastable ion with m/e = 186. 3 is consistent with this process. It is known that the nitrogen molecule could be eliminated only from 1-N-substituted triazoles [10]. Thus for 2-N substituted benzotriazole (IIb), the only possibility of such process is preliminary rearrangement of metallofragment blocking the nitrogen atom in 2-position. It should be noted that the nitrogen molecule elimination is generally specific of benzotriazole derivatives, which is a driving force

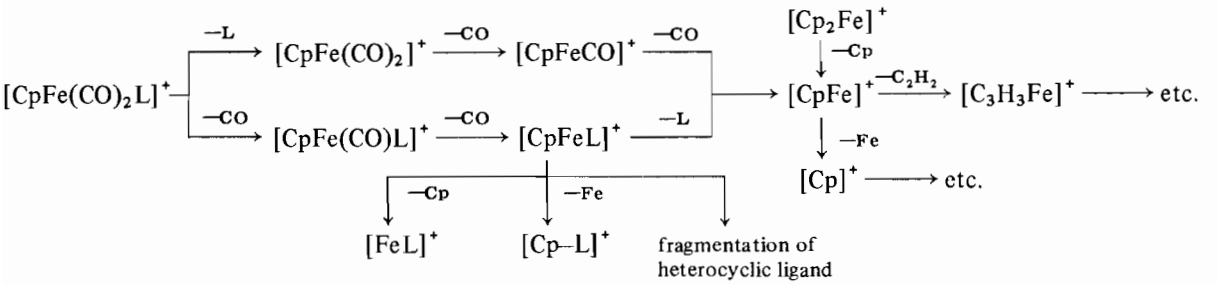
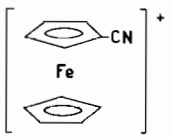


TABLE I. Mass Fragmentation

	1-N-,2-N-1,2,3- triazolyl		1-N, 2-N-benzotriazolyl		1-N, 2-N-(4-phenyl-1,2,3-triazolyl	
	Ion (m/e)	Metastable Ion (m/e)	Ion (m/e)	Metastable Ion (m/e)	Ion (m/e)	Metastable Ion (m/e)
$[C_5H_5Fe(CO)_2L]^+$	245	192.2	295	241.7	321	267.4
$[C_5H_5Fe(CO)L]^+$	217	164.6	267	213.9	293	239.7
$[C_5H_5FeL]^+$	189		239		265	
$[C_5H_5Fe(CO)_2L]^{++}$	122.5		147.5		160.5	
$[C_5H_5Fe(CO)L]^{++}$	108.5		133.5		146.5	
$[C_5H_5FeL]^{++}$	94.5		119.5		132.5	

in a number of fragmentations of benzotriazole derivatives under electron impact [11, 12], thermal decay [13] and photolysis [14]. This may involve benzene cycle contraction into a cyclopentadienylic system (almost quantitatively under pyrolysis in condensed phase [15]). Thus in scheme 6 the ion $[CpFeC_6H_4N]^+$ may have structure (IV):



IV

Further decay confirmed by metastable peaks supports this suggestion, since it is specific of ferrocenes:

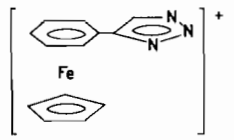
$$\underset{211}{IV} \xrightarrow[-27]{-HCN} \underset{184}{[CpFeC_5H_3]^+} \quad \text{metastable ion } 160.5 \quad (7)$$

$$\underset{211}{IV} \xrightarrow[-56]{-Fe} \underset{155}{[C_5H_5C_5H_4CN]^+} \quad \text{metastable ion } 113.9 \quad (8)$$

$$\underset{211}{IV} \xrightarrow[-90]{-C_5H_4CN} \underset{121}{[C_5H_5Fe]^+} \quad \text{metastable ion } 69.4 \quad (9)$$

The spectra also show the ions with m/e = 146, $[FeC_5H_4CN]^+$.

