Registry No.—**1**, 18623-61-5; **2**, 36794-95-3; **3**, 36794-96-4; **7**, 36807-48-4; **8**, 36794-97-5; **9**, 36870-64-1; **12**, 36807-49-5; **13**, 36794-98-6; **14**, 36870-65-2.

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Fundamental Studies of Substituted Ferrocene Systems. VI. Electronic Effects in the Alkylferrocenes

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The 220-MHz proton magnetic resonance spectra of methyl-, ethyl-, isopropyl-, and *tert*-butylferrocene are reported. The improved resolution allows differentiation of resonances in all but isopropylferrocene, thus allowing investigation of chemical shift trends for the various protons involved. Spectra were also obtained for the specifically deuterated molecules necessary to establish the identity of the various resonances. Of interest is the predominant shielding effect experienced at the 3,4-position protons contrary to previous predictions and assignments.

Proton magnetic resonance spectroscopy has proven to be a valuable tool in the analysis of ferrocenes, both for the determination of structure and for the investigation of the modes of transmission of electronic effects. A complete spectral analysis of the alkylferrocenes has been absent from the literature because of the failure of the 60- and 100-MHz instruments to resolve the weakly perturbed ring proton resonances. We wish to report here the 220-MHz spectra of methyl-, ethyl-, isopropyl-, and *tert*-butylferrocene along with the appropriately deuterated molecules necessary to unambiguously assign the various resonances.

The 60- and 100-MHz spectra of this series of alkylferrocenes have been reported by a number of research groups. Benkeser and coworkers[1,2] observed ring proton resonances for methylferrocene at δ 3.99 and 3.94 and on the basis of integration alone assigned the downfield resonance to the 1′- and 3,4-position protons and the upfield resonance to the 2,5-position protons. Resolution was not sufficient to separate the homoannular ring resonances of the other alkylferrocenes. In contrast, Rausch and Siegel[3] reported that the pmr spectrum of 2,5-dideuteriomethylferrocene exhibited a partial decrease in absorption for the upfield resonance, concluding that this resonance in the undeuterated molecule was in fact due to both the 2,5- and 3,4-position protons. Similarly, Nesmeyanov and coworkers[4] have reported the spectra of this same series of compounds and claimed to have obtained sufficient resolution to partially resolve the upfield resonance in both methyl- and *tert*-butylferrocene. Citing Benkeser, *et al.*,[1,2] and a paper by Levenberg and Richards,[5] they assigned the upfield resonance to the 2,5-position protons. These inconsistencies are mainly the result of insufficient resolution afforded by the 60- and 100-MHz spectrometers, which prohibits reliable assignment of the homoannular ring resonances and hence meaningful assessment of electronic effects of the substituents.

Recent results from this laboratory have demonstrated that for strong electron-donating substituents an upfield shift is experienced predominately by the 3,4-position protons.[6] Since alkyl groups are weak electron donors, a distinct possibility of a parallel electronic effect was seen to exist between these two systems such that the homoannular ring assignments of Benkeser, *et al.*,[1,2] and Nesmeyanov, *et al.*,[4] would need to be reversed.

Results and Discussion

The 220-MHz spectral data for these alkylferrocenes are summarized in Table I along with "corrected" chemical shift data of the previous authors. Assignments of the substituted ring resonances were made on the basis of comparison to the spectra of specifically deuterated molecules. 2-Deuteriomethylferrocene and 2,5-dideuterioethylferrocene were prepared *via* routes involving lithiation–deuteration procedures on *N*,*N*-dimethylaminomethylferrocene[7] and *N*,*N*-dimethylaminoethylferrocene,[8] respectively, in which the metalation has been demonstrated unequivocally to occur at the 2 position. 3,1′-Dideuterio-*tert*-butylferrocene was prepared by the sequence of reactions shown in Scheme I.

