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Preliminary communication

ON THE ELECTRONIC INFLUENCE OF ALKYL GROUPS IN ALKYLFERROCENES

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Summary

The ^{13}C NMR signals of α- and β-carbons in methyl-, ethyl-, isopropyl- and t-butyl-ferrocenes were assigned using deuterium labelling. The electronic influence of alkyl groups in alkylferrocenes is discussed.

In a previous ^{13}C NMR study of ferrocenylcarbenium ions we used their precursors, ferrocenylcarbinols, with deuterium atoms at the α-position of the substituted cyclopentadienyl ring [1]. The ferrocenylcarbinols are known to be reduced easily to alkylferrocenes for which a hyperconjugation effect has often been proposed [2-5]. It seemed reasonable to measure the ^{13}C chemical shifts in α,α-dideuterated alkylferrocenes and thus to assign unequivocally all the signals in the spectra of alkylferrocenes.

The deuterated samples of methyl-, ethyl- and isopropyl-ferrocenes were prepared by reduction of the respective deuterated carbinols (or acylferrocenes) by means of $LiAlH_4/AlCl_3$ [6]. α,α-Dideutero-t-butylferrocene was obtained by treatment of α,α-dideuteroacetylferrocene with CH_3MgI/MgI_2 excess [7]. The key compound in these syntheses was *N*,*N*-dimethylaminomethylferrocene, deuterated selectively by the procedure of Hauser et al. [8].

The ^{13}C chemical shifts in alkylferrocenes are listed in Table 1. It can be seen from these data that the greatest changes are observed in the signals of key atoms (C_k) whose deshielding increases with increasing branching of the alkyl group. All alkyl substituents cause some shift of the carbon signal of an unsubstituted ring (C_u) downfield with respect to ferrocene. The α- and β-carbon signals in the substituted ring are shifted upfield with an exception of methylferrocene whose α-carbons are deshielded. In neopentylferrocene (obtained by reduction of pivaloylferrocene [9] the α-carbons are deshielded as well and the chemical shift of the key atom is close to that in methylferrocene. Thus in the ground state the neopentyl group effect resembles a methyl rather than an ethyl group effect. The use of deuterium labelling demonstrated that in alkylferrocenes the relative shielding of α- and β-carbons

TABLE 1

THE ^{13}C NMR CHEMICAL SHIFTS IN ALKYLFERROCENES [a]

Compound [b]	δ(ppm) from TMS (in dichloroethane, 30 °C)						
	C_k	C_α	C_β	C_u	Substituent		
FcH	67.7	67.7	67.7	67.7			
$FcCH_3$	83.4	68.9	66.8	68.4	14.4 (CH_3)		
$FcCH_2CH_3$	90.7	67.2	66.7	68.2	22.0 (CH_2),	14.4 (CH_3)	
$FcCH(CH_3)_2$	96.6	65.8	66.5	68.0	27.4 (CH)	23.2 (CH_3)	
$FcC(CH_3)_3$	101.7	64.8	66.7	68.2	30.2 (C)	31.2 (CH_3)	
$FcCH_2C(CH_3)_3$	85.3	69.9	66.9	68.2	44.6 (CH_2)	31.3 (C),	28.9 (CH_3)

[a] The spectra were taken on a Bruker HX-90 spectrometer with Fourier transform and proton decoupling and noise modulation at 22.635 MHz. [b] Fc = ferrocenyl.

of the ring changes its sign on going from methyl and ethyl to isopropyl and t-butyl substituents while the ^{13}C chemical shifts of β-carbons are almost independent of the alkyl group character. The results obtained in the present study lead to certain conclusions on the character of effect of alkyl substituents in alkylferrocenes.

Slocum et al. [2,4] have found that the ^{1}H NMR spectra of methyl-, ethyl-, isopropyl- and t-butylferrocene manifest predominantly a resonant interaction between the alkyl groups and the ferrocenyl moiety and this resonance effect is transmitted generally to the β-position. This assumption is based on the fact that in each molecule with the exception of isopropylferrocene whose proton signals of the unsubstituted ring are unresolved even at 220 MHz) the β-protons are resonating at higher field than the α-protons and the unsubstituted ring protons [4].

Such a conclusion, however, is inconsistent with the data of ^{13}C NMR spectra. Unlike methyl- and ethyl-ferrocene, in isopropyl- and t-butyl-ferrocene the α- rather than β-carbons of the ring are more shielded.

According to the ^{13}C NMR data the alkyl groups produce considerable electron density redistribution over the ferrocene system. However, Libit and Hoffman [10] have shown for toluene that such a redistribution is not a result of general charge transfer from the substituent (only 0.019 electron) but is due to a polarization of the π-system. (The role of the π-inductive effect has been mentioned in a qualitative analysis of the ^{13}C NMR spectra of ferrocene derivatives [11]. At the same time the difference in the relative electronic influence of alkyl groups should be rather small and it is hard to estimate such influence in the case of alkylferrocenes because of complexity of the metal-containing system.

It can be noted that the greater part of the data used by different authors as evidence of the alkyl group hyperconjugation refer to heterolytic reactions [12]. Schubert et al. [13] have found that very often a "hyperconjugation" order of substituents effect $CH_3 > \cdots > C(CH_3)_3$ is determined by solvation effects. At the same time, investigation of the stability of $R\overset{+}{C}{=}O$ cations [14] in the gaseous phase gave an ordinary "inductive" series of alkyl group effects: $C(CH_3)_3 > \cdots > CH_3$. Moreover recently it has been shown that the pattern of relative influence of alkyl groups depends on the nature of centre to which they are bound [15]. For example, the tendency of alkoxide ions $R'O^-$ to undergo negative charge delocalization decreases in the series $R_3C > R_2CH > RCH_2 > CH_3 > H$ [16]. Taking into account an enhancement of electron donor properties of the ferrocenyl nucleus [17] one should assume that the hyperconjugation, if it ever takes place, should be less marked in alkylferrocenes than in alkylbenzenes.

The fact that ^{13}C chemical shifts of β-carbons in alkylferrocenes almost do not change on going from one to another group means that the hyperconjugation effect, even if it exists in these systems, is so negligible that it can be overshadowed by other effects of alkyl groups (the π-inductive effect, the substituent magnetic anisotropy). Thus the available data on shielding of ^1H and ^{13}C nuclei in alkylferrocenes cannot serve as strict evidence of hyperconjugation.

Recently the $^1J(^{57}Fe—^{13}C)$ constants have been measured for ferrocene derivatives using $^{13}C—\{^1H\}$ NMR [19]. This enabled the ^{57}Fe chemical shift to be determined for the first time, by means of heteronuclear triple resonance. It is quite possible that additional information on the electronic influence of alkyl groups may be obtained from ^{57}Fe NMR data. The preliminary experiments have demonstrated that the ^{57}Fe chemical shift is sensitive to the substitution and the ethylferrocene signal is shifted over 36.66 ppm downfield from ferrocene (CS_2, 30 °C).

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