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ESR AND ELECTRONIC ABSORPTION SPECTRA OF THE PRODUCTS OF DEPROTONATION OF IRON ARENE-CYCLOPENTADIENYL COMPLEXES

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Summary

Paramagnetic d^7 complexes have been obtained by reducing deprotonated arenecyclopentadienyliron borofluorides (arene = diphenylmethane, fluorene, hexamethylbenzene) with sodium. The interaction of deprotonated d^7 complexes with ethanol leads to neutral d^7 complexes which are formed by direct reduction of the initial cations with sodium. Hexamethylbenzenecyclopentadienyliron was shown to undergo deprotonation under the action of sodium.

The electronic absorption spectra of the deprotonated complexes have been studied. Analysis of the positions and intensities of the absorption bands made it possible to draw some structural conclusions about deprotonated arene ligands.

The deprotonation of substituted areneCpiron cations, $[RC_6H_5FeC_5H_5]^+$, with strong bases has been described in a number of papers [1–4]. The combined action of coordination to the metal and of the complex positive charge causes high lability of the hydrogen atoms positioned α to the arene ligand. In particular, deprotonation has been described for $[areneFeC_5H_5]^+$ with fluorene [1], diphenylmethane [2] and even hexamethylbenzene [3] and toluene [4] for the arene group. The deprotonation of $areneFeC_5H_5{}^+$ (of d^6 configuration) yields rather unstable π-complexes also having the d^6 configuration. The structure of these complexes is discussed in Refs. 1 and 2.

Free fluorene and diphenylmethane are also known to react with alkali metals at reduced temperatures with the formation of the corresponding anion-radicals. At higher temperatures, these radicals lose protons and undergo transformation to carbanions [5,6]. Toluene remains intact under the same conditions. We have carried out an ESR study of the reduction of $[areneFeC_5H_5]^+$ (d^6) cations to neutral $areneFeC_5H_5$ (d^7) with alkali metals [7,8]. From the above it follows

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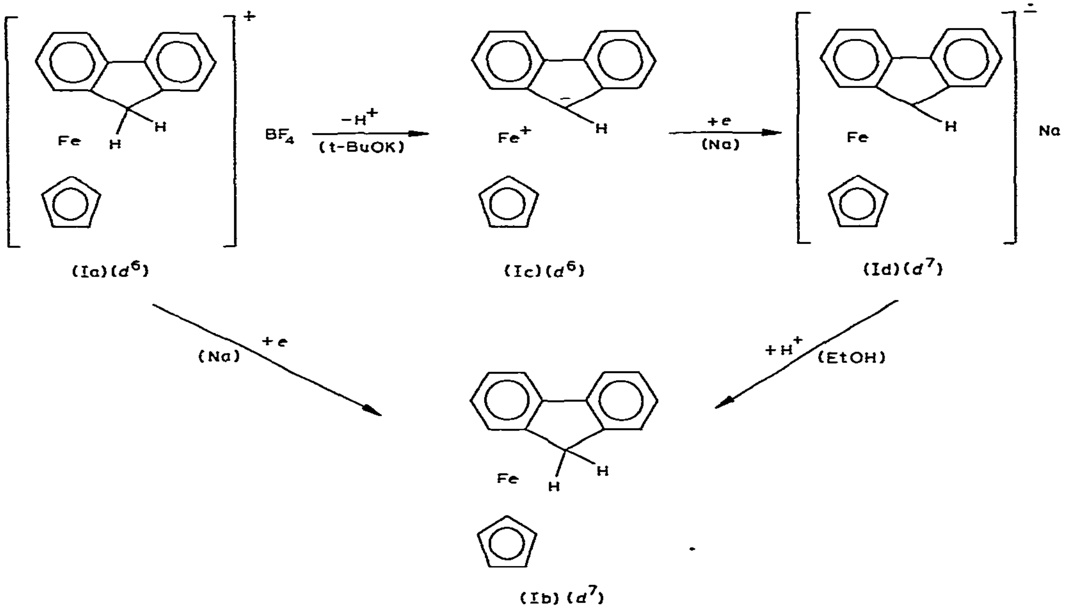
that the reduction of $[RC_6H_5FeC_5H_5]^+$ cations bearing appropriate substituents may be accompanied by deprotonation. In this work, we have studied this possibility and also the possibility of reducing the deprotonation products. We started our investigation by studying fluoreneCpiron borofluoride (Ia), see Scheme 1.

