Salts of Ferricinium Cation and its Homologues: NMR Investigation, I
On Mechanisms of Spin Delocalization in Salts of Ferricinium and 1,1'-Dimethylferricinium Cation

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1H and 13C NMR spectra of hexafluorophosphates of ferricinium (1) and 1,1'-dimethylferricinium cations (2) and the EPR spectrum of 2 were recorded. Pseudocontact and contact contributions of isotropic shift were calculated and constants of hyperfine interaction estimated according to Jesson. It is shown that the calculations of pseudocontact and contact shift via magnetic susceptibility components according to Kurland and McGarvey do not change the signs of HFS constants. According to the suggested mechanisms of spin delocalization the \( \pi \)-contribution is the dominating one.

Mechanisms of spin delocalization in paramagnetic complexes of metals are studied for the main part with the use of constants of hyperfine interaction between unpaired electrons and magnetically active nuclei. However, when calculating HFS constants \( (A_\text{c}) \) in NMR investigations of anisotropic molecules such as ferricinium cation and its homologues one must distinguish between the pseudocontact and the contact parts of isotropic shift, since pseudocontact shift \((\Delta H/H)_\text{ps} \) makes an essential contribution to isotropic shift of ferricinium salts. Incidentally, to calculate it in such systems is not an easy task.

In order to estimate pseudocontact shifts with the help of Jesson equations [1] which commonly are used, it is necessary to know the geometry of the molecule, components of g-factor \((g_x \text{ and } g_y) \) [2] and to have an idea of relations between Zeeman energy anisotropy, rotational correlation times and electronic relaxation times. Anderson and Rai have shown, however [3], that the approach based upon g-factor anisotropy is not rigorous enough for salts of ferricinium and 1,1'-dimethylferricinium cation, whose molecules contain nearby \( \Delta g_x \) and \( \Delta g_y \) levels, so that second order Zeeman effects must be considered. In this case the expressions to be used are those obtained by Kurland and McGarvey [4]. Their application requires knowledge of magnetic susceptibility components \( \chi_\| \) and \( \chi_\perp \). The physical reason of this procedure is the fact that such systems are strongly affected by intramolecular magnetic fields created by currents at the periphery of the nuclei. Mainly measurements of magnetic susceptibility make it possible to investigate these effects [5]. On the other hand, calculations carried out by Anderson and Rai [3] have shown that the correction introduced into the values estimated by the g-factor anisotropy method by the use of Kurland-McGarvey expressions does not exceed 1.5 ppm for ring protons and 4 ppm for methyl protons in the expression for the pseudocontact term.

In this paper we report 1H and 13C NMR spectra of hexafluorophosphates of ferricinium (1) and 1,1'-dimethylferricinium (2) cations and EPR spectra of 2. The 13C NMR spectra of these compounds were first reported by Köhler [6], who, however, did not discuss mechanisms of spin delocalization. On the other hand, only 1H NMR evidence was available to Anderson and Rai [3] in their discussion of spin delocalization mechanisms in these systems. The more calling was the challenge to simultaneously apply all the methods possible to investigate these salts. At the given stage we have undertaken an effort to calculate the pseudo-contact and the contact terms with the use of g-factor anisotropy approach, assuming that the corrections introduced into 1H NMR isotropic shift by considering second order Zeemans effect are small. We believe, however, that the corrections for 13C shift may be greater. Therefore, our discussion of spin delocalization...
mechanisms is based mainly on the signs of constants of hyperfine interaction with $^{13}$C nuclei rather than on their absolute values. To check our results we have estimated the pseudocontact contribution using evidence obtained by Anderson and Rai for $\gamma_0$ and $\gamma_1$ [3], and then used our own data to estimate $^{13}$C HFS constants according to Kurland and McGarvey [4]. The signs of the constants in the two calculations proved to be the same as those provided by g-factor anisotropy method.

Figure. Signs of $A_i$ constants for different nuclei of cyclopentadienyl ligands in compounds 1 and 2.

#### Experimental

**Preparation of the salts 1 and 2**

Concentrated H$_2$SO$_4$, 5 ml (0.092 mol), was added to 0.50 g (0.027 mol) of ferrocene. The solution was allowed to stand for an hour, then diluted with water to 45 ml, filtered through a sintered glass filter and treated with conc. NaPF$_6$ solution. The solids were washed with ice water (3 X 10 ml) and dried. The yield of 1 was 0.69 g (78% of the calculated value), m.p. 160 °C (decomp.).

C$_{10}$H$_{10}$FePF$_6$


2 was obtained in the same manner with 3 ml (0.054 mol) of conc. H$_2$SO$_4$ and 0.53 g (0.025 mol) of l,l'-dimethylferrocene. The yield of 2 was 0.74 g (83% of the calculated value), m.p. 183–184 °C (decomp.).

C$_{12}$H$_{14}$FePF$_6$

Calcd Fe 15.60 C 40.14 H 3.90, Found Fe 15.35 C 40.03 H 3.92.