As far as complexes with 4-phenyl-1,2,3-triazole are concerned (Ic and IIc), after elimination of two carbonyl groups the ion $[C_5H_5FeL]^+$ may rearrange into the π-system with coordinated iron at the phenyl ring (V):



V 265

$$\xrightarrow[-55]{-CHN_3} \underset{210}{[C_5H_5FeC_7H_5]^+} \quad \text{metastable ion } 166.4 \quad (10)$$

Such coordination releases triazole ring and provides elimination of CHN_3 fragment or simultaneous elimination of N_2 and HCN producing the energetically favourable tropilium system (scheme 10). Such systems are generated readily in iron π-complexes with aromatic ligands having a number of carbons $\geqslant 7$ [16].

In this case, however, the "test" for 1-N-isomers (N_2-elimination) and 2-N-isomers (HCN elimination) cannot be employed since for each isomer the ion abundances with m/e = 238 and 237 corresponding to N_2 and HCN elimination from fragment ion $[CpFeL]^+$ are nearly equal and negligible (*ca.* 0.5%).

This also takes place in 1,2,3-triazole complexes (Ia and IIa). Unlike heterocycle itself the HCN and N_2 elimination from the coordinated ligand is not specific. In both complexes (Ia and IIa) the respective peak abundances are very weak and their ratio is equal for various isomers. On the other hand the fragment ion with m/e 134 corresponding to elimination of 55 units from the heterocycle is one of the most intense in the spectrum:

$$\underset{189}{[C_5H_5FeC_2H_2N_3]^+} \xrightarrow[-55]{-CHN_3} \underset{134}{[C_5H_5FeCH]^+} \quad (11)$$

Such fragmentation may be again explained only by π-coordination of the iron group in $[C_5H_5FeL]^+$ fragment ion with triazole ligand. Moreover the absence of σ-blocking of azole triade is evident from rather essential fragment ion (m/e = 146) $[C_5H_5FeC_2H]^+$ generated from $[C_5H_5FeL]^+$ after HN_3 elimination.

IR Spectra

Infrared spectra of (I)–(II) solutions show two absorption bands in the region of stretching modes of terminal carbonyl ligands (Table II). Isomeric benzotriazole complexes (I), (II) exhibit essentially different $\nu_{C\equiv O}$ frequencies in solution. This could be understood since force characteristics are also different in benzotriazole isomers with considerable variation of mass distribution towards benzotriazole nucleus. An alternative pattern is observed in 1,2,3-

TABLE II. Infrared Data.

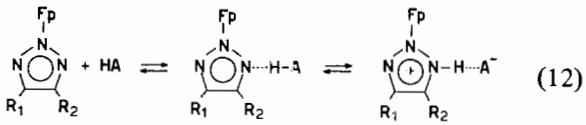
Compound	Conditions	ν (cm^{-1})	
$CpFe(CO)_2$-1-N-($C_2H_2N_3$)	THF solution	2063	2013
$CpFe(CO)_2$-2-N-($C_2H_2N_3$)	"	2062	2014
$CpFe(CO)_2$-1-N-($C_6H_4N_3$)	"	2054	2004
$CpFe(CO)_2$-2-N($C_6H_4N_3$)	"	2060	2020
$CpFe(CO)_2$-1-N-($C_8H_6N_3$)	"	2060	2010
$CpFe(CO)_2$-2-N-($C_8H_6N_3$)		2060	2010
$CpFe(CO)_2$-1-N-($C_2H_2N_3$)H_2SO_4	KBr pellet	2069	2024
$CpFe(CO)_2$-1-N-($C_8H_6N_3$)·H_2SO_4	"	2068	2019
$CpFe(CO)_2$-1-N-($C_6H_4N_3$)·H_2SO_4	"	2066	2020
"	CH_3OH solution	2075	2029
"	$(CH_3)_2SO$ solution	2064	2015
$CpFe(CO)_2$-1-N-($C_6H_4N_3$)·$H_2C_2O_4$	KBr Pellet	2069	2018

triazole and 4-phenyl-1,2,3-triazole derivatives. These isomers possess different permutations of CH and N fragments with close masses. In complexes Ic and IIc the phenyl ring position (3-position) from metal-containing group is the same, thus $\nu_{C\equiv O}$ stretching frequencies in (Ib) and (IIb) isomers as well as in (Ic) and (IIc) species are practically coincident. Differences are observed only in the stretching and bending modes of triazole ring.

