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## CARBON-13 FT NMR STUDIES OF $^{13}\text{C}$ — $^{57}\text{Fe}$ AND $^{13}\text{C}$ — $^{13}\text{C}$ SATELLITE SPECTRA OF FERROCENE, 1,1'-DIMETHYLFERROCENE AND CYCLOBUTADIENEIRON TRICARBONYL

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### Summary

Natural abundance  $^{13}\text{C}$ — $^{57}\text{Fe}$  and  $^{13}\text{C}$ — $^{13}\text{C}$  satellite spectra obtained from  $^{13}\text{C}$  Fourier transform NMR spectra of ferrocene, 1,1'-dimethylferrocene and cyclobutadieneiron tricarbonyl are reported. Spectral analysis yielded the first determination of  $^{13}\text{C}$ — $^{57}\text{Fe}$  and  $^{13}\text{C}$ — $^{13}\text{C}$  coupling constants in  $\pi$ -complexes, and the one- and two-bond  $^{13}\text{C}$ — $^{13}\text{C}$  ( $^{12}\text{C}$ ) isotope shifts. Calculated  $^{13}\text{C}$ — $^{57}\text{Fe}$  coupling constants, obtained using two MO descriptions for ferrocene, are compared with the experimental values. The one-bond and long-range  $^{13}\text{C}$ — $^{13}\text{C}$  coupling constants are outside the range usually observed for such couplings in aromatic and heteroaromatic compounds.

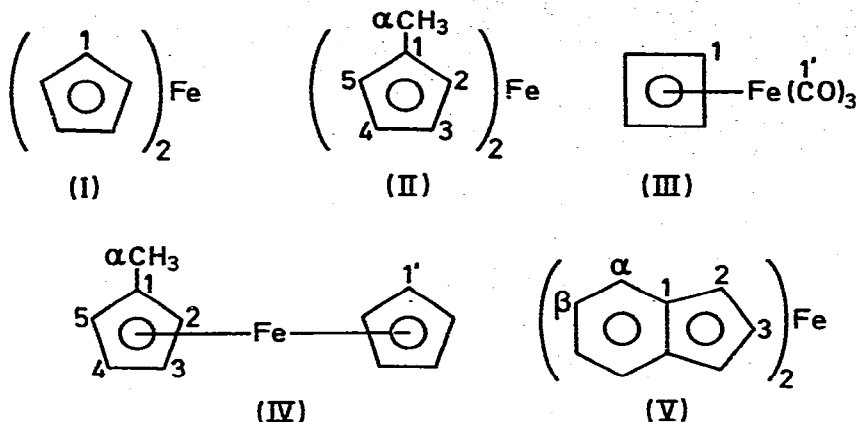
### Introduction

In the last few years numerous studies of spin-spin coupling constants between  $^{13}\text{C}$  and a large number of metals have yielded valuable information about bonding, electronic and geometric structure of organometallic compounds in solution \*\*. These parameters are most conveniently obtained as the splittings (first-order) of the  $^{13}\text{C}$ —metal satellites observed in fully proton decoupled  $^{13}\text{C}$  Fourier transform (FT) NMR spectra. To our knowledge, however, a  $^{13}\text{C}$ — $^{57}\text{Fe}$  coupling constant has been reported for only a single compound ( $\text{Fe}(\text{CO})_5$ ) [2]. Presumably, this is due to the low natural abundance of 2.19% for  $^{57}\text{Fe}$  ( $I = \frac{1}{2}$ ). Thus the degree of difficulty encountered in obtaining  $^{13}\text{C}$ — $^{57}\text{Fe}$  coupling constants from natural abundance  $^{13}\text{C}$  NMR spectra is comparable to that for obtaining  $^{13}\text{C}$ — $^{13}\text{C}$  couplings. A further complication arises in cases where the  $^{13}\text{C}$ — $^{57}\text{Fe}$  coupling is small, i.e. when the  $^{13}\text{C}$ — $^{57}\text{Fe}$  satellites tend to be hidden in the strong main  $^{13}\text{C}$  resonance signal.

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\*\* For a collection of references see ref. 1.

