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Preliminary communication

ESR SPECTRA OF ARENECYCLOPENTADIENYLIRON DICATIONS

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Summary

ESR spectra of arenecyclopentadienyliron dications have been studied at 77 K. Arenecyclopentadienyliron cations were oxidized with $SbCl_5$ in CH_2Cl_2 solution at 203 K. The $g_\parallel$ and $g_\perp$ values have been measured and splittings of the degenerate e_{2g} orbitals have been calculated. The energy differences between the split components proved to be considerably smaller than that of the e^*_{1g} level in the corresponding neutral complexes. They are, however, larger than the splittings of the e_{2g} orbitals observed in ferricinium cations.

We have recently studied the ESR spectra of arenecyclopentadienyliron derivatives, $areneFeC_5H_5$, obtained by reduction of the corresponding cations [1—3]. In this work, the ESR spectra of dications occurring in the oxidation of $[areneFeC_5H_5]^+BF_4^-$ are reported. It should be noted that the oxidation of arenecyclopentadienyliron cations to the dications has not been accomplished so far [4,5], and the present results are the first evidence for the existence of $[areneFeC_5H_5]^{2+}$.

Arenecyclopentadienyliron cations are isoelectronic with ferrocene, and have a d^6 configuration, ${}^1A_{1g}[(a_{1g})^2(e_{2g})^4]$, the neutral compounds have a d^7 configuration, ${}^2E_{1g}[(a_{1g})^2(e_{2g})^4(e^*_{1g})^1]$, and the dications should be isoelectronic with the ferricinium cation, d^5, ${}^2E_{2g}[(a_{1g})^2(e_{2g})^3]$. ESR spectra of the reduced and oxidized forms of arenecyclopentadienyliron cations afford important information on various iron orbitals, splittings of degenerate levels and interactions between iron and ligand orbitals.

Various oxidizing systems were tested, including $SbCl_5$-CH_2Cl_2 (203 K), I_2 vapour, I_2-dimethylformamide, I_2-CH_2Cl_2, Br_2 vapour, Br_2-CH_2Cl_2, $AlCl_3$-nitromethane (233 K) and tetracyanoquinodimethane-THF (203 K). The system $SbCl_5$-CH_2Cl_2 (203 K) gave the best results.

The initial borofluorides of the monocations $[areneFeC_5H_5]^+$ (arene =

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*Deceased.

$CH_3OC_6H_5$, $C_6H_5OC_6H_5$, p-FC_6H_4—C_6H_5, C_6H_5—C_6H_5, $C_{10}H_8$, $C_{14}H_{10}$) were obtained using the procedures recommended in the literature.

The reaction of α-methylnaphthalene (0.1 mol) with ferrocene (0.054 mol), $AlCl_3$ (0.06 mol) and Al powder (0.04 g-atom) in 100 ml heptane (5 h, 100°C) yields the α-methylnaphthalenecyclopentadienyliron cation, isolated as its borofluoride (yield 10%, m.p. 112—115°C). Found: Fe, 15.55. $C_{16}H_{15}BF_4Fe$ Calcd: Fe, 15.95%. $[\beta\text{-}FC_{10}H_7FeC_5H_5]BF_4$ was made from β-fluoronaphthalene and ferrocene by the same procedure (yield 13%, m.p. 138—142°C). Found: Fe, 15.43. $C_{15}H_{12}BF_5Fe$ Calcd: Fe, 15.78%. Similarly, naphthalene reacted with 1,1-diethylferrocene to give $[C_{10}H_8FeC_5H_4C_2H_5]BF_4$ (yield 14%, m.p. 99—101°C). Found: Fe, 15.33. $C_{17}H_{17}BF_4Fe$ Calcd: Fe, 15.34%.

The monocations were oxidized at 203 K under argon by the addition of the required amounts of $SbCl_5$ to concentrated solutions of $[areneFeC_5H_5]BF_4$ in CH_2Cl_2 placed in quartz ampoules.

The ESR spectra were recorded on a Varian E12 spectrometer at 77 K.