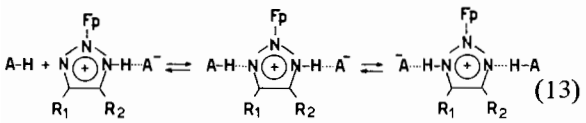
The spectra of crystals of 1-isomers (III) salts contain only two $\nu_{C\equiv O}$ bands. Intense continuous absorption is observed in the region from 2450 to 2900 cm^{-1}. No stretching modes of separate O–H, N–H groups were found in the region of 3100–3600 cm^{-1}. Thus the NH and OH fragments participate in hydrogen bonds [17].

NMR Spectra

^1H NMR spectra show the signals corresponding to cyclopentadienyl ring and heterocyclic ligand protons. In all complexes the cyclopentadienyl ring protons exhibit a singlet at 5.5 ppm (σ-scale). Asymmetric benzotriazole complex (1b) shows a four spin resonance pattern of benzogroup at 7 ppm. On the other hand, 2-isomer possesses effective C_2 symmetry of benzotriazole ligand resulting in symmetric four-spin AA'BB' system. Acid addition to 2-isomer solution in THF (IIb) immediately distorts the symmetric pattern. The spectrum resembles that of 1-isomer. This means that one of the ligand imino groups was protonated. Secondly it manifests the absence of fast prototropic rearrangement producing an effective symmetry in the NMR time scale.



(12)



(13)

Clearly, two types of exchange processes may occur in the system: hydrogen bond generation or cleavage (H-complex exchange) (12) and proton transfer via hydrogen bond (13). The absence of the latter process indicates that H-bond potentials are asymmetric and as a result the activation energies of a classical subsystem stimulation in the act of proton transfer are rather high. The cleavage and formation of hydrogen bonds (ligand exchange in H-complexes) are fast and could not be slowed down above −50 °C. On the other hand, temperature increase for observation of proton transfer causes a rearrangement of Fp fragment and formation of an insoluble 1-isomer salt. The study of salt solutions (in methanol) of asymmetric isomer (IIIb) showed that the ^1H and ^{13}C NMR spectra of these compounds are temperature dependent (Fig. 1). Since in this case the H-complex was generated via complementary hydrogen bonds it is more stable than acid H-complexes with 2-isomer. In H-complexes no ligand exchange is observed and as was shown above the IR spectra contain no bands of free OH and NH groups but exhibit diffusive absorption typical of the hydrogen bonds. We thus assume that temperature dependence of NMR spectra observed in 1-isomer complexes with sulfuric acid is due to a hindered prototropic rearrangement at low temperatures. In this case the rates of proton migration exceed those in pyrazole [18, 19] and we failed to obtain the low temperature boundary spectra. The coalescence temperature was attained only at −120 °C. Obviously in this system proton transfer in vicinal hydrogen-bridged bonds occurs consistently owing to a dynamic change of potential function of one of the bonds upon proton transfer in the adjacent hydrogen bridge. The starting migration step in N···H–O bond may stimulate proton tunnelling in the bridge balancing the levels in the quantum subsystem.

Interrelations of Isomeric Complexes

From this material it follows that relations between formations of any isomer depending on the type of triazole ligand are nontrivial. The reaction

TABLE III. ^{1}H-NMR spectra of the Complexes.

