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ELECTRONIC EFFECTS IN METALLOCENES

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SUMMARY

A comparative study of the PMR spectra of isoelectronic ferrocene and cobalticinium salt homologues has been undertaken. With cobalticinium salts the introduction of a positive charge leads to a decrease in the ring proton shielding, while the introduction of alkyl groups has a similar effect on the electronic structure of both the cobalticinium cation and ferrocene. It was found that the introduction of primary and secondary alkyl groups caused proton signal shifts not only in those rings which were directly substituted but also in unsubstituted metallocene rings. However, within the experimental accuracy of the method it was found that the tertiary butyl group has no influence on the proton chemical shifts in the free cyclopentadienyl ring. These results, as well as other chemical data, are explained by assuming that the heteroannular action of aliphatic substituents upon a metallocene system is generally controlled by resonance effects introduced by these groups.

INTRODUCTION

It has been shown earlier that the heteroannular effect in the ferrocene molecule can be explained in general in terms of an inductive component of the substituent. Such behaviour has been observed in a number of reaction series through the use of two main types of measurement: determination of the equilibrium constants of redox exchange $Fe^{II} \rightleftarrows Fe^{III}$ and studies of acid–base reactions[2]. Similar conclusions have been obtained from the study of substituents with clearly pronounced attractive properties[3] and in which the contribution of an inductive component to the total electronic effect of the substituents is greater than that due to conjugation. The values of σ_R^0 constants of the electron-releasing substituents are always greater than those for electron-withdrawing substituents, while the reverse is usually true for the σ_I parameters[4,5]. With substituents which mainly exhibit a conjugation effect, such as the methoxy group or the halides, or with entities capable of hyperconjugation (for example alkyl groups) it is often difficult to establish the exact nature of the heteroannular effect unequivocally. Thus an increase in the electron deficiency at the reaction centre increases the conjugation effect of the methoxy group to such an extent that the perturbation of the electronic system of ferrocene may be attributed solely to this effect, a result which is reflected in the enhanced value of the σ_R^0 constant for this group. If the reaction centre is provided by a carboxylate group then the value of σ_R^0 is decreased to -0.30 while the introduction of a reaction centre of even greater electron unsaturation at the iron atom reduces this value even further to -0.34. If the dependence of redox potentials[2] on the σ_I values is analysed for heteroannularly substituted ferrocenes it is found that compounds containing methoxy groups and halides as substituents do not fit any such correlation, and, in addition that the effect of alkyl groups on the ferrocene system is masked because of the similarity between their various σ_I constants (Me_3, -0.05; Et, -0.05; i-Pr, -0.03). For these reasons it seemed interesting to estimate the value and character of the electronic effects of alkyl substituents upon each cyclopentadienyl ligand of ferrocene. To this end we have prepared homo- and heteroannular homologues of ferrocene and cobalticinium salts[6] and have studied their PMR spectra.

RESULTS AND DISCUSSION

A comparison of the PMR spectra of isoelectronic homologues of ferrocene and cobalticinium salts revealed that in homologues of ferrocene with primary (Me, Et), secondary (i-Pr) and tertiary alkyl groups (t-Bu) the tertiary butyl group exhibits approximately the same high-field shift in its adjacent cyclopentadienyl ring (0.10 ppm from the ferrocene protons) as those observed with other alkyl groups. The tertiary butyl group does not however affect the proton chemical shift of any unsubstituted rings in the molecule[7,8], and this distinguishes this group from those of normal or iso-structure, at least in the alkylferrocene series. Secondary alkyl groups cause signal shifts not only in adjacent rings but also in unsubstituted rings. The value of the proton chemical shift in unsubstituted rings is only about half the magnitude of those in substituted rings and for the proton signals in ferrocene cyclopentadienyl rings is equal to 0.05 ppm. This behaviour is even more pronounced in the PMR spectra of 1,3-isomers of ferrocene with ethyl and tertiary butyl substituents. If the chemical shift of the unsubstituted ring protons in 1,3-diethylferrocene is taken as 0.12 ppm (with reference to the ferrocene proton signal) then the corresponding chemical shift for the 1,3-di-tert-butyl derivative is equal to zero within experimental accuracy (*cf.* Table 1).

