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Preliminary communication

ELECTRONEUTRAL NAPHTHALENECYCLOPENTADIENYLIRON

A.N. NESMEYANOV, S.P. SOLODOVNIKOV, N.A. VOL'KENAU*, L.S. KOTOVA and N.A. SINITSYNA

Institute of Organo-Element Compounds, Academy of Sciences, Moscow V-312 (U.S.S.R.)

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Summary

Electroneutral naphthalene- and tetralin-cyclopentadienyliron complexes have been obtained by reduction of the corresponding cationic [AreneFeC_5H_5]BF_4 compounds. Their chemical behaviour is described. Benzene- and naphthalene-cyclopentadienyliron EPR spectra have been obtained and are discussed.

In extension of our previous studies [1—4] on a novel class of electroneutral arene-cpd-iron derivatives (cpd = cyclopentadienyl ligand) we now describe the preparation and properties of naphthalene-cpd-iron, $C_{10}H_8FeC_5H_5$. This complex was obtained by reduction of $[C_{10}H_8FeC_5H_5]BF_4$ with 1% sodium amalgam in dimethoxyethane (in 75% yield) or in tetrahydrofuran (in 40% yield).

$$[C_{10}H_8FeC_5H_5]BF_4 + Na/Hg \xrightarrow{\text{DME or THF}} C_{10}H_8FeC_5H_5 + NaBF_4$$

DME = dimethoxyethane; THF = tetrahydrofuran

Naphthalene-cpd-iron is a dark violet crystalline substance, soluble in DME, THF and pentane. The mass spectrum of $C_{10}H_8FeC_5H_5$ contains the molecular ion $[C_{10}H_8FeC_5H_5]^+$ of m/e 249 and fragmentation products of m/e 128 $[C_{10}H_8]^+$, 121 $[C_5H_5Fe]^+$, 65 $[C_5H_5]^+$ and 56 $[Fe]^+$. Moreover, in the mass spectrum the ferrocene molecular ion (m/e 186) and ions of m/e 312 and 250 were found. Possibly, there occurs a partial pyrolysis of the initial complex. Electroneutral naphthalene-cpd-iron is paramagnetic as is benzene-cpd-iron [2]. The electron paramagnetic resonance (EPR) of $C_6H_6FeC_5H_5$ and $C_{10}H_8FeC_5H_5$ was investigated in DME solution. The EPR spectrum of $C_6H_6FeC_5H_5$ was observed in the 14—60 K temperature range. At 60 K the spectrum virtually disappears. g-Factors were found at 14 K: $g_\parallel = 2.00$ and $g_\perp = 1.85$ (Fig. 1a). The EPR spectrum of $C_{10}H_8FeC_5H_5$ is observed in a wider temperature range (77—293 K). We found $g_\parallel = 2.096$ and $g_\perp = 2.002$ (Fig. 1b) at 77 K. The EPR signal with isotropic g-factor $g_{iso} = 1/3\ (2g_\perp + g_\parallel)$ appears as the temperature is raised to 150 K and the signal is observed until 293 K. The repeated decrease in tempera-