SCHEME 1



The compound was deprotonated with t-C_4H_9OK in 1,2-dimethoxyethane (DME). The diamagnetic product isolated from this reaction (Ic) was reduced with Na-mirror to obtain paramagnetic Id. The ESR spectrum of Id is shown in Fig. 1a; the g values are: $g_1 = 2.078$, $g_2 = 2.00$, $g_3 = 1.926$. Addition of ethanol resulted in transformation to the spectrum shown in Fig. 1b ($g_1 = 2.100$, $g_2 = 2.00$, $g_3 = 1.990$) without a noticeable decrease in signal intensities.

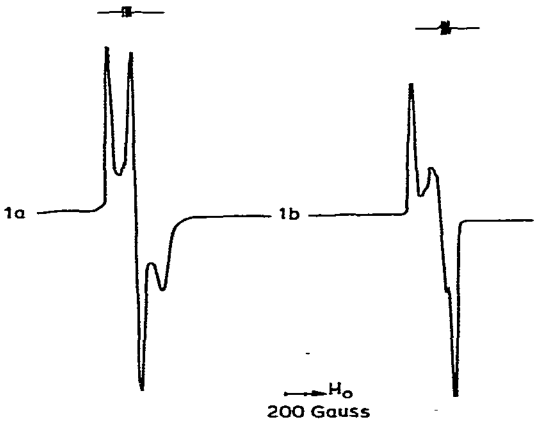


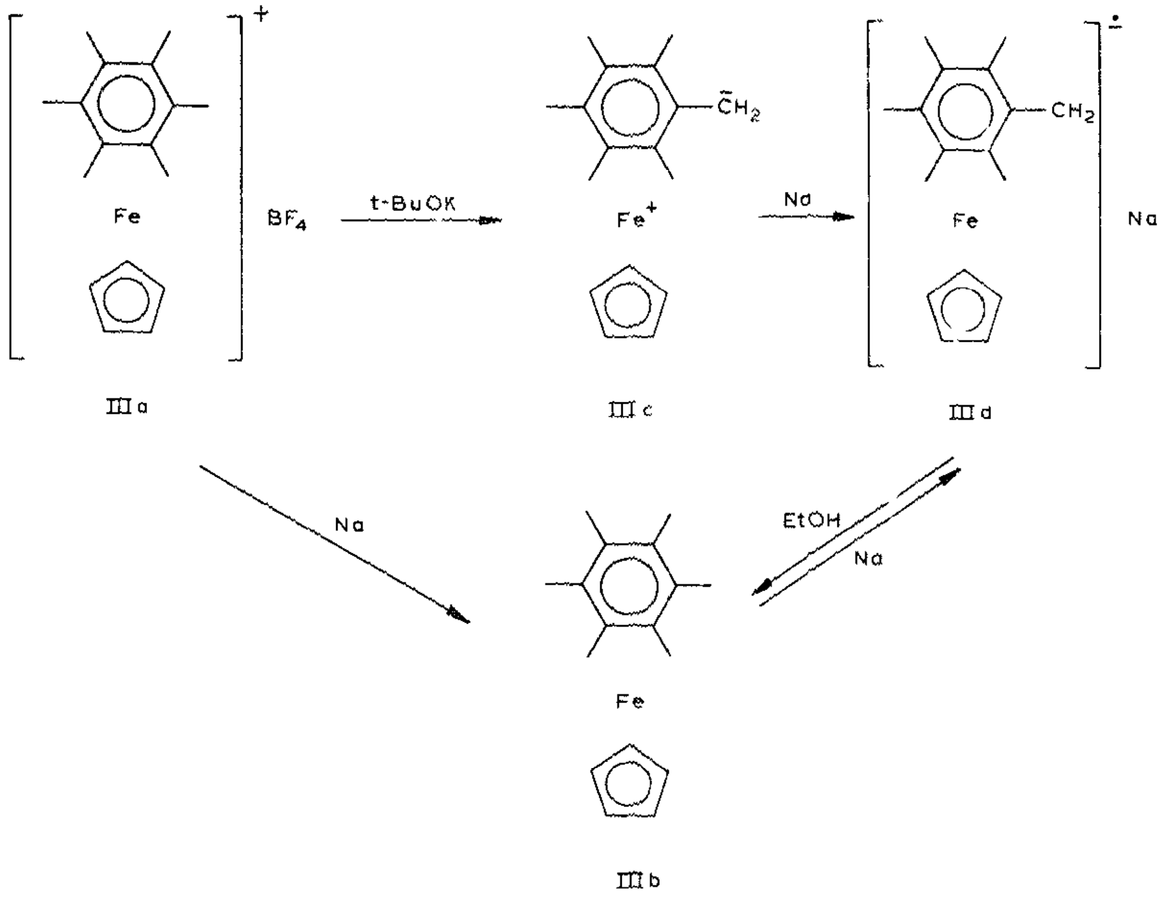
Fig. 1. ESR spectra of (a) $[C_{13}H_9FeC_5H_5]^-$ Na (Id) and (b) $[C_{13}H_{10}FeC_5H_5]$ (Ib).