SCHEME I

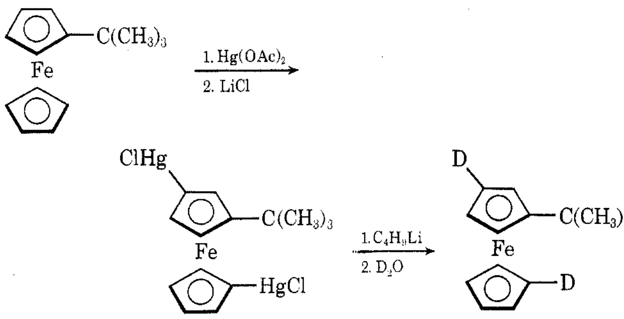

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TABLE I

CHEMICAL SHIFT DATA FOR ALKYL FERROCENES DETERMINED AT 220 MHz[a]

Registry no.	Substituent	$H_{1'}$	$H_{2,5}$	$H_{3,4}$	α^{b}	β^{c}
1271-44-9	Methyl	3.964 (3.95, 3.99)	3.932 (3.92, 3.99)	3.895 (3.89, 3.94)	1.877 (—, 1.96)	
1273-89-8	Ethyl	3.977 (3.98, 4.01)	3.936 (3.94, 3.97)	3.927 (3.94, 3.97)	2.31 (2.30, 2.29)	1.18 (1.15, —)
12126-81-7	Isopropyl	3.991 (3.97, 4.02)	3.927 (3.92, 3.96)	3.927 (3.92, 3.96)	2.57 (2.58, 2.59)	1.18 (1.15, —)
1316-98-9	*tert*-Butyl	4.018 (4.02, 4.02)	3.945 (3.95, 3.92)	3.909 (3.89, 3.92)		1.21 (1.20, —)

[a] In parts per million. Values in parenthesis are those reported by Nesmeyanov[4] and Benkeser,[1,2] respectively. Assignments have been reversed to coincide with our revised data. [b] Chemical shifts of the protons of the alkyl group located on the carbon atom attached to the ferrocene ring. [c] Chemical shift of the protons of the alkyl group located on the carbon atoms other than those attached to the ferrocene ring.

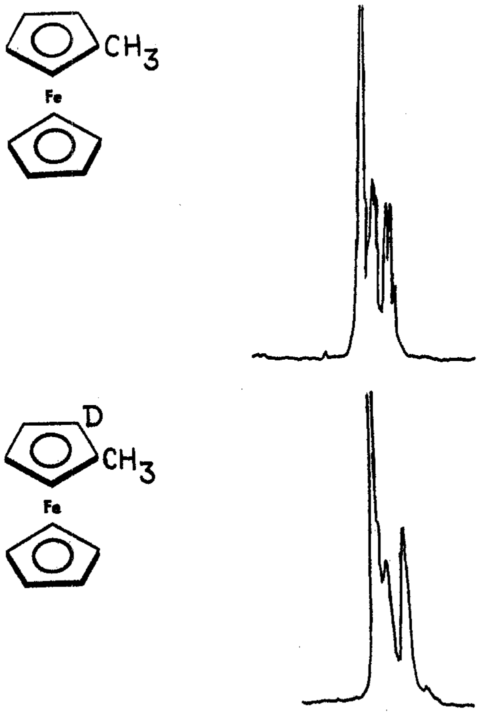

Figure 1.—Pmr spectra of methyl- and 2-deuteriomethylferrocene at 220 MHz.

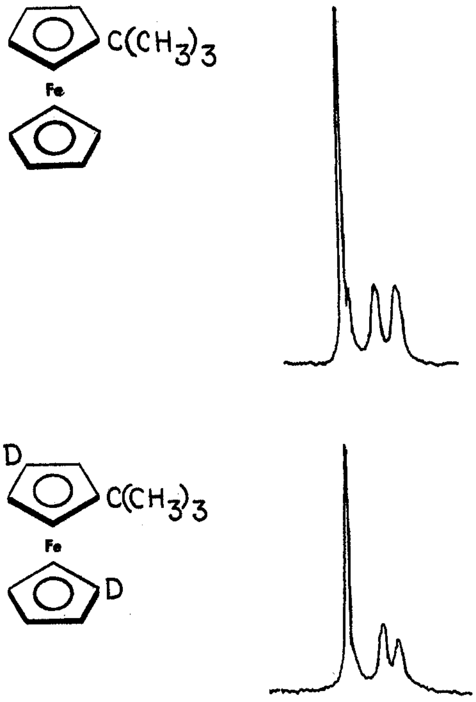

Figure 2.—Pmr spectra of *tert*-butyl- and 3,1′-dideuterio-*tert*-butylferrocene at 220 MHz.