**Spectra**

The $^1$H NMR spectra of 1 and 2 in acetone-d$_6$ were obtained on a Bruker WP-60 instrument operated at 15.1 MHz, 30 °C. The $^{13}$C NMR spectra were recorded using Fourier transform $^{13}$C NMR without $^1$H decoupling on a Bruker WH-180 spectrometer using acetone as solvent and internal reference. The operating conditions were 45.28 MHz, 35 °C. EPR spectrum of 2 (as polycrystalline sample) was obtained on an EPR-3 instrument operated at the frequency of magnetic field modulation 20 kHz, 15 K.

**Results**

The pseudo-contact component of isotropic shift in ferricinium salts was calculated according to an equation reported by Jesson [1]:

$$ (\Delta H/H)_{ps} = -\frac{\beta S (S+1)}{3 kT R^3} \cdot \frac{(g_+^2 - g_\perp^2)}{3} $$

The g-factor components for 1 were taken from Prins's paper [7] ($g_\parallel = 4.30, g_\perp = 1.26$), those for 2 were calculated from the EPR spectrum measured at 20 K. They equal $g_\parallel = 3.90$ and $g_\perp = 1.76$. Geometrical factors were calculated from X-ray structural analysis data [8, 9]. The geometrical factors and the values of pseudo-contact shift for various nuclei are given in the table. $A_i$ constants were estimated by the equation for Fermi-contact contribution reported by McConnell and Robertson [11]:

$$ (\Delta H/H)_F = -\frac{\beta S (S+1)}{(\gamma N/2 \pi)^2} 3 kT \cdot A_i $$

<table>
<thead>
<tr>
<th>Nucleus</th>
<th>Geometrical factor, G $\times 10^{21}$ [cm$^{-3}$]</th>
<th>Pseudocontact shift, (\Delta H/H)$_{ps}$, ppm</th>
<th>Observed shift, (\Delta H/H)*, ppm</th>
<th>Fermi-contact shift, (\Delta H/H)$_F$, ppm</th>
<th>HFS constant, $A_i \cdot 10^4$, Tesla</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{13}$C(Cp)</td>
<td>113,00</td>
<td>-342,0</td>
<td>-231,0</td>
<td>-231,0</td>
<td>314,0</td>
</tr>
<tr>
<td>$^1$H(Cp)</td>
<td>2,99</td>
<td>9,0</td>
<td>6,0</td>
<td>26,8**</td>
<td>30,7</td>
</tr>
<tr>
<td>$^{13}$C(key)</td>
<td>113,00</td>
<td>-231,0</td>
<td>-231,0</td>
<td>314,0</td>
<td>-266,0</td>
</tr>
<tr>
<td>$^{13}$C(Me)</td>
<td>-4,40</td>
<td>9,0</td>
<td>9,0</td>
<td>14,3</td>
<td>14,3</td>
</tr>
<tr>
<td>$^1$H(Me)</td>
<td>-9,35</td>
<td>19,1</td>
<td>9,6</td>
<td>7,5</td>
<td>0,095</td>
</tr>
</tbody>
</table>

* The shifts are given relatively $^1$H and $^{13}$C nuclei of TMS, the shifts to lower fields are negative. For chemical shifts of nuclei of diamagnetic counterparts of 1 and 2 see e.g. I.e. [16]; ** eq. [10].
where \( g \), as usual, is the rotation average of the g-tensor, \( \gamma_N \) is the gyromagnetic ratio for a proton or for a \(^{13}C\) nucleus. The values of the Fermi-contact member and of \( A_1 \) constants are given in the Table.

It is noticeable that the \( A_1 \) constants of non-substituted ring carbons in 1 and 2 are negative. The HFS constants for methyl carbons in 2 are also negative. Only the key carbon in 1,1'-dimethylferricinium hexafluorophosphate (2) has a positive constant. As for the signs of \( A_1 \) constants for hydrogen atoms, they are positive both for the ring and for the methyl protons (Figure).

Discussion

The negative \( A_1 \) values of ring carbons in 1 and 2 indicate at once that delocalization of spin density occurs largely by spin polarization mechanism. Assuming the ground state of ferricinium salts is \(^2E_g\) with configuration \((a_{1g})^2(e_{2g})^2\), the unpaired electron would occupy a MO formed mainly by \( d_{xy}, d_{z^2} \) nonbonding atomic orbitals of iron. By their transformation properties these orbitals are related to the wave functions giving significant contribution to metal ligand bonding in approximately the same manner as \( p \)-orbitals of an aromatic radical are related to C–H \( \sigma \)-fragments. In this case negative spin density on the ligand may arise from configuration interaction involving occupied \( e_{1g} \)-symmetry MO’s of essentially ligand nature. This mechanism, known as Levy–Orgel’s model [12], is considered by Prins [13] as a second-order process involving the \( \pi \)-skeleton of the ligand (\( \pi \) 2 mechanism). Further delocalization of spin density from the carbon atoms to ring protons obeys the common \( \sigma,\pi \)-polarization mechanism [14]. At the same time it is noteworthy that whereas the \((\Delta H/H)^{1/2} : (\Delta H/H)^{1/3}\) ratio for ferricinium cation (about –6) is close to the regular one for \( \sigma,\pi \)-mechanism, its value for 1,1’-dimethylferricinium cation (about –2) indicates that the distribution of the spin density in cyclopentadienyl rings is affected by a competing mechanism [15]. As shown by the sign of the key carbon \( A_1 \) constant, the mechanism is that of direct delocalization [15, 16]. One may think that this case, again, involves \( \pi \)-delocalization. This is indicated by alternation of signs of \( A_1 \) constants in the \( C(\text{key})-C(\text{Me})-H(\text{Me}) \) fragment, a phenomenon typical of spin transfer according to hyper-conjugation mechanism. Hyperconjugational alternation of the \( A_1 \) signs on the nuclei of this fragment requires that the positive spin density be located namely on the \( \pi \)-orbital of the key carbon.