The ESR spectra of the naphthalenecyclopentadienyliron and α-methylnaphthalenecyclopentadienyliron dications are shown in Fig. 1. Fig. 2 presents the ESR spectra of the dications $[\beta\text{-}FC_{10}H_7FeC_5H_5]^{2+}$, $[C_{10}H_8FeC_5H_4C_2H_5]^{2+}$ and $[CH_3OC_6H_5FeC_5H_5]^{2+}$. Alongside the dication signals, the spectra contain narrow symmetrical signals with g = 2.0023 arising from the aromatic ligand

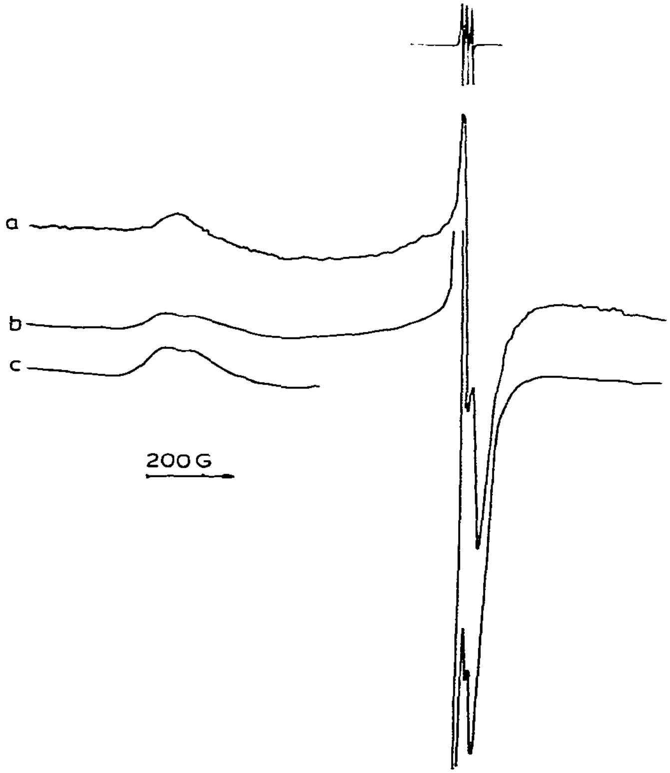


Fig. 1. ESR spectra of dications: a) naphthalenecyclopentadienyliron, b) and c) α-methylnaphthalenecyclopentadienyliron at 77 K.

Fig. 2. ESR spectra of dications: a) β-fluoronaphthalenecyclopentadienyliron, b) naphthalene-ethylcyclopentadienyliron, c) anisolecyclopentadienyliron at 77 K.

cation-radicals formed by partial decomposition of the dications [7]. The data in Figs. 1 and 2 show that the relative yields of dications and cation-radicals are subject to considerable variation, depending on both the stability of the initial cations and ligands to oxidation and the stability of the paramagnetic species.

The $g_{\parallel}$ and $g_{\perp}$ dication signals are positioned to the right and to the left, respectively, of the ligand cation-radical signals. The dication signals disappear irreversibly as the sample temperature rises to room temperature; and only the cation-radical signal remains in the spectrum, as follows from spectra taken after recooling the samples to 77 K. The decomposition of the dications may be due to their instability and/or the possible presence of excess $SbCl_5$ causing their further oxidation.

The $g_{\parallel}$, $g_{\perp}$ and $\Delta E = E_{d_{x^2-y^2}} - E_{d_{xy}}$ values, calculated by the formula

$$g_{\parallel} = 2\left(1 - \frac{2\lambda_0}{\Delta E}\right) \qquad \lambda_0 = -400\ \mathrm{cm}^{-1}$$

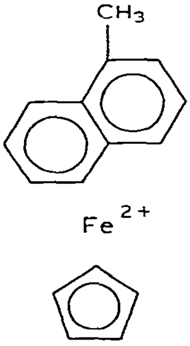
TABLE 1

THE $g_{\parallel}$, $g_{\perp}$ AND ΔE VALUES IN THE ESR SPECTRA OF ARENECYCLOPENTADIENYLIRON DICATIONS, $[\text{areneFeC}_5\text{H}_5]^{2+}$

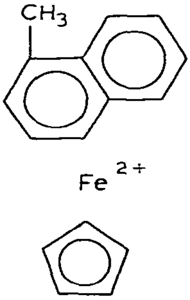
Arene ligand	$g_{\parallel}$	$g_{\perp}$	ΔE (cm^{-1})
$CH_3OC_6H_5$	3.14	1.940	1400
$C_6H_5OC_6H_5$	3.14	1.920	1400
p-$FC_6H_4C_6H_5$	3.16	1.898	1380
$C_6H_5C_6H_5$	3.04	1.930	1540
$C_{10}H_8$	2.80	1.976	2000
β-$FC_{10}H_7$	2.83	1.976	1930
α-$CH_3C_{10}H_7$ (A)	2.81	1.977	1970
α-$CH_3C_{10}H_7$ (B)	2.71	1.988	2260
$C_{14}H_{10}$	2.86	1.964	1860

are listed in Table 1. The ΔE values thus obtained are far larger than the λ_0 one. For this reason, this formula yields practically the same ΔE values as that used for $g_{\parallel}$ by Prins [6] in his study of the ESR spectra of ferricinium cation derivatives.