Chloromercuration of *tert*-butylferrocene yielded an intermediate primarily consisting of 3,1′-dichloromercuri-*tert*-butylferrocene. The assumption was made that little or no 2- or 2,1′-dichloromercuri compound would be formed because of the bulk of the *tert*-butyl group. This material was converted to the corresponding dilithio intermediate by reaction with *n*-butyllithium in ether. Condensation of this solution with deuterium oxide yielded 3,1′-dideuterio-*tert*-butylferrocene containing 1.53 atoms of deuterium per molecule as determined by mass spectral analysis. Although the orientation of the product of chloromercuration of *tert*-butylferrocene has not been established, previous electrophilic substitution reactions on this molecule have been shown to occur predominantly at the 3 and 1′ positions.[9]

Comparative pmr spectra of the deuterated and undeuterated methyl- and *tert*-butylferrocene are shown in Figures 1 and 2. The ring proton resonances in the spectra of the undeuterated molecules were clearly resolved in all but isopropylferrocene, which exhibited singlets for both the substituted and unsubstituted rings. In each of the remaining molecules the 3,4-position protons appeared upfield with respect to the 2,5- and 1′-position proton resonances. The observed relative shielding orders are contrary to the assignments previously suggested and are indicative of a predominantly resonance mode of interaction of the alkyl groups with the ferrocene ring. The transmission of this effect primarily to the 3,4 positions is also established.

The improved resolution obtained has revealed some interesting chemical-shift trends for the various positions in this series of alkylferrocenes. Figure 3 is a graphical representation of the ortho, meta, and para protons for the series methyl- through *tert*-butylbenzene.[10] Figure 4 is a similar representation of the 2,5- and 3,4-position protons for the series methyl- through *tert*-butylferrocene. We note that there is a fairly similar trend in the plots of the para benzene

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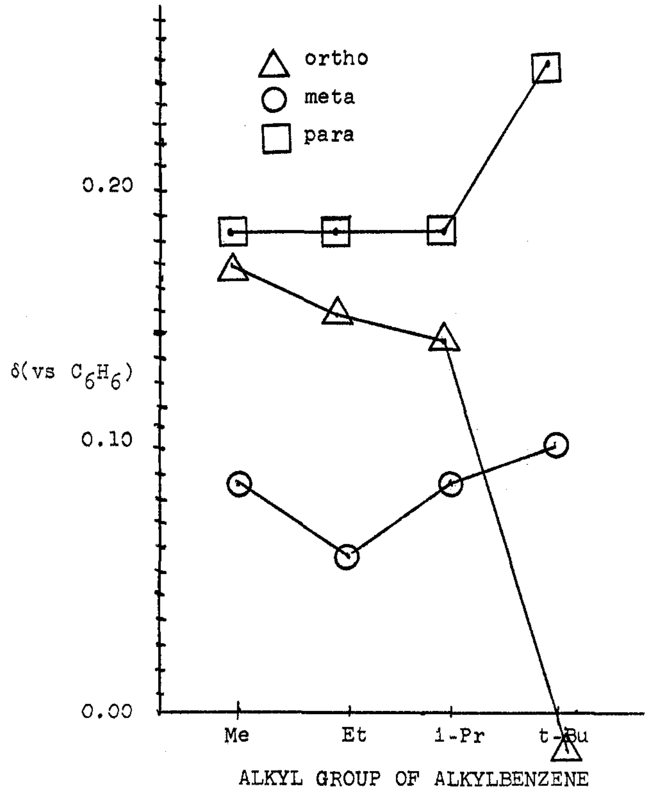

Figure 3.—Chemical shifts of ring protons of alkylbenzenes.

