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The ^{13}C–H Proton Magnetic Resonance Spectra of Ferrocene and Some Related Metallocenes

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The ^{13}C–H satellite proton magnetic resonance spectra of ferrocene, ruthenocene, and cobaltocene chloride have been obtained and analyzed. The results provide detailed information concerning the H–H and ^{13}C–H coupling parameters for these molecules as well as the isotopic displacement of the ^{13}C nucleus on the proton shifts. The data have been considered from the standpoint of the electronic structure of the ring system and the effect of charge on the central metal atom.

Introduction

Of the large number of metallocenes now known ferrocene has been studied most extensively. A number of investigators have described the various molecular spectra of ferrocene, which are of particular interest as a source of information concerning the structure and properties of this complex.[1,2] Heretofore, however, nuclear magnetic resonance (nmr) investigations of ferrocene have been relatively limited in scope. One of the reasons for this is that the protons in each cyclopentadienyl ring comprise a system of five chemically equivalent spins, yielding but a single spectral peak. Some nmr studies have been carried out with simple derivatives of ferrocene, but the principal interest in these compounds appears to have been the behavior of the chemical shifts.[3-8] Information concerning the effect of a wide range of substituents on the H–H coupling parameters is not yet available. A value for the bonded ^{13}C–H coupling has been obtained from the ^{13}C spectrum by Lauterbur.[9] The long-range ^{13}C–H coupling parameters, of considerable current interest, have not been previously reported.

Because of the widespread interest in the properties of ferrocene, we have now carried out a detailed study of the ^{13}C–H satellite proton magnetic resonance (pmr) spectrum of this molecule. This is the proton spectrum which arises solely from the isotopic species containing a single ^{13}C nucleus. Because of the reduction of symmetry in this species, the pmr spectrum is relatively complex and is capable of yielding a considerable amount of information.

A similar approach has also been used to study ruthenocene and cobaltocene chloride in order to examine the effect of the central metal atom on the spectral parameters. Theoretical analyses of the spectral patterns have yielded values for all the ^{13}C–H couplings and H–H couplings for both ferrocene and cobaltocene chloride. Because of the lower solubility of ruthenocene, the results in this case are somewhat limited in both scope and reliability. However, the values obtained do permit some comparison with the data for the other two compounds. All of the coupling data obtained here have been compared with the values found in other unsaturated five- and six-membered ring systems. The value of the directly bonded ^{13}C–H coupling in ferrocene seems to support the MO calculations which indicate that a small charge separation exists between the rings and metal atom in the neutral metallocenes.[10] Also limited correlations between the interior ring angles and long-range ^{13}C–H couplings have been noted for the five-membered ring systems.

Experimental Section

Ferrocene and ruthenocene were the commercially available compounds. Since the former contained a paramagnetic impurity, as indicated by its pmr spectrum, it was purified by vacuum sublimation. Cobaltocene perchlorate, prepared by Dr. Arthur F. Dratz, was converted into the chloride by ion exchange. No interfering impurities were detected in either the ruthenocene or cobaltocene chloride. Since all of the compounds are solids, suitable solvents were chosen so that the ^{13}C–H satellite patterns could be recorded at natural abundance of ^{13}C. Ferrocene and cobaltocene chloride were dissolved in carbon disulfide and water, respectively, to give satisfactory concentrations ($\sim$40%). Ruthenocene, however, was found to be only marginally soluble in a large number of solvents, from which chloroform was finally selected.

All spectra were obtained using a Varian A-60A nmr spectrometer operating at 38°. Calibrations were performed by the usual audio-side-band method using the parent peak of each compound as the internal reference. Each spectral frequency represents at least four forward and four reverse sweeps and the maximum average deviations of the observed frequencies for ferrocene and cobaltocene chloride were 0.04 and 0.06 Hz, respectively. Owing to the limited solubility of ruthenocene, only the inner satellite lines were intense enough to calibrate (average deviation of 0.04 Hz).

Results and Calculations

The theoretical analyses of these spectra were carried out with the aid of an iterative computer program