A similar spectrum was described by us earlier [7] as arising from the electroneutral π-complex Ib formed by reduction of Ia with a Na-mirror. The formation of Ib in the protonation of Id substantiates the structure suggested for that product.

The reduction of the fluoreneCpiron cation, Ia, with a Na-mirror under the conditions described gave only the electroneutral complex Ib (d^7). Increasing the temperature and the reaction time did not affect the deprotonation, as judged from the absence of the spectrum of Id shown in Fig. 1b. Marked decomposition of Ib only occurred.

The transformations of diphenylmethaneCpiron (IIa) carried out in this work were as follows: the deprotonation to IIc [2] and reduction of IIc to the paramagnetic d^7 complex $[C_6H_5CHC_6H_5FeC_5H_5]^{-}Na^{+}$ (IId). The g values in the ESR spectrum of IId were $g_{\parallel} = 2.120$, $g_{\perp} = 2.006$. In the spectrum of $C_6H_5CH_2C_6H_5FeC_5H_5$, $g_{\parallel} = 2.240$, $g_{\perp} = 2.006$ [7]. Attempts to deprotonate IIb with sodium proved a failure. The transformations of hexamethylbenzeneCpiron (IIIa) are shown in Scheme 2.

SCHEME 2



According to Scheme 2, the reduction of IIIa with a Na-mirror results in the electroneutral π-complex IIIb, having the spectrum shown in Fig. 2a ($g_1 = 1.840$, $g_2 = 2.000$, $g_3 = 2.050$) *.

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* Compound IIIb was earlier [4] prepared by reduction of IIIa with sodium amalgam in DME at room temperature Its ESR spectrum was reported ($g_1 = 1.864$, $g_2 = 2.000$, $g_3 = 2.063$).

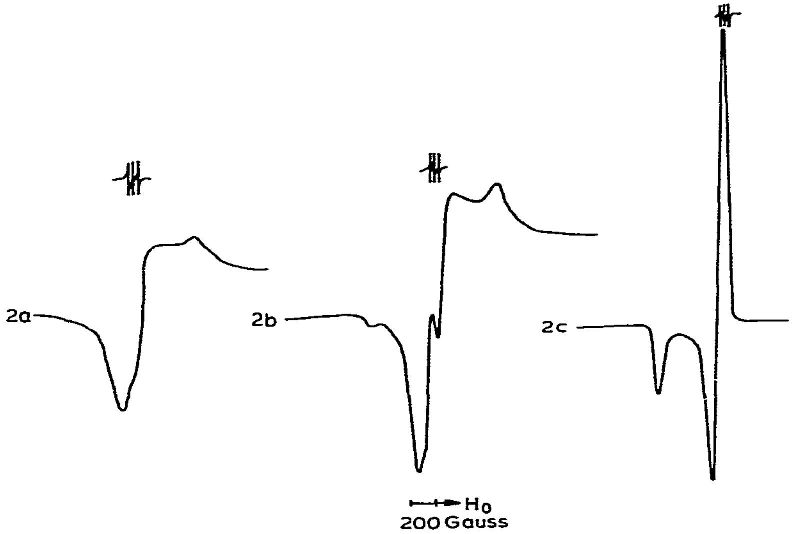


Fig. 2. ESR spectra of (a) $C_6(CH_3)_6FeC_5H_5$ (IIIb), (b) $C_6(CH_3)_6FeC_5H_5$ (IIIb) + $[C_5H_5FeC_6(CH_3)_5CH_2]^{\dot{-}}$ Na (IIId) and (c) $[C_5H_5FeC_6(CH_3)_5CH_2]^{\dot{-}}$ Na (IIId).

