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EFFECT OF COORDINATION WITH THE METAL ON THE REACTIVITY OF π-BONDED ORGANIC LIGANDS

V*. THE ELECTRONIC EFFECT OF THE CYCLOPENTADIENYL ANION. THE σ- AND π-ORBITAL CHARGE DISTRIBUTION

A. A. KORIDZE, S. P. GUBIN, A. A. LUBOVICH, B. A. KVASOV AND N. A. OGORODNIKOVA
Institute of Organo-Element Compounds, Academy of Sciences, Moscow (U.S.S.R.)

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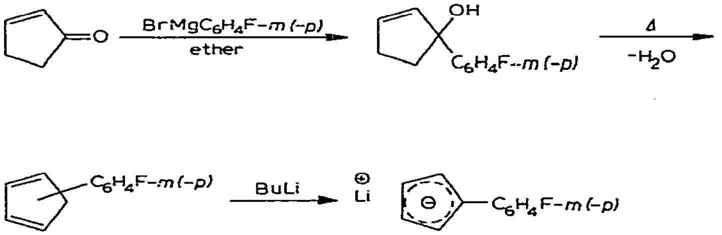
SUMMARY

The electronic effect of the cyclopentadienyl anion has been determined from the ^{19}F NMR spectra for the lithium salts of the (*m*- and *p*-fluorophenyl)cyclopentadienyl anions. The values of σ_I and σ_R^0 obtained lead to the assumption that in the cyclopentadienyl anion a considerable portion of the negative charge is localized in the σ-orbitals.

In previous papers in this series we have reported studies of the effect of metal coordination on the reactivity of organic ligands which are stable under ordinary conditions and which may be comparatively easily studied by different methods. In order to employ the same approach to experimental information now available regarding the reactivity of metallocenes and other π-cyclopentadienyl compounds it has been found necessary to estimate quantitatively the reactivity of a free ligand *viz.*, the cyclopentadienyl anion.

Ordinary methods for the quantitative estimation of ligand reactivity obviously cannot be applied to such unstable materials, and thus in the present work the ^{19}F NMR spectra have been measured for the lithium salts of the (*m*- and *p*-fluorophenyl)cyclopentadienyl anions, the latter having been prepared by the following scheme:



(*m*- and *p*-Fluorophenyl)cyclopentadienyls were obtained through the use of a

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* For part IV see ref. 1.

procedure similar to that employed for the synthesis of 1-phenyl-1,3-cyclopentadiene[2,3] *i.e.*, the reaction of 1-cyclopentene-3-one with the appropriate (fluorophenyl)magnesium bromide in ether followed by the subsequent thermal dehydration of the resulting 1-(fluorophenyl)-2-cyclopentene-1-ols. Reaction of BuLi with (*m*- and *p*-fluorophenyl)cyclopentadiene in n-hexane gave the lithium salts of the respective anions which could be isolated in the form of white powders stable under an inert atmosphere. The structures of the anions so prepared was confirmed from their proton magnetic resonance spectra and from their conversion to the respective metallocene derivatives. The ^1H and ^{19}F NMR spectra of 0.5 *M* acetonitrile solutions of these compounds were measured. In the PMR spectrum, in addition to a multiplet from the four phenyl protons, two distinct triplets from the aromatic ring α- and β-protons centered at 5.97, 5.64 (for *meta* isomer) and 5.80, 5.52 ppm (for *para* isomer) were also obtained (Fig. 1). Treatment of *m*- and (*p*-fluorophenyl)cyclopentadienyl anions with Fe, Ru and Os chlorides led to the formation of the respective metallocenes. Thus, the reaction[4] of $FeCl_2 \cdot 4H_2O$ with a mixture of cyclopentadienyl and (fluorophenyl)cyclopentadienyl anions, followed by the normal work-up procedure and alumina chromatography, gave ferrocene and the respective fluoro-substituted mono- and 1,1'-diphenylferrocenes*: (*m*-fluorophenyl)ferrocene, m.p. 62–63°, (*p*-fluorophenyl)ferrocene, m.p. 106–107°, 1,1'-bis(*m*-fluorophenyl)ferrocene, m.p. 147–148°, 1,1'-bis(*p*-fluorophenyl)ferrocene, m.p. 172–173°**.