The ESR spectrum of the α-methylnaphthalenecyclopentadienyliron dication is noteworthy. The $g_{\parallel}$ and $g_{\perp}$ signals in that spectrum are both split into two components. We have observed a similar splitting of the $g_{\parallel}$ signal in the spectrum of the neutral complex α-methylnaphthalenecyclopentadienyliron [3]. The splitting was attributed to the presence of two isomers, with iron bonded to either the substituted or unsubstituted naphthalene nucleus. The stronger signals in the spectrum of the α-methylnaphthalenecyclopentadienyliron dication were assigned to isomer A, as follows from the $g_{\parallel}$ and $g_{\perp}$ values found for the unsubstituted naphthalene derivative.



(A)



(B)

For $[\beta\text{-CH}_3\text{C}_{10}\text{H}_7\text{FeC}_5\text{H}_5]^+$, the occurrence of isomers of types A and B has been proved by NMR spectra. The A:B ratio was found to be 55:45 [8]. With the α-fluoronaphthalenecyclopentadienyliron cation, one isomer only exists, with iron bonded to the unsubstituted ring [8]. We also observed a single signal in the spectrum of $[\beta\text{-FC}_{10}\text{H}_7\text{FeC}_5\text{H}_5]^{2+}$, which should, according to its $g_{\parallel}$ and $g_{\perp}$ values, be assigned to the isomer containing iron—unsubstituted ring bonds. Unlike the neutral naphthalenecyclopentadienyliron complex and its α-methyl and β-fluoro derivatives, where the Jahn-Teller effect causes the iron atom to migrate between the naphthalene nuclei at temperatures above 77 K [3], the dications feature no such migration.

The nature of the aromatic ligand significantly affects the $g_{\parallel}$ and $g_{\perp}$ values, signal linewidths and dication yields. An increase of ligand electron-donor strength results in a decrease of $g_{\parallel}$ and increase of $g_{\perp}$, signal narrowing and growth of dication yields from the oxidation of monocation salts. As a consequence of this, we failed to register spectra of the benzenecyclopentadienyliron dication and some of its derivatives at 77 K. In contrast, oxidation of $[CH_3OC_6H_5FeC_5H_5]BF_4$ and $[C_6H_5OC_6H_5FeC_5H_5]BF_4$ gives high yields of the corresponding dications.

Linewidths corresponding to $g_{\perp}$ are some 30—40 Gauss in the spectra of the dications with naphthalene and phenanthrene ligands (at 77 K), whereas it is 150 Gauss in the diphenyl ligand complex. In the spectrum of $[C_6H_5C_6H_5FeC_5H_5]^{2+}$, the linewidth corresponding to $g_{\perp}$ varies from 70 to 150 Gauss in the range 15—77 K. With the $[C_{10}H_8FeC_5H_5]^{2+}$ dication, a temperature rise from 77 to 150 K results in a dramatic broadening of the spectral lines and, finally, to the disappearance of the signal.

The study of the ESR spectra of dicationic and neutral arenecyclopentadienyliron complexes shows that the splitting of degenerate e_{2g} orbitals in the dications is far smaller than the splittings of $e^{\star}_{1g}$ orbitals in the neutral complexes [2]. The reason for this is that in the dication the unpaired electron occupies the $d_{x^2-y^2}$ and d_{xy} orbitals, whereas in the neutral complexes, the unpaired electron should occupy the d_{xz} and d_{yz} iron orbitals. The stronger overlapping of the latter with the ligand π-orbitals results in the larger splitting observed in the electroneutral complexes. Comparison of the dications studied with the ferricinium cation and its derivatives [6] shows that dications show far stronger splittings of the e_{2g} orbitals than ferricinium cations do.

Attempts to use the other oxidation reagents mentioned above proved a failure.

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