Increase of the time of contact of IIIb with the sodium mirror to ca. 30 min results in a gradual fading out of the spectrum shown in Fig. 2a and the appearance of a new spectrum with $g_{\parallel} = 2.180$, $g_{\perp} = 2.000$ (Fig. 2b, c). We explain this as the deprotonation of IIIb under the action of sodium metal and the formation of IIId:

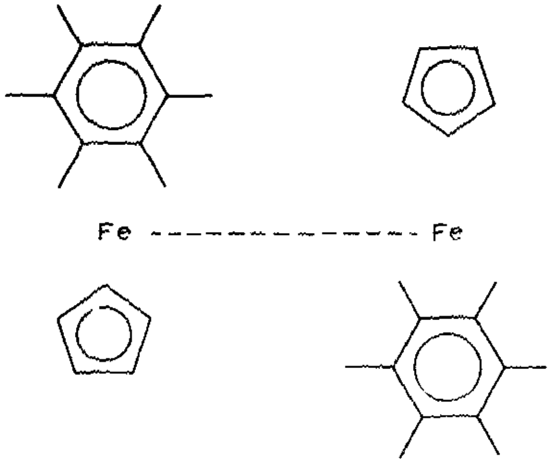
$$C_6(CH_3)_6FeC_5H_5 + Na \rightarrow [C_5H_5FeC_6(CH_3)_5CH_2]^{\dot{-}} Na^+ + H^{\cdot}$$

$$\text{(IIIb)} \qquad\qquad\qquad \text{(IIId)}$$

In fact, addition of ethanol to the ampoule led to transformation of the spectrum shown in Fig. 2c into the spectrum of Fig. 2a, i.e. to the reverse protonation and formation of IIIb. Following the procedure given in ref. 3 we deprotonated IIIa with t-C_4H_9OK and reduced the diamagnetic product from that reaction, IIIc, with a Na-mirror to obtain IIId and the spectrum shown in Fig. 2c by another route. This is the first example of the deprotonation of an electroneutral complex of the type $RC_6H_5FeC_5H_5$. It is noteworthy that IIIb does not react with t-C_4H_9OK (the addition of t-C_4H_9OK to $C_6(CH_3)_6FeC_5H_5$ left the ESR spectrum unchanged). The reason for this is not quite clear. A hydrogen positioned α- to the arene ligand of the electroneutral π-compound should, of course, be less labile than the corresponding hydrogen atom of $RC_6H_5FeC_5H_5^+$. However, mechanistically, hydrogen abstractions from the electroneutral π-complex and from $[RC_6H_5FeC_5H_5]^+$ may differ significantly.

We also made an attempt to prepare $[C_6H_5CH_2FeC_5H_5]^{\dot{-}}Na^+$ (IVd). The corresponding cation (IVa) was deprotonated under the action of t-C_4H_9OK [3] and the deprotonation product (IVc) was reduced to IVd with a Na-mirror. The appearance of an ESR signal showed the reduction to occur. However, the product, IVd proved to be rather unstable, and decomposition to iron metal interfered with its spectral study. The results obtained show that, apart from the neutral d^7 complexes areneFeC_5H_5 [7], there is evidence for the existence of d^7 complexes containing arene ligands in the carbanionic state.

The temperature dependences of the ESR spectra of IIIb and IIId differ from each other. Temperature increase from 77 to 100 K results in broadening of lines and decrease of line intensities in the spectrum of IIIb. The line intensities in the spectrum of this compound depend strongly on the rate of freezing the solution. Slow freezing leading to vitrification of the solvent causes a drastic decrease in signal intensities. Fast freezing with crystallization of the solvent results in intensity increase. These findings may be explained in terms of different effects of the crystalline and vitreous solvent states on manifestations of the dynamic Jahn-Teller effect [4]. On the other hand, fading out of the spectrum of IIIb during slow vitrification of the solution may be caused by the formation of diamagnetic dimers with weak metal—metal bonds. In consideration of the latter possibility, it should be noted that removal of the solvent from an ampoule containing IIIb under vacuum failed to make the ESR spectrum of IIIb detectible at 77 K With IIId subjected to the same treatment, an ESR spectrum having the same parameters as observed in frozen solution was registered;



The temperature behaviour of the spectrum of IIId is typical for d^7 complexes [7] which retain spectral anisotropy up to solution m.p.'s and show no rate-of-freezing effects on the spectral intensities.