TABLE 1

PROTON CHEMICAL SHIFTS OF FERROCENE HOMOLOGUES (ppm)

Compound	*δ of protons of unsubs. ring*	*δ of protons of subst. ring*				*Solvent*
		2	3	4	5	
$C_5H_5FeC_5H_5$	4.04					THF
$C_5H_5FeC_5H_5$	4.04					C_6H_{12}
$CH_3C_5H_4FeC_5H_5$	3.97	3.94	3.94	3.94	3.94	C_6H_{12}
$C_2H_5C_5H_4FeC_5H_5$	4.00	3.92	3.95	3.95	3.92	C_6H_{12}
$i\text{-}C_3H_7C_5H_4FeC_5H_5$	3.99	3.94	3.94	3.94	3.94	C_6H_{12}
$t\text{-}C_4H_9C_5H_4FeC_5H_5$	4.04	3.92	3.98	3.98	3.92	C_6H_{12}
$1,3\text{-}(t\text{-}C_4H_9)_2C_5H_3FeC_5H_5$	4.04	3.80		3.87	3.87	C_6H_{12}

When the acetyl group of 1-alkyl-1'-acetylferrocene is combined with methyl, ethyl or isopropyl groups a transmission of the donor effect of the alkyl substituent apparently occurs through the metal and influences the proton chemical shift of an acetylated ring. With the tert-butyl substituent no additional effect was observed on the proton chemical shift of the acetylated ring. It is impossible to explain the difference in the PMR spectra of ferrocene homologues containing primary and tertiary alkyl groups on purely steric grounds: thus, Stewart models of 1,3-di-tert-butylferrocene show no hindrance to free rotation of the rings about the iron atom (*cf.* Fig. 1). It is possible that the introduction of donor alkyl groups leads to hyperconjugation, certainly the available data on the chemical behaviour of ferrocene homologues agree with such a conclusion. In collaboration with Setkina, Kislyakova and Kursanov[10], the authors have found that at early stages in the isotopic hydrogen exchange between ethyl- and tert-butylferrocenes the percentage of hydrogen exchange in the unsubstituted cyclopentadienyl ligand of the former compound (as estimated from the integral intensity of the proton signals) is twice that of the latter compound. In addition, a study of the reaction products of the competitive acylation[11] of ferrocene derivatives (Me, Et, i-Pr, t-Bu) and ferrocene, using acetic anhydride in the presence of boron trifluoride etherates, showed that (at least in the authors' opinion) an increase in the relative reaction rates for the acylation of unsubstituted cyclopentadienyl rings (heteroannular effect) is governed by the resonance contribution of the substituent, since the reaction rate decreases in the series Me > Et > i-Pr > t-Bu. The same authors[11] have shown that in the desilylation of 1-alkyl-1'-(triethylsilyl)ferrocenes in glacial acetic acid the relative rates of protodesilylation decrease in the same sequence depending on the electronic effects of alkyl groups: Me > i-Pr > t-Bu. These data indicate that the heteroannular effect is absent with the tert-butyl group whereas normal and secondary alkyl substituents transmit an electron-releasing effect through the metal atom. All these results demonstrate that the conjugation effect plays a role in the transmission of the electronic effect of the alkyl group to an unsubstituted cyclopentadienyl ring via the iron atom.

A study of the PMR spectra of cobalticinium salt homologues in THF and DMSO indicates that their behaviour is similar to that of the respective ferrocenes

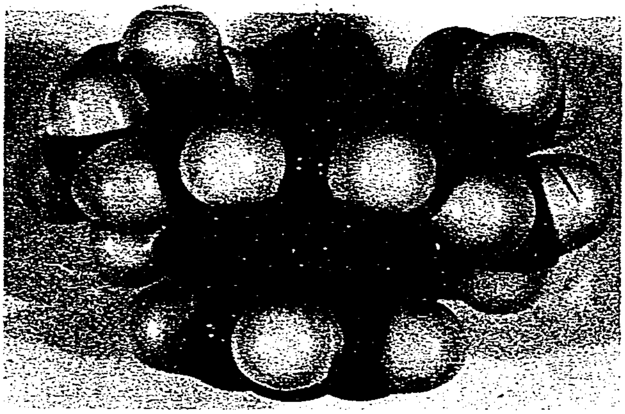
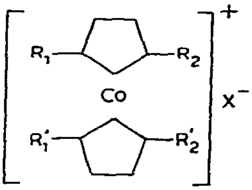


Fig. 1. Stewart model of 1,3-di-tert-butylferrocene.

(*cf.* Tables 1 and 2). However, the general decrease in electron density in the cobalticinium system in comparison with the ferrocene system results in a greater downfield shift for the ring proton signal (5.93 and 4.04 ppm respectively for cobalticinium salts and ferrocene in tetrahydrofuran). Thus, the introduction of a positive charge as occurs in the cobalticinium system influences the proton ring shielding but probably does not materially affect the distribution of additional electron density (introduced by the alkyl substituents) throughout the system. Thus the upfield shift on the proton signals for the substituted ring relative to those for the unsubstituted molecule is found to be 0.10 and 0.07–0.10 ppm respectively for the ferrocenes and the associated alkylcobalticinium salts (*cf.* Tables 1 and 2). It should be noted, however, that in the alkylcobalticinium salts the effect of the ethyl group is almost equally divided between the proton chemical shifts for the substituted (δ 0.12 ppm) and unsubstituted rings (δ 0.008 ppm), while in the respective ferrocenes the transannular effect is almost twice as small as the homoannular effect (δ 0.04 and 0.09 ppm respectively). A comparison of the homoannular di-tert-butyl analogues of these metallocenes leads to the conclusion that although in the cobalticinium ion the effect of tert-butyl groups on their adjacent ring is an order of magnitude greater than their transannular effect, in the ferrocene system this effect is much weaker. Although geometrical factors may not play an important role in the ferrocene system they could be more significant in the cobalticinium system, which although isoelectronic with ferrocene, has a positive charge situated at the metal atom and may possess shorter metal–cyclopentadienyl ring separations. Such an effect probably occurs in 1,1′,3,3′-tetra-tert-butylcobalticinium salts where there is a noticeable difference in the chemical shifts for the protons in the 2 and 4 positions.