Compound	Solvent	C_5H_5	Chemical Shift (ppm, σ-value) Triazoles			N–H
$CpFe(CO)_2$-1-N-($C_2H_2N_3$)	THF	5.30 S(5)[a]	7.19 S(1)	7.38 S(1)		
$CpFe(CO)_2$-2-N-($C_2H_2N_3$)	THF	5.32 S(5)	7.39 S(2)			
$CpFe(CO)_2$-1-N-($C_2H_2N_3$)·H_2SO_4	CH_3OH	5.62 S(5)	8.27 S(1)	8.35 S(1)		17.01 S[b] (broad)
$CpFe(CO)_2$-1-N-($C_8H_6N_3$)	THF	5.18 S(5)	7.26 S(1)	6.85m (2.5)	7.34m (2.5)	
$CpFe(CO)_2$-2-N-($C_8H_6N_3$)	$(CH_3)_2CO$	5.26 S(5)	7.49 S(1)	6.97m (2.5)	7.41m (2.5)	
$CpFe(CO)_2$-1-N-($C_8H_6N_3$)·H_2SO_4	CH_3OH	5.61 S(5)	8.57 S(1)	7.58m (2.5)	7.87m (2.5)	17.10 S[b] (broad)
$CpFe(CO)_2$-1-N-($C_6H_4N_3$)	THF	5.51 S(5)	7.18m(2)	7.78m (2)		
$CpFe(CO)_2$-2-N-($C_6H_4N_3$)	THF	5.48 S(5)	7.04m (2)	7.66m (2)		
$CpFe(CO)_2$-1-N-($C_6H_4N_3$)·H_2SO_4	CH_3OH	5.54 S(5)	7.82m (2)	8.07m (2)		17.29 S[b] (broad)
$CpFe(CO)_2$-2-N-($C_6H_4N_3$)·H_2SO_4	THF	5.90 S(5)	8.20m (2)	8.62m (2)		14.00 S

[a]S = singlet, m = multiplet. [b]Broad signals appear at t < −70 °C, recorded at −90 °C.

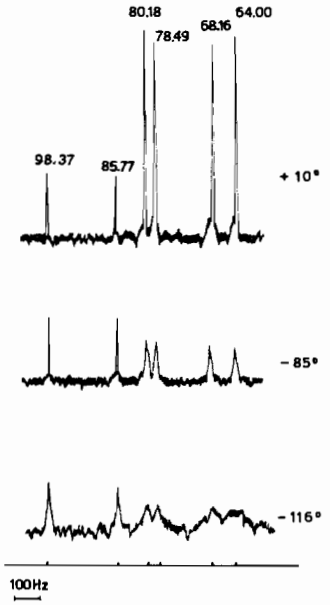


Figure 1. ^{13}C NMR spectra. The temperature dependence of the complex $Fp(-1N-C_6H_4N_3)\cdot H_2SO_4$ benzo group (methyl alcohol as internal standard, operating frequency 22.635 MHz).

course depends on the conditions, kinetic and thermodynamic factors. This reaction is a nucleophilic substitution in the iron pseudooctahedral coordination sphere. The reactions are carried out in highly donor strength media (DN_{THF} = 20.0, DN_{CH_3CN}= 14.1) [20], thus the first step may involve halogen substitution by solvent (THF or acetonitrile) molecule