It should be noted that the deprotonated complex, $C_5H_5\overset{+}{Fe}C_6(CH_3)_5\ddot{C}H_2$ (IIIc), also gives a paramagnetic product under the action of oxidizing agents. Thus, the addition of iodine dissolved in isopropyl alcohol to dimethoxyethane solutions of diamagnetic Ic and IIIc leads to the appearance of ESR spectra with $g_{\parallel} = 2.10$, $g_{\perp} = 2.005$ and $g_{\parallel} = 2.080$, $g_{\perp} = 2.005$, respectively. It is likely that oxygen also oxidizes IIIc at a low rate, because solutions of IIIc kept in the air show a weak ESR signal ($g_{\parallel} = 2.110$, $g_{\perp} = 2.005$). The action of atmospheric oxygen also gives rise to a weak ESR signal in solutions of IIc ($g_{\parallel} = 2.090$, $g_{\perp} = 2.005$). Oxidation of the deprotonated d^6 complexes studied may seemingly be written as follows

$$C_6(CH_3)_5\ddot{C}H_2\overset{+}{Fe}C_5H_5 \xrightarrow[O_2 \text{ or } I_2]{-e^-} C_6(CH_3)_5\dot{C}H_2\overset{+}{Fe}C_5H_5$$

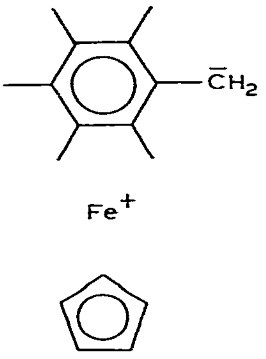
(IIIc) (IIIe)

Noticeable anisotropy of the *g* value implies that a structure having a d^7 metal configuration contributes to IIIe.

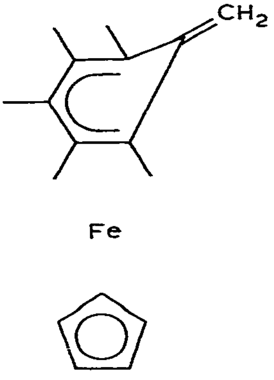
$$\underset{(d^6)}{C_6(CH_3)_5\dot{C}H_2\overset{+}{Fe}C_5H_5} \longleftrightarrow \underset{(d^7)}{C_6(CH_3)_5\overset{+}{C}H_2FeC_5H_5}$$

If this is the case, IIIe is the first example of an iron arene-Cp derivative with the arene ligand having carbocationic nature.

The electronic structure of the products of deprotonation of iron arene-Cp complexes has been discussed in a number of publications [1—3]. The limiting resonance structures describing the electronic structure of deprotonated complexes contain six-membered ligands as either carbanions with a symmetric distribution of the negative charge (A) or non-planar cyclohexadienyl rings with free exocylic double bond (B) [3].



(A)



(B)

We have studied the electronic absorption spectra of the deprotonated complexes Ic—IVc to compare the results obtained with the spectra of the corresponding carbanions and initial cations. Figure 3 shows the electronic spectra of $C_{13}H_9FeC_5H_5$ (Ic), $C_6H_5CHC_6H_5FeC_5H_5$ (IIc) and $C_6(CH_3)_5CH_2$-FeC_5H_5 (IIIc). The absorption band positions and molar extinctions for the deprotonated complexes and the corresponding $[areneFeC_5H_5]^+$ cations are listed in Table 1. Analysis of the absorption spectra of the cations shows that three weak bands (ϵ ca. 10^2) in the visible region arise from *d*—*d* transitions and that their positions depend somewhat on the nature of the arene ligand [9,10].

