Paramagnetic Metallocenes:  Interannular Electron Transfer

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Previously we described the oxidation of ferrocenyl ketones which contain an α methylene group to the paramagnetic semidione (2).  The esr spectra of these semidiones indicated a very small amount of spin delocalization into the metallocene ring and it was apparent that little, if any, electron spin was on the metal atom.  We now wish to report facile interannular electron transfer in the ketyl derived from 1,1' dibenzoylferrocene; our studies implicate the involvement of the metal atom in this intramolecular electron transfer I.  In view of the importance of metal ions in electron transport processes in biological systems and organometallic semiconductors we are prompted to report our initial results on the metallocene model system.



I
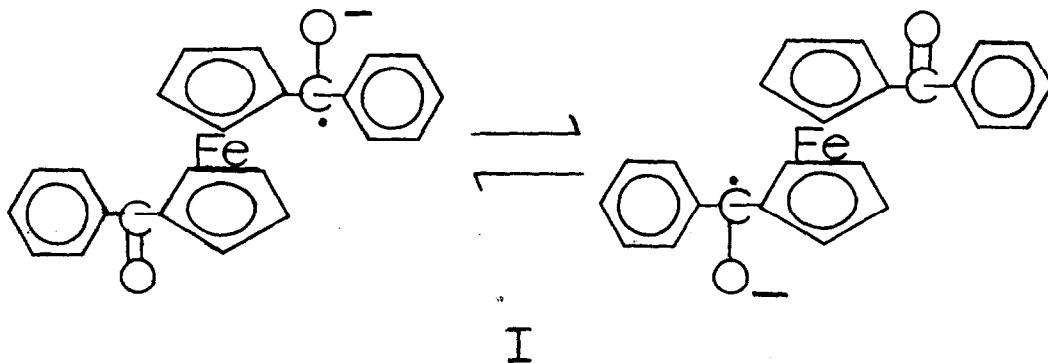
The ketyl derived from monobenzoylferrocene exhibits a high resolution esr spectrum.  The assignment of hyperfine splitting constants to individual hydrogen atoms were proven by ketyl derivatives listed in Table I.

| Ketyl | ferrocene ring | | benzene ring | | | |
|---|---|---|---|---|---|---|
| | o | m | o | m | p | g |
| benzoylferrocene | 0.80(2H) | 0.0 | 3.1(2H) | .8 (2H) | 4.5(1H) | 2.0062 |
| benzoylruthenocene | 0.80(2H) | 0.0 | 3.1(2H) | .8 (2H) | 4.5(1H) | 2.0035 |
| benzoylferrocene-$d_9$ | 2D (not observed) | 0.0 | 3.1(2H) | .8 (2H) | 4.5(1H) | 2.0062 |
| benzoyl 2,5-dideuteroferrocene | 2D (not observed) | 0.0 | 3.1(2H) | .8 (2H) | 4.5(1H) | 2.0062 |
| <u>para</u> trifluoromethylbenzoyl-ferrocene | 0.7 (2H) | 0.0 | 3.3(2H) | .7 (2H) | 14.7(3F) | 2.0062 |
| <u>para</u> fluorobenzoylferrocene | 0.9 (2H) | 0.0 | 3.3(2H) | .7 (2H) | 8.7(1F) | 2.0062 |

Table I

The results are contrary to the suggestion of Russian workers (3) that hyperfine splitting of 1.0 gauss (4H) originate from the four hydrogens of the metallocene ring. The data in Table I establishes that the <u>ortho</u> hydrogens of the ferrocene ring and the <u>meta</u> hydrogen of the benzene ring are fortuitously equivalent. Spin density distribution calculated by Huckel-McLachlan method using reasonable parameters (4) for the coulombic integral of oxygen and ferrocenyl ring carbon agree with the experimental spin distribution. The difference in g value between the benzoyl-ferrocene and benzoylruthenocene ketyls - 2.0062 and 2.0035 respectively - is viewed as proof that the metallocene moiety is intact (4). An interesting observation is that $g_{Fe} > g_{Ru}$, an order opposite to that of the spin-orbit, LS, coupling constants for the metals involved ($\zeta$ $Ru^{+2}$ = 1140 $cm^{-1}$, $\zeta$ $Fe^{+2}$ = 410 $cm^{-1}$). These results imply very little free electron density at the metal atom itself. These experimental facts are most explicable in terms of an electron occupying a ligand molecular orbital which is not involved in metal-ligand bonding. This is in sharp contrast to the ferrocenylphenylnitroxide which has a g value of 2.015. This high g value is a clear indication of interaction between the metal atom and the unpaired electron (5). We wish to reserve our comments on the nature of this metal-free electron interaction until our studies in this area are completed. We wish, however, to point out that involvement of the metal atom with unpaired spin causes a substantial increase in g value.