$$FpX + solv \rightleftharpoons [Fp{-}solv]^+ X^-$$

Then solvent molecule exchanges with heterocyclic ligand in the coordination sphere. However, the ligand has at least three donor centers. Thus various attacks are possible even in symmetrical triazoles. In benzotriazolide and triazolide anions these are N-(1), N(3) and N(2) positions. In 4-phenyl-1,2,3-triazole anion all three nitrogen atoms are different. Under the minimally drastic conditions the reaction course will be defined by kinetics *i.e.* activation parameters of the process. The primary attack is performed by the nitrogen with the highest electron density. In benzotriazolide anion and 1,2,3-triazole anion it is N(2) position. In 4-phenyl-1,2,3-triazole anion it is N(1) [3]. Thus reactions of sodium salts of these heterocycles with cyclopentadienyldicarbonyliron halides at room temperature afford predominantly the (IIa, b) and (Ic) complexes with iron coordinated to N(2) and N(1) atoms respectively. Upon increasing temperature when activation barriers are not decisive for reaction course the primary function is played by thermodynamics: systems ability to redistribute its electronic density. In these cases coordination with 1 and 2-positions in benzotriazole and 4-phenyl-1,2,3-triazole respectively is more energy-favoured. In terms of the hard–soft acid–base theory (HSAB) [21] this could be explained as preferable ability of soft acid $(C_5H_5Fe(CO)_2)^+$ to coordinate the softer centers in ambidentate ligands. Namely the thermodynamic factors are decisive in isomeric rearrangements [2, 3]. On the other hand, in various isomers the free Gibbs energies should not be essentially different. Thus in 4-phenyl-1,2,3-triazole derivatives with additional stabilization by complementary hydrogen bonds to a bifunctional acid the less stable 1-isomer (Ic) will be more stable in the form of salt (IIIc). 1-Isomer of 5-phenyl-1,2,3-triazole could be destabilized due to effective steric hindrance since its bulky phenyl and Fp groups are closely located.

Experimental

All syntheses and sample preparations for spectral measurements were performed under argon.

The ^{1}H-NMR spectra were registered on R-12 (Perkin–Elmer) R-20 (Perkin–Elmer–Hitachi), RYa-2310 (USSR) instruments. The ^{13}C-NMR spectra were taken on a Bruker HX-90 model instrument. The IR spectra were obtained on UR-10 (DDR) spectrometer. The mass spectra were measured on CH-8 (Varian) and MS-30 (AEI) instruments.

Reactions of Cyclopentadienyldicarbonyliron Halides with Sodium Benzotriazolide

5.14 g (0.02 mol) of $CpFe(CO)_2Br$* and 2.82 g (0.02 mol) of $C_6H_4N_3Na$ were stirred in THF at 20 °C for 1 hr. The mixture was concentrated to minimum volume and chromatographed in THF on alumina column (II–d Brokman's activity grade). Initial halide, then 2-isomer (IIb) and 1-isomer (Ib) were eluted. 0.59 g (10%) of (IIb), and 0.01 g (0.02%) of (Ib) were obtained.

At 45 °C for 2.5 hr. the yields of complexes were 0.24 g (4%) (complex IIb) and 1.95 g (33%) (Ib) (chromatography in THF on alumina (IV-th Brokman's activity grade)).

Rearrangement of Cyclopentandienyldicarbonyl-2-N-benzotriazolyliron (IIb) into Cyclopentadienyldicarbonyl-1-N-benzotriazolyliron (Ib)

0.30 g of (IIb) was refluxed in benzene for 1 hr. The solution was chromatographed to give 0.09 (30%) of compound (Ib).

		C%	H%	N%
Anal.	Calculated for $C_{13}H_9N_3O_2Fe$	53.0	3.06	14.3
	Found for (Ib)	52.5	2.8	13.9
	Found for (IIb)	53.0	3.14	14.03

Synthesis of Bifunctional Acid Salts of Cyclopentadienyldicarbinyl-1-N-benzotriazolyliron (IIIb)

Tetrahydrofuran solution of sulfuric or oxalic acids was added to a solution of 1-isomer (Ib) in THF. The precipitated yellow cristalline solid was crystallized from methanol in quantitative yield.

		C %	H %	N %	Fe %
Anal.	Calculated for $C_{13}H_{11}N_3O_6$-FeS	39.69	2.80	10.69	14.25
	Found	38.93	2.96	10.46	14.30
	Calculated for $C_{15}H_{11}N_3O_6Fe$	46.75	2.86	10.91	
	Found	46.75	2.86	10.87	

Rearrangement of 2-isomer (IIb) into 1-isomer (Ib) of Benzotriazole Complexes in Sulfuric Acid Medium

A solution of 2-isomer (IIb) in THF acidified with sulfuric or oxalic acids was heated to 45 °C. The solution first opalesced, then in 15 min the crystals of 1-isomer (IIIb) salt precipitated.