The ϵ values for the deprotonated complexes are in the range 10^3 to 10^4. We compared the spectra of Ic and IIc with the spectra of the corresponding carbanions to see whether the increase of ϵ on going to the deprotonated complexes was caused by the π—π origin of the bands or by an increase in the *d*—*d* transition probabilities.

The spectrum of the fluorene carbanion [11] is dominated by an intense ($\epsilon \approx 10^4$) band at 345 to 375 nm. A number of weaker bands are observed at 400 to 600 nm. Band positions and intensities depend on the alkali metal, solvent and temperature [11]. The spectrum of Ic retains the principal carbanion band system; a correspondence is also observed between the transition

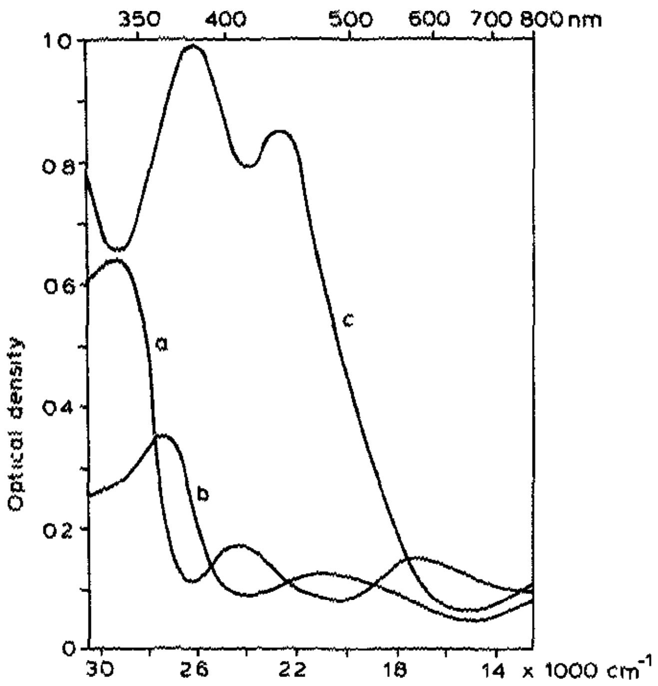


Fig. 3. Electronic absorption spectra of (a) $C_{13}H_9FeC_5H_5$ (Ic), (b) $C_6H_5CHC_6HFEC_5H_5$ (IIc) and (c) $C_6(CH_3)_5CH_2FeC_5H_5$ (IIIc).

intensities. The same is true of the spectra of the diphenylmethane carbanion [12] as compared with IIc.

Deprotonated complexes IIIc and IVc show a somewhat different behaviour;

TABLE 1

ELECTRONIC ABSORPTION SPECTRA OF THE CATIONS AND THE DEPROTONATED COMPLEXES ARENEFeC_5H_5

Complexes (solvent)	Absorption band positions (cm^{-1}) and molar extinctions		
	I	II	III
$C_{19}H_{10}FeC_5H_5^+$	21700	25200	30000
(THF)	(100)	(270)	—
$C_{13}H_9FeC_5H_5$	17000	24300	29200
(THF)	(1.4 × 10^3)	(1.7 × 10^3)	([illegible] 3 × 10^3)
$C_{13}H_9FeC_5H_5$	17000	24200	29200
(toluene)	(2 × 10^3)	(2.7 × 10^3)	(1.4 × 10^4)
$C_6H_5CH_2C_6H_5FeC_5H_5^+$	22000	26000	31000
(THF)	(100)	(120)	—
$C_6H_5CHC_6H_5FeC_5H_5$	21000	27500	—
(THF)	(8 × 10^3)	(2.3 × 10^4)	—
$C_6H_5CH_3FeC_5H_5^+$	21800	27600	31000
(THF)	(140)	(160)	—
$C_6H_5CH_2FeC_5H_5$	21000	25000	29800
(THF)	(300)	(500)	(1.1 × 10^3)
$C_6(CH_3)_6FeC_5H_5^+$	22000	25100	30000
(DME)	(150)	(200)	—
$C_6(CH_3)CH_2FeC_5H_5$	20000	25100	30000
(DME)	(3 × 10^3)	(5 × 10^3)	(6.2 × 10^3)
$(C_6H_6FeC_5H_5)_2$	20000	23700	28200
(DME)	(300)	(900)	(3 × 10^5)

although band intensities do increase on going to these complexes, their positions remain close to those in the spectra of the initial [areneFeC_5H_5]$^+$. The spectra are interesting to compare with that of the dimer, [$C_6H_6FeC_5H_5$]$_2$. In the latter compound, six-membered ligands have the cyclohexadienyl structrure [13]. Its spectrum [10], however, contains three d—d transitions, like those of [areneFeC_5H_5]$^+$. The positions of the corresponding bands are close to those in deprotonated IIIc and IVc.

