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MONO- AND DI-CATIONIC SPECIES OF A [1,1-DIMERCURIO]FERROCENOPHANE BISDIMETHYLAMINOMETHYL DERIVATIVE

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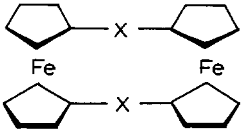
Summary

Oxidation of iron atoms in a neutral ferrocenophane with two ferrocene moieties and two mercury atoms, $\overline{C_5H_4FeC_5H_3(CH_2NMe_2)HgC_5H_4FeC_5H_3(CH_2NMe_2)Hg}$, gives corresponding mono- and di-cationic species. Ferrocenium, substituted ferrocenium salts and TCNQ were chosen as oxidizing agents. Electronic absorption and Mössbauer spectra of the oxidized species are discussed.

Introduction

For the past several decades metallocenes are in the focus of interest of organometallic chemists. Nevertheless metallocenophanic derivatives are very scarce compared with the numerous and varied metallocenes of other types. They are not easily available and their direct implementation is limited to some special cases, e.g. when a necessity arises to prove the stereochemical pattern of a chemical reaction (if conformationally rigid structures are employed). Metallocenophanes are also used in planning syntheses of compounds of new structural types, because phanic * bridges have a specific stabilizing effect on structures otherwise unstable.

Derivatives of the structural type I containing two sandwich moieties bridging each other make up a separate class of metalloceneophanes



(I)

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* Phanic refers to metallocenophane derivatives and non-phanic to metallocene derivatives.

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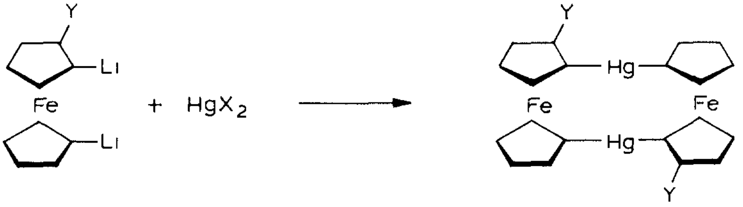
The structural rigidity of these molecules and the possibility of varying the distance between the iron through changing the size of the X groups are valuable for investigation of the nature of intermetallic interactions. Variation of the properties of C–X bonds and X fragments from non-phanic to phanic structures are also of interest.

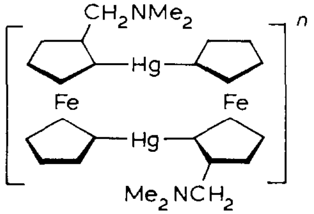
Results and discussion

Earlier, we reported the synthesis of two compounds which are the first examples of structural type I, with metal atoms for X. Actually, we prepared complexes II and IIa [1].



(Y = CH_2NMe_2 , (40% yield), II ,
Y = H , (5% yield), IIa)

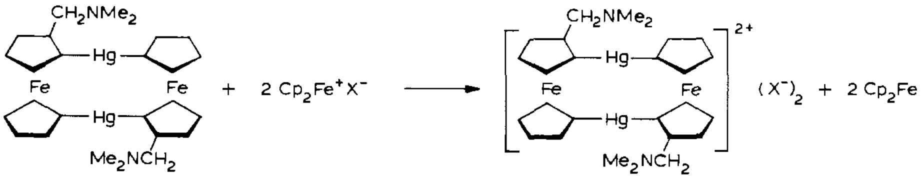
Here we describe the synthesis and the properties of mono- and di-cationic species III and IV. These are obtained through a sequential direct electron abstraction from the neutral complex II. Only the iron centres are affected.



(n = 1+ . III ,
n = 2+ ; IV)

The oxidizing agents used do not affect the dimethylamino groups and the C–Hg bonds. Thus in this case the C–Hg bonds do not dissociate by the one-electron transfer mechanism. We admit, however, that we were not the first to discover such a behaviour of a C–Hg bond in ferrocenium compounds. Recently, evidence for the formation of a ferrocenium mercuric non-phanic species, $[C_5H_5FeC_5H_4HgCl]^+$, was reported. No solid salts have been isolated, however [2].

The dicationic salts IV are more easily isolated than those of the monocation III. Ferrocenium BF_4^- and PF_6^- salts are employed as one-electron oxidizing agents in



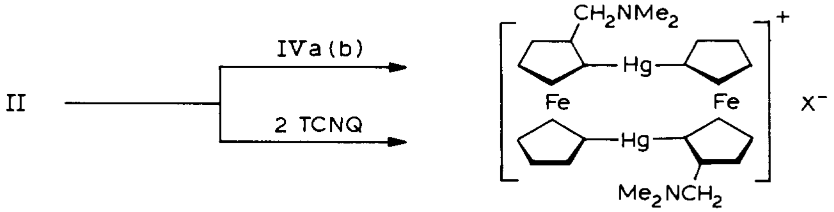
(II)

(X = BF_4 IVa ,
X = PF_6 IVb)

the synthesis of IV. Two equivalents of the oxidizer are stirred with one equivalent of II in an aromatic hydrocarbon medium. The microcrystalline salts IVa and IVb are precipitated almost quantitatively.