Reaction of Cyclopentadienyldicarbonyliron Halides with 4-Phenyl-1,2,3-triazolyl Sodium

5.14 g (0.02 mol) of $CpFe(CO)_2Br$ was stirred with 3.34 g (0.02 mol) of $C_8H_6N_3Na$ in acetonitrile for 1 hr at 25 °C. The solution was evaporated, THF added and chromatographed as above. 0.1 g (7.9%) of (Ic) and 0.22 g (3.4%) of (IIc) were obtained. At 45 °C for 2.5 hr the yields of complexes were 0.39 g (6.1%) for (Ic) and 2.34 g (36.5%) for (IIc).

Rearrangement of Cyclopentadienyldicarbonyl-1-N-(4-phenyl-1,2,3-triazolyl)iron (Ic) into Cyclopentadienyldicarbonyl-2-N-(4-phenyl-1,2,3-triazolyl)iron (IIc)

A solution of 0.27 g of 1-isomer in THF was heated to 60 °C for 2 hr, then chromatographed. 0.16 g (59%) of 2-isomer was obtained.

		C%	H%	N%
Anal.	Calculated for $C_{15}H_{11}N_3O_2Fe$	56.07	3.43	13.08
	Found for (Ic)	56.03	3.58	13.06
	Found for (IIc)	55.93	3.81	13.30

Synthesis of Cyclopentadienyldicarbonyl-1-N-(4-phenyl-1,2,3-triazolyl)iron Sulfate

A solution of sulfuric acid in THF was added to THF solution of 1-isomer. The yellow solid precipitated was crystallized from ethanol–tetrahydrofuran mixture. Gold scaly crystals correspond to a composition $CpFe(CO)_2(C_8H_6N_3)\cdot H_2SO_4\cdot C_4H_8O\cdot \frac{1}{2}H_2O$

		C %	H %	N %
Anal.	Calculated for $C_{19}H_{22}N_3O_{7.5}SFe$	45.60	4.40	8.40
	Found	45.54	4.42	8.38

Fischer's water analysis gave 5.0%, calculated 4.5%.

Rearrangement in Acid Medium of 2-Isomer of Cyclopentadienyldicarbonyliron Complex with 4-Phenyl-1,2,3-triazole (IIc) into 1-Isomer (IIIc)

Tetrahydrofuran solution of 2-isomer acidified with sulfuric acid was heated to 60 °C for 2 hr. The 1-isomer (IIIc) sulfate precipitated.

Reaction of $CpFe(CO)_2Br$ with 1,2,3-Triazolyl Sodium

5.14 g (0.02 mol) of $CpFe(CO)_2Br$ and 1.82 g (0.02 mol) of $C_2H_2N_3Na$ were stirred in acetonitrile at 45 °C for 2.5 hr. The solution was evaporated, THF added and chromatographed. 1.30 g (26.5%) of 1-isomer and 0.22 g (4.5%) of 2-isomer were obtained.

*Use of iodide or chloride in these reactions lowers the yield.

Rearrangement of cyclopentadienyldicarbonyl-2-N-(1,2,3-triazolyl)iron into Cyclopentadienyldicarbonyl-1-N-1,2,3-triazolyliron

A solution of 2-isomer (0.67 g) in THF was refluxed for 1.5 hr, then chromatographed. 0.22 g (32.9%) of 1-isomer was obtained.

Synthesis of Cyclopentadienyldicarbonyl-1-N-1,2,3-triazolyliron Sulfate (IIIa)

Tetrahydrofuran solution of sulfuric acid was added to a solution of 1-isomer in THF. Precipitated crystals were crystallized from methanol.

		C %	H %	N %
Anal.	Calculated for $C_9H_9N_3O_6SFe$	31.49	2.62	12.24
	Found	31.20	2.76	12.09

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