TABLE 2

NMR SPECTRA OF ALKYLCOBALTICINIUM SALTS



R_1	R_2	R'_1	R'_2	*Anion* X^-	*δ of protons of unsubs. ring*	*δ of protons of subst. ring*				*δ*(C_6H_6)	*Solvent*
						2	3	4	5		
H	H	H	H	Br_3	5.93						THF
					5.85						DMSO
					5.36						CF_3COOH
				BPh_4	5.75					6.90 7.15	DMSO
				$\frac{1}{2}$ $PtCl_6$	5.84						DMSO
Et	H	H	H	$\frac{1}{2}$ $PtCl_6$	5.76	5.73	5.73	5.73	5.73		DMSO
				BPh_4	5.70	5.67	5.67	5.67	5.67	6.88 7.11	DMSO
Et	H	Et	H	$\frac{1}{2}$ $PtCl_6$		5.66	5.66	5.66	5.66		DMSO
				BPh_4		5.60	5.60	5.60	5.60	6.87 7.10	DMSO
t-Bu	H	t-Bu	H	Br_3		5.87	5.87	5.87	5.87		THF
						5.81	5.81	5.81	5.81		DMSO
t-Bu	t-Bu	H	H	Br_3	5.92	5.78		5.90	5.90		THF
					5.85						DMSO
t-Bu	t-Bu	t-Bu	t-Bu	Br_3		5.57		5.80	5.80		THF

Thus the nature of the changes occurring in the proton chemical shifts in homo- and heteroannular ferrocenes and cobalticinium salts appears to be dependent upon the ease of transmission of the electronic effects of donor substituents (particularly alkyl groups) relative to groups possessing a $-R$-effect. It appears that the heteroannular effect of alkyl substituents in metallocenes is mainly governed by the contribution of conjugation.

EXPERIMENTAL

The PMR spectra were measured on a Hitachi–Perkin–Elmer R-20 spectrometer with hexamethyldisiloxane (HMDS) as internal standard (δ_{HMDS} 0.05 ppm).

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Note added in proof. The spectra of 1,3-di-tert-butylferrocene, its cobalticinium salt analogue and related 1,1′,3,3′-tetra-tert-butyl derivatives consist of a strong doublet (protons in positions 4 and 5) to low field and a weak triplet (proton in position 2) to high field. These spectra give strong evidence for our assignment (see Tables 1 and 2) (*cf.* D. W. Slocum and C. R. Ernst, *Advan. Organometal. Chem.*, 10 (1972) 79). Our data were reported at the IVth International Organometallic Conference (Bristol, 1969).

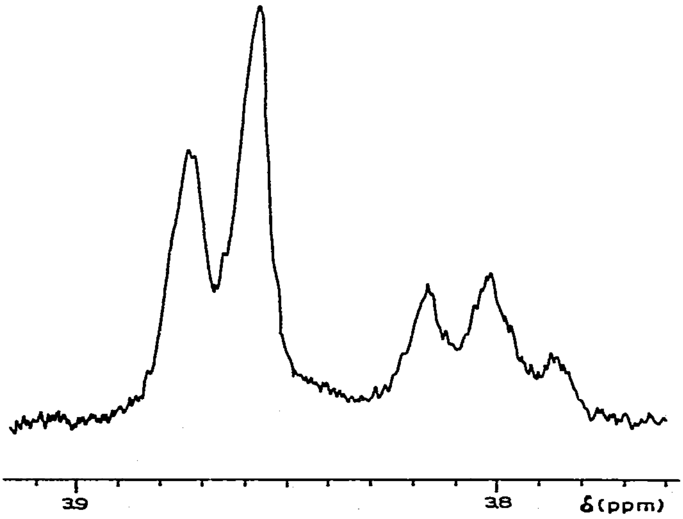

Fig. 2. PMR-spectrum of the substituted ring in 1,1′,3,3′-tetra-tert-butylferrocene (Spectrometer "Bruker-90").