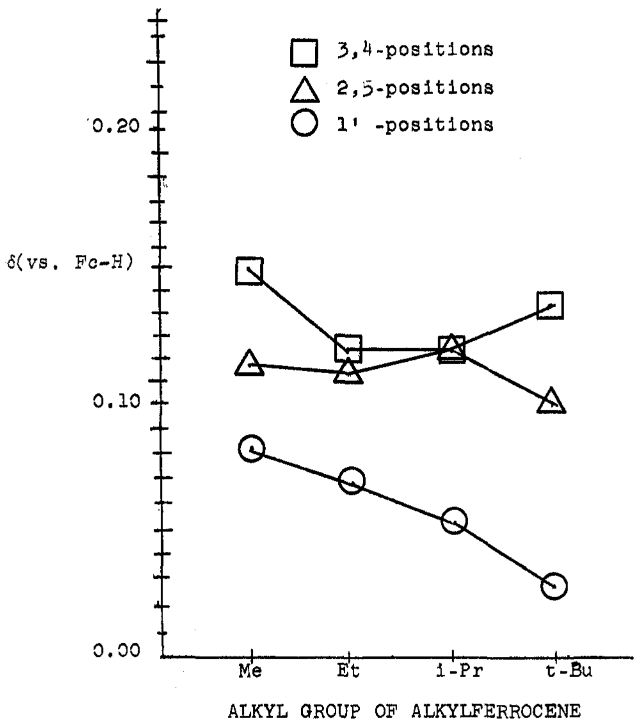

Figure 4.—Chemical shifts of homoannular ring protons of alkylferrocenes.

protons and the 3,4-position ferrocene protons, particularly with regard to the anomalous upfield trend for the respective *tert*-butyl compounds. This observation in turn reinforces our arguments of the position of chloromercuration of *tert*-butylferrocene and hence also the position of deuteration. A lesser correlation is noted between the ortho benzene protons and the 2,5 protons of the alkylferrocenes.

Although too few substituents were studied to obtain a meaningful correlation of chemical shift data with substituent constants, a positive correlation did exist for the 3,4-position data with σ_{para} and Lupton–Swain σ_R[11] constants. A similar correlation could not be obtained for the 2,5 and 1′ positions, however. The lack of correlation for the 2,5-position protons was due principally to an abnormal shift for these protons in *tert*-butylferrocene. A similar shift for the ortho protons in *tert*-butylbenzene has been attributed to a van der Waals interaction with the substituent.[10] The downfield trend for the 1′-position protons through the series suggests that such an interaction may also be involved for these protons.

In conclusion, the assignment of the resonances in this series of alkylferrocenes should be of great aid in the future analysis of alkylferrocene spectra. An evaluation of the relative importance of resonance (hyperconjugation) and induction to the electronic effects of the alkyl substituents and a better understanding of the transmission of resonance effects in the ground state of alkylferrocenes has also been provided.

Experimental Section

General.—The 220-MHz spectra were obtained at an ambient temperature of 20° on a Varian HR 220 spectrometer located at the University of Illinois. All samples were 3% (molar) in carbon tetrachloride with tetramethylsilane as an internal standard. Mass spectra were obtained on a CEC 21-109 spectrometer at an inlet temperature of 200°. Gas chromatography was carried out on a Varian Aerograph 90-p gas chromatograph on a 6% Apiezon L on Chromosorb W column. The undeuterated alkylferrocenes except for isopropylferrocene were prepared by published procedures.[12,13] Methylferrocene was prepared by the Na/NH_3 reduction of dimethylaminomethylferrocene methiodide.[14] The *n*-butyllithium used in the following reactions was 1.6 *M* in hexane and was provided by Foote Mineral Co.