The structural data on $C_{13}H_9FeC_5H_5$ (Ic) [1] and $C_6(CH_3)_5CH_2FeC_5H_5$ (IIIc) [3] and the spectral data reported here show that the ligand structures resemble the carbanionic structure A in Ic and IIc and the cyclohexadienyl structure B in IIIc and IVc. The structures A and B differ from each other in the degrees of negative charge shift from the arene ligand to the Fe—arene bond (structure A corresponds to a weaker and B to a stronger shift). The ESR data, however, show that the iron atom has the d^6 configuration, irrespective of the structure of the deprotonated ligand. Reduction leads to conversion to the d^7 state. The g value for [$C_6(CH_3)_5CH_2FeC_5H_5$]$^-$ Na^+ ($g_\parallel$ = 2.180, $g_\perp$ = 2.000) characterizing the d^7 state of the deprotonated complex is close to the g values found for the neutral d^7 complexes $C_6R_xH_{6-x}FeC_5H_5$ ($g_\parallel$ = 2.26—2.21, $g_\perp$ = 2.00) [7].

Arene ligands with higher degrees of conjugation (fluorene and diphenylmethane) cause larger splittings of the e^*_{1g} metal level in Id and IId, as well as the polyconjugated ligands in areneFeC_5H_5 ($g_\parallel$ = 2.07—2.10, $g_\perp$ = 2.00) [7].

Experimental

The ESR spectra were registered with a Varian-E12 spectrometer at 77 K.

The electronic absorption spectra were obtained on a Specord UV-VIS spectrophotometer.

The deprotonation of [areneFeC_5H_5]BF_4 (0.08 mmol; arene = $C_{13}H_{10}$, $C_6H_5CH_2C_6H_5$, $(CH_3)_6C_6$, $CH_3C_6H_5$) was carried out by treatment with t-BuOK (0.1 mmol) in DME at —70°C in a quartz ampoule under vacuum. After 10 min, the solvent and t-BuOH formed were distilled off from the brightly coloured deprotonation product. A 1/1 mixtnre of DME and ether or 1/2 mixture of DME and THF was vacuum transferred onto the dry residue. The reduction with sodium mirror was carried out at —80 to —100°C; a characteristic green colouration appeared during the process.

After recording the ESR spectrum of the reduced deprotonated complex, two drops of ethanol were added to the sample and the sample was evacuated. After stirring at —80°C, the spectrum was registered once more. The action of atmospheric oxygen (at 20°C) on the deprotonation products from [$C_6(CH_3)_6FeC_5H_5$]BF_4 and [$C_6H_5CH_2C_6H_5FeC_5H_5$]BF_4 resulted in the appearance of a weak signal ($g_\parallel$ = 2.08—2.11, $g_\perp$ = 2.005) whose intensity increased rapidly on addition of 1 or 2 drops of iodine in isopropyl alcohol. The signal with $g_\parallel$ = 2.100 and $g_\perp$ = 2.005 was recorded after the addition of 2 drops of 0.5% iodine solution to $C_{13}H_9FeC_5H_5$ under argon at —80°C. A signal was also observed with $C_6(CH_3)_5CH_2FeC_5H_5$ under similar conditons.

Reduction of the [areneFeC_5H_5]BF_4 cations with sodium mirror was run in the same solvent mixture at reduced temperatures (—90 to —100°C).

The electronic absorption spectra of the cations [areneFeC_5H_5]BF_4 were corded in THF or DME at concentrations of 10^{-4} mol/l (see Table 1). To tain the spectra of the deprotonated compounds, solutions of the cations the concentration indicated were placed in optical cells; argon was bubbled rough the solution for 5 to 10 min, excess t-BuOK was added, and the osed cell was shaken until the reaction ceased. The reaction was monitored absorption spectrum measurements.

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