Now we are facing a natural question: due to what is the change of spin density sign on the key carbon, or why the mechanism of direct spin delocalization is so efficient on this carbon atom. The most obvious interpretation would apparently be based upon the use of nodal characteristics of MO of cyclopentadienyl rings and an assumption that the \((a_{1g})^1(e_{2g})^4\) electron configuration (the \(^2A_{1g}\) state) is thermally available. Indeed, it is well-known that the \( e \)-symmetry orbitals of cyclopentadienyl rings have a node on the key carbon [17]. Moreover, the low symmetry distortion, which plays a larger role in case of 1,1’-dimethylferricinium cation, may eliminate degeneration of \( e \)-orbitals. This is what creates conditions for experimental manifestation of nodal properties, if the configuration interaction involves the \( e \)-orbital. This will eventually lead to sharp changes in the effect of the spin polarization mechanism on the relevant atom. However, the effect is not confined to such reduction of the role played by spin-polarization transfer of unpaired electron density, since the rather considerable low-field contact shift of the key carbon indicates that the direct spin delocalization mechanism is manifested. As shown by Gächter, Königstein and Aleksanjan [18], the ferricinium salt displays an electron Raman transition \(^2E_g \rightarrow ^2A_{1g}\) of energy about 200 cm\(^{-1}\). Evidence on magnetic properties also indicates that an energy gap about 200 cm\(^{-1}\) exists between the ground state \(^2E_g\) and the first excited state \(^2A_{1g}\). Thus at room temperature the thermal population of the \(^2A_{1g}\) level must be quite considerable. As long as the \( a_{1g} \) MO is formed largely by the iron \( d_z^2 \)-orbital, populating of the \(^2A_{1g}\) state may provide for direct delocalization of the unpaired spin. One gets an impression that direct transfer of spin density from the \( a_{1g} \) orbital (\( \pi \) 1 mechanism) on account of the energy gap of kT order of magnitude does play an important role in 1,1’-dimethylferricinium cation [19]. Another fact which is possibly significant in this case is that the electron-donating methyl groups increase the donor ability of the cyclopentadienyl ligand by expanding its electron cloud and improving the conditions of overlapping in the area of the metal-ligand bond. It is essential to emphasize once again that direct
delocalization of spin density necessarily involves the \( \pi \)-skeleton of the cyclopentadienyl ligand, though in principle the \( \sigma \)-skeleton may also be expected to participate. The positive spin density of the key carbon \( p_z \) orbital delocalizes to the methyl group by hyperconjugation mechanism, so that the \( A_1 \) constants are negative on C(Me) and positive on H(Me).

Of course, our interpretation is not the only one possible. In particular, one can not disregard the probable manifestation of Jahn–Teller’s dynamic effect, which, in its turn, can provide for axial symmetry distortions in the molecule, as it occurs in the C5H5 radical [20]; another not unlikely effect is intraligand spin polarization.

Conclusion
The most important points resulting from our considerations are as follows:
1. The predominant mechanism of spin delocalization in the ferricinium salt is spin polarization.
2. In the 1,1′-dimethylferricinium salt one must distinguish between the C2(Cp)–C5(Cp) fragment of cyclopentadienyl ligands, where like in the foregoing case the sign of HFS constants is determined by spin polarization mechanism, and the C(key)–CH₃ fragment, where direct spin delocalization from the metal atom to C(key) is predominant and then occurs hyperconjugation mechanism to the CH₃ group.
3. A generalization of (1) and (2) would be that two leading mechanisms for these salts are \( \pi \) 1 and \( \pi \) 2 [14].
4. The results obtained in this paper indicate that the \( e_{2g} \) orbitals are nonbonding and agree with the notion about \( 2E_{2g} \) as the ground state of ferricinium and 1,1′-dimethylferricinium. It is also clear that the \( 2A_{1g} \) state is thermally available, since it is situated only 200 cm\(^{-1}\) above the \( 2E_{2g} \) state.

In the future we intend to examine the picture of spin delocalization in salts of other cations of polymethylferricinium series.

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