Preparation of Isopropylferrocene.—α-Methylvinylferrocene[15] (1.08 g, 4.8 mmol) was placed in a hydrogenation flask along with 10 ml of ethanol, 3 ml of benzene, and 0.03 g of Pd/C catalyst. Hydrogenation was carried out at an operating pressure of 52 psi for 2.0 hr. The resulting mixture was filtered, diluted with 200 ml of water, and extracted repeatedly with ether. The ether extracts were combined, dried over anhydrous $MgSO_4$, and stripped under vacuum. The remaining oil was chromatographed on 100 g of neutral alumina I; elution with petroleum ether (bp 40–60°) afforded 1.04 g (95%) of a red oil. An ir of this product was identical with that of isopropylferrocene as described in the literature.[16]

Preparation of 2-Deuteriomethylferrocene.—Dimethylaminomethylferrocene (10 g, 41.2 mmol) was dissolved in about 125 ml of anhydrous ether in a 250-ml flask equipped with a nitrogen inlet tube. *n*-Butyllithium (40 ml, 60 mmol) was added and the resulting solution was stirred for 1.5 hr, after which time excess deuterium oxide was added.[7] After sitting for 2 hr at room temperature, the reaction mixture was filtered and the filtrate was stripped of solvent. The resulting oil was dissolved in ether and treated with excess methyl iodide. A copious precipitate of the methiodide was collected. This methiodide (1.68 g, 4.25 mmol), sodium amalgam (23.94 g, 10%), water (117 ml), and benzene (75 ml) were combined and allowed to set for several hours. The benzene layer was separated and stripped and the resulting oil was chromatographed on alumina I. Elution with petroleum ether yielded 2-deuteriomethylferrocene (0.32 g, 37%) which

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was identified by its pmr spectrum. The product's vpc retention time was equal to that of an authentic sample of methylferrocene. Pmr analysis indicated that approximately 0.6 atom of deuterium had been incorporated into the molecule. Mass spectral analysis of the m/e 200 and 201 peaks corrected for natural isotopic abundance indicated the incorporation of 0.55 atom of deuterium.

Preparation of 2,5-Dideuterioethylferrocene.—*N,N*-Dimethylaminoethylferrocene (2.57 g, 10 mmol) along with 25 ml of anhydrous ether were placed in a flame-dried, round-bottom flask equipped with a magnetic stirrer, gas inlet, and reflux condenser. *n*-Butyllithium (10 ml, 15 mmol) was added under an argon atmosphere and the solution was stirred at room temperature for 2 hr,[8] after which time the reaction mixture was hydrolyzed with 1 ml of deuterium oxide. The resulting mixture was stirred for 30 min, diluted with ether, and dried over anhydrous $MgSO_4$. The dried ethereal solution was stripped of its solvent, yielding a red oil. The lithiation and deuteration of this oil was repeated twice, yielding 2,5-dideuteriodimethylaminoethylferrocene (2.40 g, 95%). Pmr analysis of the resulting amine indicated that *ca.* 1.8–2.0 atoms of deuterium were incorporated into the molecule.

The above deuterated amine (2.40 g, 9.4 mmol) was treated with excess methyl iodide (2.48 g, 20 mmol) at room temperature. Upon cooling, precipitation of the ammonium salt occurred. Subsequent isolation and air drying afforded 1.85 g (50%) of the methiodide. In a 250-ml flask sodium (2 g, 87 mmol) was dissolved in about 150 ml of ammonia and the blue solution obtained was poured over the methiodide (1.8 g, 4.5 mmol) contained in another 250-ml flask. After about 45 sec ammonium chloride was added followed by water. The reaction mixture was extracted with ether. Evaporation of the ether left a crude oil which was chromatographed on activated alumina. The first band was eluted with petroleum ether and yielded 2,5-dideuterioethylferrocene (0.50 g, 5%), identified by its pmr spectrum and by comparison of its retention time at 187° with that of an authentic sample of ethylferrocene.[12] A second band was eluted with petroleum ether–benzene, and was identified by its ir and pmr spectra as 2,5-dideuteriovinylferrocene (0.223 g, 22%), mp 51–52.5° (lit.[3] mp 51–52°). The pmr spectrum was identical in appearance with that reported by Rausch and Siegel,[3] although chemical shifts varied slightly.