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(PROSPECT 1). For this purpose the cyclopentadienyl ring was treated as an ABB′CC′X (X = ^{13}C) spin system, which allows for the simultaneous calculation of both the upfield and the downfield satellite patterns, as well as the inner satellite pattern. In the cases of ferrocene and cobaltocene chloride, eight adjustable parameters were employed to account for a total of 30 and 20 observed frequencies, respectively. Although the number of theoretical lines is the same in each instance, there were fewer observable lines in the latter compound because of somewhat poorer resolution in the aqueous solution. Three of the parameters were isotopic effects on the proton shifts, approximately 0.1 Hz in magnitude; the remaining parameters were the three ^{13}C–H couplings and the two H–H couplings. The iterative phase of the calculations was allowed to continue until agreement between the observed and computed frequencies was judged to be satisfactory, in the present instances equivalent to rms errors of 0.04 and 0.03 Hz, respectively, between the observed and calculated frequencies. The resulting calculated probable errors for the nmr parameters were not greater than 0.03 Hz. The final values of these parameters so obtained are listed in Table I and the corresponding theoretical spectra are shown in the lower portion of Figure 1 for ferrocene. The spectra for cobaltocene chloride and also the inner satellite region of ruthenocene showed only minor differences from those of ferrocene and therefore have not been illustrated. In the calculations all of the coupling parameters were assumed to be positive. However, attempts to fit the spectra using negative long-range ^{13}C–H couplings led to significantly poorer results, as indicated by incorrect relative intensities in the inner satellite spectral region.

TABLE I

THE PMR SPECTRAL PARAMETERS FOR SOME METALLOCENES[a]

Parameters	Ferrocene	Cobaltocene chloride	Ruthenocene
ν_1	0.14	0.25	...[b]
ν_2, ν_5	0.10	0.16	...
ν_3, ν_4	0.08	0.15	...
J_{12}, J_{23}	2.40	2.58	...
J_{13}, J_{24}	1.24	1.46	...
J_{CH}	174.81	185.54	176.3
J_{CCH}	6.30	6.26	6.3
J_{CCCH}	7.22	7.17	7.3

[a] All values in hertz. Shift values are at 60 MHz relative to the parent proton peak of compound. [b] These values could not be determined accurately.

Although the fine structure of the ^{13}C–H outer satellite pattern of ruthenocene was obscured by noise, the general shape of the satellites resembled that of ferrocene. No attempt was made to analyze these patterns fully; J_{CH} was measured from the centers of gravity of these satellite regions. For ruthenocene the inner satellite pattern is more intense and could be satisfactorily calibrated. The calculated frequencies in this pattern were dependent to some extent on the H–H coupling constants. However, when iterative calculations were carried out for only the interior region of ferrocene, they yielded a set of H–H coupling values inconsistent with those obtained for the total spectrum. Consequently, because of the obvious marked similarity between the outer satellite patterns of ferrocene and ruthenocene, the H–H couplings from the former were adopted in order to calculate the ^{13}C–H long-range couplings in ruthenocene shown in Table I. The errors in these values are probably somewhat higher than those of the other two metallocenes and are estimated to be about ±0.3 Hz.

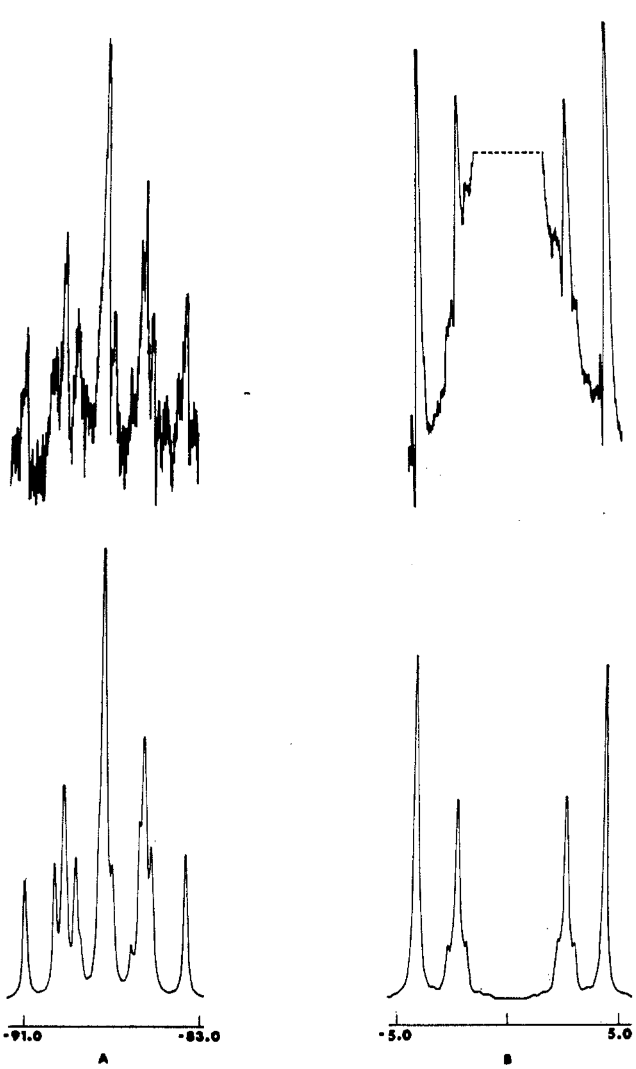

Figure 1.—Observed and calculated outer downfield (A) and inner ^{13}C–H satellite (B) patterns of ferrocene at 60 MHz. The intensity scales for the outer and inner satellites are not the same.