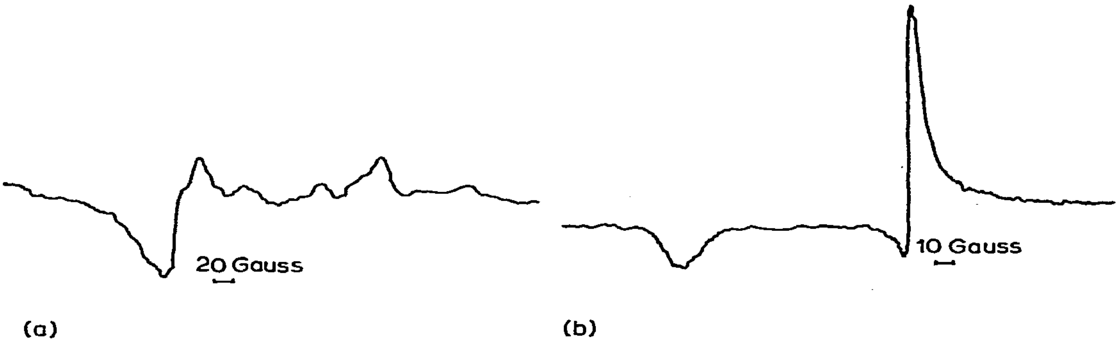


Fig.1. (a) EPR spectrum of $C_6H_6FeC_5H_5$ at 14 K, (b) EPR spectrum of $C_{10}H_8FeC_5H_5$ at 77 K.

ture to 77 K leads to the initial anisotropic spectrum. It means that the heating for a short time to room temperature does not destroy the complex. The narrowing of the EPR signal on going from anisotropic to isotropic *g*-factor is replaced by broadening of the line as the temperature is raised further. The narrowest line width (peak to peak $\Delta H = 10$ Gauss) is observed at 173 K. At room temperature the line is two times as broad and the signal intensity is greatly diminished. The observed *g*-factor anisotropy and the line width dependence on temperature are characteristic of a paramagnetic sandwich complex of iron [5]. It is important to note that $C_{10}H_8FeC_5H_5$ is the only sandwich complex of iron of which the EPR spectrum can be recorded at room temperature.

The EPR spectra of the ferricenium cation and its derivatives having 17 electrons (five 3*d* electrons) have been widely discussed, but the EPR spectra of 19 electron iron systems (d^7) have been investigated to a much lesser extent. Data are available on the EPR and NMR of the bis(hexamethylbenzene)iron(I) cation [6,7]. The supposition was made [6] that the unpaired electron is taken up in the bis(hexamethylbenzene)iron(I) cation by the e_{2u} nonbonding ligand orbitals. Later, however, on the basis of NMR investigations [7], it was proved that the unpaired electron is mainly located on the iron atom. The energy sequence of the molecular orbitals of iron complexes is now well established [5,7,8]. The ligand orbitals are below the metal ones and the metal orbitals sequence is now mainly discussed. This discussion is generally concerned with the closely located a_{1g} and e_{2g} levels and there is no doubt that the $e_{1g}^{\star}$ level is above the a_{1g} and e_{2g} levels. So the unpaired electron is apparently on the $e_{1g}^{\star}$ level in the complexes investigated. It occupies the d_{xz} or d_{yz} orbitals of the iron atom because on the basis of the low symmetry of these complexes the degeneracy must be removed.

The conclusions about the unpaired electron localization may be proved by analysis of the line width of the naphthalene-cpd-iron EPR spectrum. The line width at 173 K is only 10 Gauss, indicating low unpaired electron density on the ligands. It is interesting that the peak-to-peak width of the well resolved vanadium components in the bis(naphthalene)vanadium(0) spectrum equals 15 Gauss [9]. The hyperfine splitting value a_V is equal to 62.5 Gauss, which corresponds to the localization of the unpaired electron on the a_{1g} $(3d_{z^2})$ metal orbital, whereas the hyperfine proton splitting of the ligands is 3.8 Gauss [9].

Naphthalene-cpd-iron is oxidized instantly by atmospheric oxygen. Such an oxidation in the presence of aqueous $NaBF_4$ leads quantitatively to the initial cationic complex $[C_{10}H_8FeC_5H_5]BF_4$ (melting point 132—133°C, and the ^1H NMR spectra of the obtained and authentic samples are identical).