The dicationic salts IVa and IVb readily exchange the anions for BPh_4^- and $B(CN)Ph_3^-$ in solution in methylcyanide, nitromethane, alcohol, etc. The finely crystalline residues of the salts IVc and IVd are formed slowly and they are quite insoluble in all the solvents used. The samples of these salts are actually under X-ray structural investigation; the details of the structure are to be presented later.

It is worth noting that the oxidation of II with ferrocenium salts in aromatic solvents cannot stop with formation of the monocationic species. The salts of III are obtained by mutual redox reaction on mixing equivalent amounts of II with IVa or IVb in aprotic polar solvents, e.g. acetone, methylcyanide. Reaction of one molecule of II with two molecules of 7,7,8,8-tetracyanoquinodimethane (TCNQ) in acetone gives a similar salt of the monocation III with the complex $(TCNQ)_2^-$ anion.



($X^- = BF_4^-$: IIIa ,
$X^- = PF_6^-$: IIIb ;
$X^- = (TCNQ)_2^{\bar{\cdot}}$: IIIc)

The salts of the monocation III are far less stable than those of the dication IV, both in the solid state and in solution.

The distance between the iron atoms in all the species II, III and IV is almost the same due to the structural rigidity of these phanes. Interaction between iron centres in these electron-saturated and electron-deficient systems is an interesting problem for investigation. The odd electron in the monocation III may be completely delocalized or there may arise a state with two different Fe^{II}: Fe^{III} atoms. There are some examples of both modes of behaviour with bridged diferrocenylenes. Some of the monocationic species contain two identical iron centres and some of them have two different ferrocenylene moieties. It seems that the mode of behaviour realized in each case depends mostly on the chemical character of the bridges, and on their length [3–8].

TABLE 1

ELECTRONIC SPECTRA OF II, IIIa AND IVa (298K)

II		IIIa		IVa	
$\nu(cm^{-1})$	$\epsilon(cm^{-1}/mol)$	$\nu(cm^{-1})$	$\epsilon(cm^{-1}/mol)$	$\nu(cm^{-1})$	$\epsilon(cm^{-1}/mol)$
–	–	15700	460	15900	620
22200	650	21500	410	–	–
27000	4400	28500	2300	25600	460

Mössbauer and the electronic absorption spectra of II, III and IV have been studied. Taken together they provide mutually complementary information on the electronic state of the iron atoms. In the diferrocenylene complexes discussed here these spectra prove the independance of the iron centres. They testify against any direct, through space, or indirect, through the ligands, interaction between the two iron atoms. The pairs of ferrocenylene moieties are identical in II and IV, but they are spectrally different in III. Spectral parameters of II are quite typical of non-oxidized mononuclear ferrocene derivatives. And the situation with complex IV is typical of ferrocenium salts. See the Table 1 and 2 for numerical data. The Mössbauer spectrum of IV, for example, is characterized by significantly lower quadrupole splitting than that of II. The electronic absorption spectra of II and IV are different in two points: the low energy iron *d–d* electron transition band undergoes significant bathochromic shift and an increase of intensity on transformation of II into IV.

The spectra of III are somewhat more complicated but they can be satisfactorily treated as resulting from superposition of the corresponding spectra of II and IV. However, the absence of strict numerical coincidence of spectral parameters of III with those of II and IV and their dependence upon the nature of the anion demonstrate that the salts III are not mere mixtures of equimolecular amounts of II and the salts IV.

Thus, the above salts of the monocationic species III could be classified as dissymmetrical mixed-valence compounds; the iron centres differing from one another. In general, mixed-valence compounds can follow either this pattern or on the contrary they may contain undistinguishable metallic centres, and this significantly affects their chemical and spectral appearances. Only a few mixed-valence binuclear π-complexes of transition metals are known. Many of them are diferrocenylenes, but only some of them have been studied in detail [3–8]. Our present data augment the knowledge of such compounds and provide a new example of a molecule with strictly independent ferrocenylene fragments.

TABLE 2

MÖSSBAUER PARAMETERS OF II, IIIb, IIIc and IVb

Compound	*T*(K)	*IS* (isomer shift) (mm/sec)	*QS* (quadrupole splittings) (mm/sec)	*I* (%) (ferrocene-ferrocenium content)
II	78	0.81	2.32	
II	293	0.72	2.30	
IIIb	78	0.81	2.26	57
IIIb	78	0.83	0.35	43
IIIc	78	0.76	2.36	53
		0.72	0.40	47
IIIc	201	0.74	2.28	50
		0.72	0.35	50
IVb	78	0.83	$\Sigma\Gamma^a \simeq 0.68$	
IVb	293	0.70	$\Sigma\Gamma^a \simeq 0.64$	

[a] Γ = line width (mm/sec).