Chloromercuration of *tert*-Butylferrocene.—*tert*-Butylferrocene (1.8 g, 7.4 mmol) was dissolved in ether in a 250-ml flask, to which was added an ether–hexane solution of mercuric acetate (2.5 g, 9.7 mmol). After about 16 hr lithium chloride (0.5 g, 12 mmol) was added in ether solution. The heterogeneous mixture was stripped and chromatographed on alumina III with benzene–ether. A small band of *tert*-butylferrocene was eluted first followed by a larger band which yielded 3,1′-di(chloromercuri)-*tert*-butylferrocene (0.30 g, 8.5%), a brown sold which melted at 163–166°. A portion of this material (0.184 g, 0.26 mmol) was added to about 30 ml of ether in a 100-ml flask. To this heterogeneous mixture was added about 3 ml of *n*-butyllithium solution upon which the solid material dissolved immediately. After the resulting solution was allowed to sit for 1 hr, excess deuterium oxide was added and the resultant mixture was extracted twice with ether. The crude ether extracts were stripped of solvent and purified by vapor phase chromatography, yielding 3,1′-dideuterio-*tert*-butylferrocene (retention time equal to that of an authentic sample of *tert*-butylferrocene[13]). The 60-MHz pmr spectrum of this compound was consistent with the incorporation of approximately 1.6 atoms of deuterium. The 100-MHz and 220-MHz spectra indicated that approximately 1.1 of these deuterium atoms were in the unsubstituted ring, and 0.6 of these were in the 3,4 positions, with essentially no deuterium incorporation in the 2,5 position. Mass spectral analysis of the m/e 242, 243, and 244 peaks corrected for natural isotopic abundance indicated that 70% of the molecules contained two atoms of deuterium, that 13% of the molecules contained one deuterium, and that 17% of the molecules contained no deuterium.

Registry No.—2-Deuteriomethylferrocene, 36862-98-3; 3,1′-dideuterio-*tert*-butylferrocene, 36862-99-4.

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The Conformational Analysis of 1-Butene

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The temperature dependences of two nmr spectral parameters have been utilized in the conformational analysis of *1,1,4,4,4*-d_5-1-butene (1). The three-bond vinyl–allylic coupling constant and the chemical shift of the methylene protons were observed to have a small but real temperature dependence which was correlated with the cis–skew conformational equilibrium of 1. A qualitative estimate of the enthalpy difference between the two conformers was made on the basis of the coupling constant data. It was concluded that the cis conformer is more stable than the skew one by 100 ± 50 cal/mol with $\Delta S = 1.376$ eu.

A wide variety of open-chain organic compounds containing a single bond between tetrahedral and trigonal carbon atoms have been shown to exist as a mixture of rotational conformers.[1b] The majority of these compounds contain one or more heteroatoms and the effect of unsaturation on the conformational equilibrium is not clear. In the case of propene, microwave spectroscopy has confirmed that the most stable conformation is that in which a methyl carbon–hydrogen bond is eclipsed with the carbon–carbon double bond.[2]

Various spectroscopic methods (infrared,[3] Raman,[3,4] nuclear magnetic resonance,[5] and microwave[6]) have been applied to establish the conformational preference of the ethyl group in 1-butene (**1**). The nmr work of Bothner-By[5a,b] and coworkers suggested that two conformers, the cis (**1a**) and skew (**1b**) forms, were present in about equal proportions. Kondo,[6] *et al.*, confirmed the existence of **1a** and **1b** from a detailed microwave study of 1-butene and estimated **1b** to be more stable than **1a** by 150 ± 150 cal/mol. Empirical and theoretical estimates of the enthalpy difference for eq 1 are −400 and −690 cal/mol, respectively.[5c,7]

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