Discussion

Although the cyclopentadienyl rings in the metallocenes are aromatic in nature and show some of the chemical properties of such systems,[11] the H–H couplings do not reflect this. The vicinal H–H couplings are very much smaller than the values characteristic of ethylenic and aromatic systems. For example,

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[11] M. Rosenblum, "Chemistry of Iron Group Metallocenes," Part I, John Wiley & Sons, Inc., New York, N. Y., 1965.

these couplings in ferrocene, cyclopentadiene,[12] and benzene[13] are 2.40, 5.06, and 7.54 Hz, respectively. The corresponding couplings in the five-membered heterocyclic rings vary considerably depending on the heteroatom.[14] On the other hand, the *meta* couplings in these latter compounds, as well as that in benzene (1.37 Hz), are of about the same magnitude as those in the metallocenes.

Our H–H coupling values for ferrocene fall well within the range of values previously reported for several methyl- and acetyl-substituted derivatives.[6] In terms of absolute magnitude, the effect of these substituents on the H–H coupling is not very large, covering a range of approximately 0.7 Hz.

The ^{13}C–H coupling values reported here for the neutral metallocenes agree with that previously reported for ferrocene[9] and are somewhat larger than those usually found for aromatic systems (~160 Hz). It has been proposed that, at least for hydrocarbons, this parameter is linearly dependent on the s character of the carbon orbital in the corresponding C–H bond.[15,16] Because of the Z^3 dependence in the Fermi contact contribution to J_{CH}, the effect of net positive charge in the five-membered ring will be to increase the value of the coupling. Thus, it appears reasonable that J_{CH} should be larger in $(CoCp_2)^+Cl^-$ than in the neutral metallocenes. In addition, in the latter compounds the value of J_{CH} will be augmented if bonding to the central metal atom leads to positively charged rings. It is interesting, in this connection, that J_{CH} increases in the five-membered ring systems in the order: cyclopentadienyl anion[17] < cyclopentadiene (ethylenic carbons[17]) < ferrocene and ruthenocene < cobaltocene chloride. The results of theoretical calculations for ferrocene disagree as to the sign of the net charge on the rings, the difference apparently arising from the choice of the AO basis used.[10,18] Shustorovich and Dyatkina reported a value of −0.69 as the charge on the rings, whereas Dahl and Ballhausen obtained a value of +0.69. To the extent that charge is the principal factor producing variations in J_{CH} in these ring systems, the coupling value in ferrocene appears to support the value of Dahl and Ballhausen.

It is worth noting that the theoretical reproduction of the outer satellite pattern is not possible without including long-range ^{13}C–H coupling, but these are involved solely as differences. The absolute values of the long-range couplings are, in principle, determinable from the inner satellite pattern, although as a practical matter interference with the parent peak often makes this impossible. There have been a few instances where the inner satellite systems have been studied in some detail at the natural abundance of ^{13}C.[19–21] Freeman and Govil have demonstrated the utility of double-resonance techniques in studying these inner satellite patterns.[22,23] Fortunately, for the metallocenes studied here, sufficient spectral detail was observed in the interior satellite region to permit a fairly reliable determination of the long-range ^{13}C–H coupling parameters without recourse to more advanced techniques.

The values of the ^{13}C–C–H and ^{13}C–C–C–H couplings are essentially constant for the three compounds in this study, indicating that the effect of the metal atom on the long-range coupling is small. The observed values for the latter couplings follow the previously noted trend that the longer range three-bond coupling is usually larger than the two-bond ^{13}C–C–H coupling.[23] Recently the long-range ^{13}C–H couplings in some five-membered heterocyclic rings have become available;[24] our values fall in the same range as those reported. We have tried to correlate these long-range couplings with several commonly used parameters (electronegativity of the heteroatom, directly bonded ^{13}C–H coupling, and inner-ring angles).[25] For the three-bond couplings to the α proton in ferrocene, furan, thiophene, and selenophene, there seems to be a linear relation between the magnitude of these couplings and the intervening inner-ring angle. No satisfactory correlations were obtained for any of the other couplings.

Small long-range ^{13}C isotopic effects on the proton shifts were required in order to account for the slight upfield displacement of the inner satellite lines. These isotopic effects, although small, are undoubtedly real. The values found here are consistent with the differences in the isotopic shifts that have been determined for *p*-dihalobenzenes.[26]

Apparently the three different metal atoms in the compounds studied in this report perturb the cyclopentadienyl rings in the same way, since only minor changes in the spectral parameters are required to fit the pmr spectra. The predominant effect on the coupling parameters that are transmitted through the ring system appears to arise from the geometry of the unsaturated five-membered rings themselves.

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