The ketyl derived from 1,1' dibenzoylferrocene exhibits a single line spectrum (hyperfine splitting cannot be resolved) with a g value of 2.0086. The ketyl derived fron 1,1' bis <u>para</u> - trifluoromethylbenzoylferrocene (6,7) shows an esr spectrum with hyperfine splitting due to 6 equivalent fluorine atoms $a^F$ = 1.0 gauss g = 2.0086 (figure 1). The equivalency of the six fluorine atoms as well as the increase in g value requires the rapid interannular conduction of an electron <u>via</u> the metal atom. We are currently studying the stereospecificity of this electron transfer process. This is an excellent model system for studying the role of metal ions in
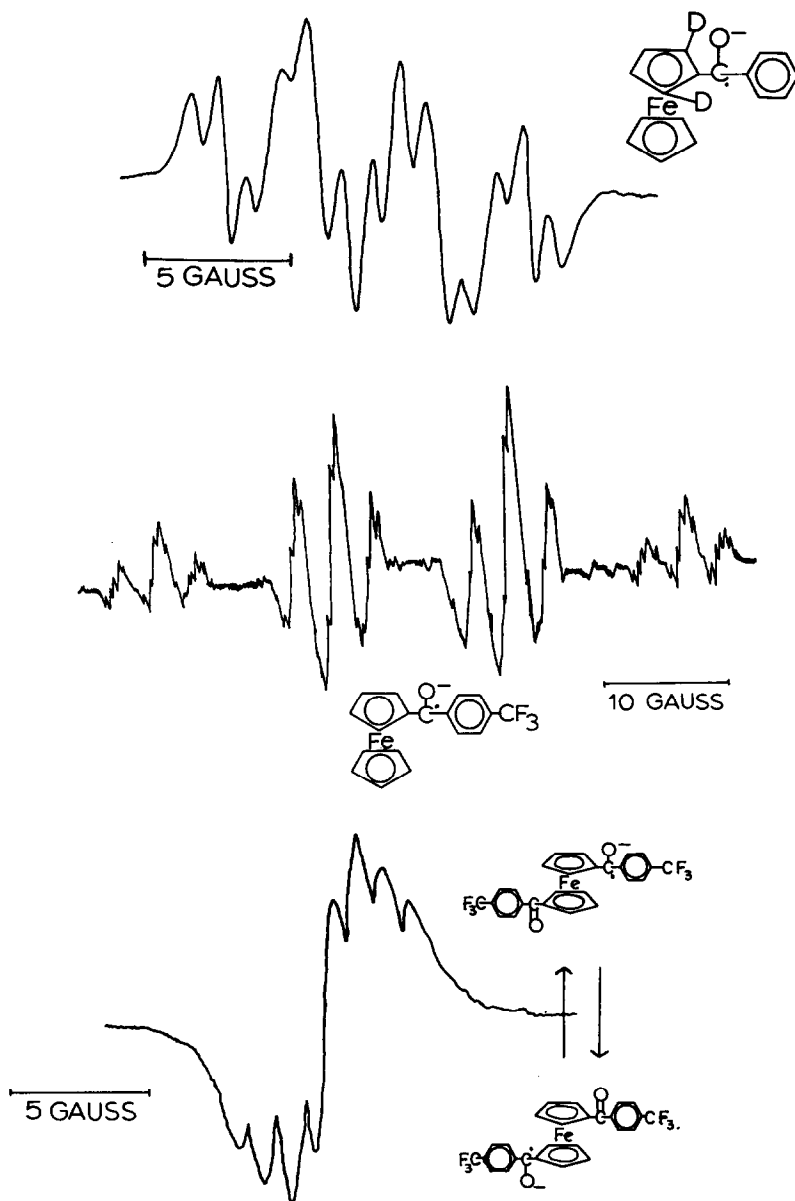
Figure I

electron transfer processes and electron exchange interactions in diradicals.

1) This work was supported by the Petroleum Research Fund, administered by the American Chemical Society (Grant 1375-G1).

2) John J. McDonnell, Tetrahedron Letters, 2039 (1969).

3) V. M. Kazakava and Ya. K. Syrkin, Zh. Strukt. Khim. $\underline{3}$, 536 (1962).

4) $\alpha o = \alpha c + 1.8 \beta$ and $\alpha c_{ferrocene} = \alpha c - 0.3 \beta$, $\alpha c_{Ruthenocene} = \alpha c - 0.2 \beta$
   Alteration of the carbon coulombic integral because of stronger metal ligand bonding in Ruthernocene places the odd electron in a lower energy orbital and accomodates the difference in g value. $\Delta G = a + b\lambda$ where b is a negative number and $\lambda$ is the $\beta$ coefficient of the HOMO: see A. J. Stone, Mol. Phys., $\underline{6}$, 509 (1963).

5) A. R. Forrester, S. P. Hepburn, R. S. Dunlop, and H. H. Mills, Chem. Commun., 698 (1969). The g value of t-Butylferrocenylnitroxide is reported to be 2.0146.

6) These ketyls were produced both by electrolysis and Na/K alloy reduction.

7) C. Elschenbroich and Micheal Cais, J. Organometal. Chem., $\underline{18}$, 135 (1969).