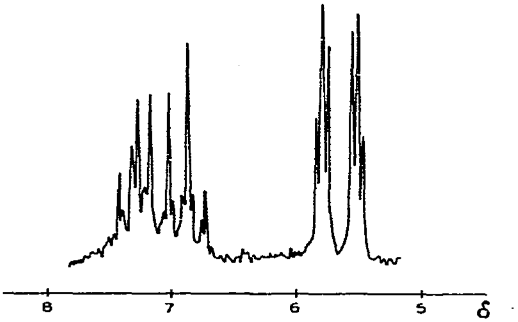
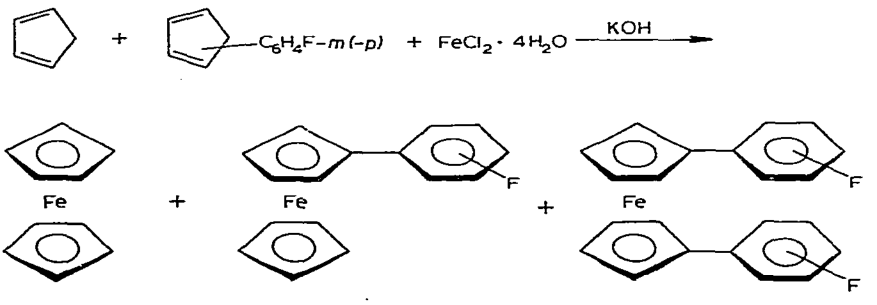


Fig. 1. ^1H NMR spectra of (*p*-fluorophenyl)cyclopentadienyl anion.



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* Satisfactory analytical and spectroscopic data were obtained for all compounds.

** Some of these compounds have previously been obtained by the arylation of ferrocene with the respective diazonium salts[5].

It should be noted that the polarographic behaviour of [(*p*-fluorophenyl)-cyclopentadienyl]lithium on DME (0.1 *M* $BuNBF_4$, DMF) is similar to that of unsubstituted cyclopentadienyllithium, and exhibits two waves, a reversible anodic wave ($E_{\frac{1}{2}}$ 0.43 V) and an irreversible wave corresponding to the reduction of the lithium ions ($E_{\frac{1}{2}}$ −2.43 V). The characteristics of the reduction wave are identical to those of the cathodic wave for unsubstituted $C_5H_5^-Li^+$ and to the reduction wave of the Li^+ ion at the same concentration. The shift of the anodic wave for the fluorophenyl derivative with respect to that for the substituted compound, ($\Delta E_{\frac{1}{2}}$ −0.25 V) indicates a reduced oxidation tendency for the fluorophenyl derivative and is quite reasonable in view of the strong electron attractive effect of the fluorophenyl group.

The ^{19}F chemical shifts of the fluorophenyl substituted cyclopentadienes were obtained in CH_3CN using C_6H_5F as an internal standard. A slight, but quite definite dependence of the chemical shift upon concentration was established, the signal shifting downfield upon dilution. The values of the chemical shifts were obtained by extrapolating to infinite dilution and were used for estimating σ_I and σ_R^0 constants. From the polarographic measurements and ^{19}F NMR analyses evidence was obtained suggesting that solvent-induced ion-pair formation occurred in dilute solutions of the compounds under investigation.

Chemical shifts of +2.2 and 10.65 ppm obtained respectively for the (*m*- and *p*-fluorophenyl)cyclopentadienyl anions using the above extrapolation method yielded values of σ_I −0.22 and σ_R^0 −0.29 when used in conjunction with the equation of Taft *et al.*[6,7]. These values indicate, as might be expected, that the cyclopentadienyl anion as a substituent introduces a strong electron-releasing effect. Comparable substituents which exhibit simultaneously such strong inductive and resonance electron releasing effects could not be found in published tables of σ constants, the inductive component of the effect being much larger than that for the trimethylsilyl group (σ_I −0.12) which is one of the strongest inductive electron-releasing neutral groups.