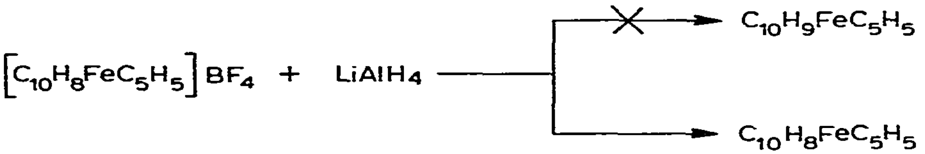
$$C_{10}H_8FeC_5H_5 \xrightarrow[NaBF_4/H_2O]{O_2} [C_{10}H_8FeC_5H_5]BF_4$$

Iodine also oxidizes $C_{10}H_8FeC_5H_5$ immediately into $[C_{10}H_8FeC_5H_5]I$. Contrary to benzene-cpd-iron [10], water does not oxidize $C_{10}H_8FeC_5H_5$, but partially hydrolizes it with the loss of both ligands, and partially converts it into ferrocene. On standing in DME or THF solutions naphthalene-cpd-iron gives ferrocene, naphthalene and elemental iron as well.

$$2C_{10}H_8FeC_5H_5 \xrightarrow{H_2O} (C_5H_5)_2Fe + 2C_{10}H_8 + Fe$$

$$2C_6H_6FeC_5H_5 \xrightarrow{H_2O} 2[C_6H_6FeC_5H_5]OH + H_2$$

In spite of our numerous attempts, we were not able to perform a dimerization of naphthalene-cpd-iron, although such a transformation is typical of $C_6H_6FeC_5H_5$ [3]. Earlier we established [3] that dimerization of electroneutral arene-cpd-iron derivatives takes place with the formation of a C—C bond between six-membered ligands of two π-complex molecules. During this conversion each arene ligand transforms into a cyclohexadienyl one having sp^3-hybridized carbon which is shifted out of the plane of the other five carbons by approximately 40° [11]. Possibly the naphthalene ligand is incapable of such a transformation because of the steric rigidity. In order to confirm this assumption we tried to perform a nucleophilic addition of hydride ion to the naphthalene ligand of $[C_{10}H_8FeC_5H_5]^+$. This reaction is general for $[AreneFeC_5H_5]^+$ and usually leads to cyclohexadienyl-cpd-iron derivatives [12]. However, in the case of $[C_{10}H_8FeC_5H_5]BF_4$, instead of hydride-ion addition one-electron reduction takes place.



The reaction of $[C_{10}H_8FeC_5H_5]BF_4$ with C_2H_5Li also leads to $C_{10}H_8FeC_5H_5$ (cf. [13]).

Thus the properties of electroneutral naphthalene-cpd-iron are markedly different from those of benzene-cpd-iron described earlier [1—4]. The former is more able to eliminate an arene ligand, more stable to oxidants and cannot be transformed into cyclohexadienyl π-complexes.

It is of interest to note that electroneutral tetralin-cpd-iron, $C_{10}H_{12}FeC_5H_5$ has properties very similar to $C_6H_6FeC_5H_5$. The dark green, crystalline paramagnetic substance, $C_{10}H_{12}FeC_5H_5$, was obtained from $[C_{10}H_{12}FeC_5H_5]BF_4$ by the standard method (DME; 1% Na/Hg; –50°C, 1 h) in a 30% yield. The mass spectrum of $C_{10}H_{12}FeC_5H_5$ contains the molecular ion (m/e 253) and characteristic fragmentation products. Tetralin-cpd-iron, similarly to $C_6H_6FeC_5H_5$, does not give an EPR spectrum down to liquid nitrogen temperature. Water oxidizes

$C_{10}H_{12}FeC_5H_5$ very readily to give $[C_{10}H_{12}FeC_5H_5]OH$ with quantitative H_2 evolution. Tetralin-cpd-iron dimerizes easily to form a red diamagnetic dimer. Thus the features of naphthalene-cpd-iron behaviour have to be considered a consequence of a planar conjugated structure of its fused arene ligand.

We intend to continue our research of arene-cpd-iron complexes with fused polynuclear arene ligands.

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Erratum

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Page C47, to be inserted between the seventh and sixth line from the bottom:

If intermediate V were involved in this reaction, the Diels—Alder adducts (Xa and Xb) arising from V and VII should be formed as main products. Care-