Experimental

Preparation of complexes

Synthesis of IV tetrafluoroboronate (IVa). A mixture of 0.22 g (0.29 mmol) II with 0.15 g (0.54 mmol) $Cp_2Fe^+BF_4^-$ in dry benzene (20 ml) was stirred vigorously at room temperature for 2 hours. The colour of the residue changed from deep to pale blue. The residue was filtered off, washed with dry benzene and dried in vacuo. 0.23 g (82% yield) salt IVa was obtained. When heated rapidly, the compound decomposed at ~ 150°C (the colour changed from blue to orange); when the temperature was made to rise slowly the decomposition began at 80°C. Found: C, 29.74; H, 2.92; N, 2.88. $C_{26}H_{30}F_8B_2N_2Hg_2Fe_2$ calcd.: C, 29.55; H, 2.86; N, 2.64%. IR (cm^{-1}): 3150m, 2790w, 1175w, 1143w, 1125m, 1105m, 1060s, 854m, 720m, 687w, 517w.

Synthesis of IV hexafluorophosphate (IVb). The compound was obtained through the above described technique, ferrocenium hexafluorophosphate being used as an oxidizing agent. The yield of IVb was ~ 90%. IR (cm^{-1}): 3130m, 2790w, 1175w, 1150w, 1030m, 900–820s, 750m, 725m, 705w, 583w.

Compounds IVa and IVb are readily soluble in water, light alcohols, acetone, methylcyanide and nitromethane. Solutions in thoroughly purified organic solvents are stable at room temperature for several hours. When commercially available solvents without purification are used the decomposition is observed some minutes after dissolving.

Synthesis of IV tetraphenylboronate (IVc). A solution of 0.10 g (0.1 mmol) IVa in pure CH_3CN (1 ml) was mixed with a solution of 0.10 g (0.29 mmol) $NaBPh_4$ in pure CH_3CN (1 ml). After an hour some deep-blue needles were formed. The residue was separated, washed with water and dried in vacuo. 0.14 g (94% yield) of salt IVc was obtained. IVc decomposed at ~ 150°C to form an orange derivative with m.p. 153–154°C. Found: C, 58.74; H, 4.68; N, 2.01; Hg, 26.45. $C_{74}H_{70}N_2B_2Hg_2Fe_2$ calcd.: C, 58.40; H, 4.64; N, 1.84; Hg, 26.36%.

Synthesis of IV triphenylcyanoboronate (IVd). The salt IVd was obtained through the technique employed for IVc.

Unlike IVa and IVb the salts IVc and IVd are insoluble in both organic solvents and in water.

Synthesis of III tetrafluoroboronate (IIIa). 0.088 g (0.1 mmol) II was added to a solution of 0.106 g (0.1 mmol) IVa in acetone (40 ml) at −78°C. The mixture was stirred for an hour at −78°C. Then the solution was filtered and the product was precipitated by adding 200 ml of ether at −78°C. 0.180 g (93% yield) IIIa was obtained. The compound decomposed slowly at room temperature; the degradation became rapid above 50°C. Found: C, 31.92; H, 3.45. $C_{26}H_{30}F_4Fe_2Hg_2N_2B$ calcd.: C, 32.19; H, 3.12%.

The same technique was used to isolate III hexafluorophosphate (IIIb).

Synthesis of the salt of III with the $(TCNQ)_2^-$ anion (IIIc). 0.883 g (1 mmol) II and 0.408 g (2 mmol) TCNQ were dissolved in benzene (100 ml). A deep green solution resulted. Fine black crystals were precipitated on adding ether. 1.260 g (quantitative yield) IIIc was obtained. The compound decomposed above 70°C. Found: C, 47.11; H, 2.41. $C_{50}H_{38}N_{10}Fe_2Hg_2$ calcd.: C, 46.45; H, 2.63%. IR (cm^{-1}): 2160s, 1710w, 1455s, 1350s, 1250w, 1170s, 1015w, 985w, 937w, 915m, 850m, 825m, 810m, 720m, 525w, 485w, 440w.

Spectra

IR spectra of Nujol mulls were recorded on a IKS-29 instrument. Electronic absorption spectra were studied with a Cary-219 spectrometer in C_6H_6 (II) or in CH_3CN (IIIa and IVa). Mössbauer spectra were measured with an electrodynamic type instrument of the Institute of Chemical Physics of the Academy of Sciences of the U.S.S.R. A ^{57}Co source in a chromium matrix was used. The spectra were recorded at temperatures of the samples of 78, 201 and 293 K and the isomeric shifts were correlated with $Na_3[Fe(CN)_5NO_2]$; the accuracy of determination of chemical forms content (I) was ±5%.

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