In general, to a first approximation, the results obtained are in agreement with the usual representation of the structure of the cyclopentadienyl anion as that of an aromatic system. However, it is possible to note certain interesting differences when the electronic effects for two isoelectronic aromatic systems *e.g.*, phenyl and cyclopentadienyl (*cf.* the Table) are compared. One surprising point is that the ability of the above substituents to undergo nonpolar conjugation, as measured by their σ_R^0 values, is only slightly different from one substituent to another. Similar changes in σ_R^0 values are observed when NH_2 groups (−0.76) are substituted by $N(CH_3)_2$ groups (−0.93) in a particular compound. It should be noted also that the value σ_R^0 for $C_5H_4^-$ is considerably less than the values for substituents having lone electron pairs (NH_2, OCH_3) and it is even less than the σ_R^0 value for F. However, from the basis of quantum chemical calculations for aromatic systems using the π electron approximation it might be expected that the cyclopentadienyl anion in its behaviour as a substituent would exhibit a greater ability to polarise the π-electron charge and thus indulge in nonpolar conjugation.

It might be expected that resonance would not be hampered by steric hindrance in the (*p*-fluorophenyl)cyclopentadienyl anion system, *i.e.* the molecule should have a planar, or almost planar, conformation. X-ray analysis of 4-biphenylferrocene[8], indicates that two independent structures exist in the crystalline state of this compound, with one structure having a dihedral angle between the planes of cyclopentadienyl and its adjacent benzene ring equal to 2.1°. This result provides evidence that an interaction of the *ortho*-protons occurs between neighbouring rings although this interaction is quite small. In addition, calculations using an extended Hückel method carried out by Hoffmann *et al.*[9] show that the plot of the potential energy of the phenylcyclopentadienyl anion *vs.* the dihedral angle between the aromatic rings has a slope which exhibits a minimum at a twist angle equal to $\theta \approx 20°$ and a very weak maximum at $\theta = 0°$.

Thus there are sufficient grounds to assume that in solution the twist angle between the two aromatic rings in the (fluorophenyl)cyclopentadienyl anion is smaller than that between the phenyl rings in biphenyl and hence the comparatively small resonance effect of this substituent cannot be associated with ring noncoplanarity.

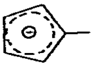
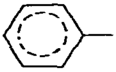
Recently Brownlee and Taft[10] have shown that there is a linear relationship between an empirical scale of σ_R^0 parameters, which characterize the ability of a substituent to delocalize the π charge, and a theoretical scale of such effects based on the use of the CNDO/2 method (complete neglect of differential overlap) for calculating the excess π-electron charge $\Sigma \Delta q(\pi)$.

On the basis of such a relationship it is possible to suggest that the replacement of a C_6H_5-substituent by a $C_5H_4^-$-group should lead to only a small change in the total excess π-electron charge in the phenyl ring ($\Delta\Sigma\Delta q(\pi) \approx 0.03$ e).

Thus the overall strong electron releasing effect of the cyclopentadienyl anion as a substituent is probably mainly due to the inductive effect rather than to its resonance effect which is comparatively small.

TABLE 1

COMPARATIVE TAFT EQUATION PARAMETERS FOR PHENYL AND CYCLOPENTADIENYL ANION SUBSTITUENTS

Substituent	σ_I	σ_R^0	$\Delta\sigma_I$	$\Delta\sigma_R^0$
	−0.22	−0.29	−0.30	−0.20
	−0.08	−0.09		

In Table 1 the electronic effects produced by the use of two isoelectronic aromatic systems *i.e.*, phenyl and $C_5H_4^-$, as substituents are compared. It will be seen that replacing a phenyl substituent by a cyclopentadienyl anion substituent leads to a considerable change in the constant relating to the inductive effect (σ_I), the change being 35 % of the entire range of values of σ_I constants.

The inductive effect is usually associated with the change of charge on the σ orbitals, and if this viewpoint is adopted it will be seen that the net effect of the introduction of the $C_5H_4^-$ substituent is an increase in the effective negative charge at the aromatic ring σ orbitals with respect to the phenyl substituent.

Thus the data obtained indicates that although the $C_5H_4^-$ substituent induces only a small change in the total effective π-electron charge it has a considerable influence on the effective σ charge in the adjacent aromatic ring.

At the same time it must be assumed that the negative charge distribution in the $C_5H_4^-$ substituent itself produces a similar electronic effect, a considerable portion of the negative charge of this substituent being localized in its σ orbitals.

Although the only quantum chemical calculation of cyclopentadienyl anion known at the present time[11] which assumes the inclusion of electrons of a σ core provides no information on the σ- and π-orbital charge distribution in the ligand, it shows that the bonding σ orbitals are arranged in such a manner that species are located among the sequence of π orbitals, *i.e.* their energies are quite close to those of the bonding π-orbitals.

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