This paper describes the determination of the magnitudes of  $^{13}\text{C}$ — $^{57}\text{Fe}$  coupling constants in ferrocene (I), 1,1'-dimethylferrocene (II), and cyclobutadieneiron tricarbonyl (III) from proton decoupled  $^{13}\text{C}$  FT NMR spectra. The experimentally easier accessible  $^{13}\text{C}$ — $^{103}\text{Rh}$  couplings ( $^{103}\text{Rh}$ : 100% natural abundant,  $I = \frac{1}{2}$ )



have earlier been investigated for some related rhodium olefin complexes\*. Due to the chemical shift non-equivalence of the carbon atoms in II it was necessary to completely analyze the  $^{13}\text{C}$ — $^{13}\text{C}$  satellite spectra in order to unambiguously assign the  $^{13}\text{C}$ — $^{57}\text{Fe}$  satellites for this compound. The results of this analysis, i.e. one-, two-, and three-bond  $^{13}\text{C}$ — $^{13}\text{C}$  coupling constants as well as  $^{13}\text{C}$  induced isotope shifts, are also reported. For monomethylferrocene (IV) and diindenyliron (V) only the  $^{13}\text{C}$  chemical shifts were obtained since the much lower sample concentration available for these compounds prevented observation of the  $^{13}\text{C}$ — $^{57}\text{Fe}$  satellite spectra, except for the cyclopentadienyl ring in IV.

## Experimental

### Materials

All data were obtained from natural abundance  $^{13}\text{C}$  and  $^{57}\text{Fe}$  materials. Ferrocene (I) was synthesized by established procedures and purified by vacuum sublimation. 1,1'-Dimethylferrocene (II), cyclobutadieneiron tricarbonyl(III), and diindenyliron (V) were obtained from Strem Chemicals Inc., Massachusetts, and used without any further purification. The  $^{13}\text{C}$  NMR spectrum of II showed the presence of ca. 11 mol % monomethylferrocene (IV) and ca. 2 mol % ferrocene (I). These impurities, however, did not interfere with the satellite measurements for II and were finally used as internal references for determination of the methyl group substituent effects on the  $^{13}\text{C}$  chemical shifts in II. Sample solutions were ca. 10% w/w in  $\text{CS}_2$ —acetone- $d_6$  (74 and 15% w/w) for I, ca. 31% w/w in  $\text{CS}_2$ —acetone- $d_6$  (52 and 16% w/w) for II, and ca. 30% w/w in acetone- $d_6$  for III. All samples contained ca. 1% w/w TMS. The sample for V was a saturated solution in benzene- $d_6$ . The samples were sealed off under vacuum in 12 mm o.d. tubes.

\* For a collection of  $^{13}\text{C}$ — $^{103}\text{Rh}$  coupling constant see ref. 3.

### <sup>13</sup>C NMR spectra

Proton decoupled <sup>13</sup>C FT NMR spectra were obtained at 25.16 MHz using internal deuterium lock and at a temperature of 33°C on a Varian XL-100-15 spectrometer equipped with a S124-XL Fourier transform accessory and a Varian 620L 16K computer. Free induction decays for each of the carbon resonances were stored into 8 K data points and were transformed to give real spectra of 256 Hz spectral width in 4 K points; i.e. an acquisition time of 16 sec was used throughout. No exponential weighting was applied to the FID's. For coupling constants less than 25 Hz the relative line positions were measured from expanded spectra of spectral width 0.5 Hz/cm with an accuracy of ±0.03 Hz. For larger coupling constants ( $^1J(^{13}\text{C}-^{13}\text{C})$ ) the relative line positions were determined from 1.0 Hz/cm expansions (±0.05 Hz accuracy). Since several of the coupling constants obtained from the <sup>13</sup>C—<sup>57</sup>Fe and <sup>13</sup>C—<sup>13</sup>C satellite spectra were smaller than 5 Hz, the measurements required very good magnet homogeneity (lineshape) [4]. In the present study a linewidth for the central peaks at the satellite level (ca. 1% peak height) of less than 2 Hz was obtained.

<sup>13</sup>C—<sup>13</sup>C AB satellite spectra were analyzed in terms of <sup>13</sup>C—<sup>13</sup>C coupling constants and <sup>13</sup>C chemical shifts (<sup>13</sup>C isotope induced shifts) using a modified version of the iterative LAOCN3 computer program [5].

## Results and discussion

### (a). <sup>13</sup>C NMR spectra

Proton decoupled <sup>13</sup>C NMR spectra of some of the <sup>13</sup>C—<sup>57</sup>Fe and <sup>13</sup>C—<sup>13</sup>C satellites for I, II, and III are shown in Figs. 1–3. Apart from the <sup>13</sup>C—<sup>57</sup>Fe satellites, the spectrum of ferrocene (I) (Fig. 1a) also shows a small peak (\*) on the highfield side of the main signal. This arises from the one-bond <sup>13</sup>C—<sup>13</sup>C satellite spectrum ( $A_2$  spectrum) of I and becomes observable due to a <sup>13</sup>C isotope induced shift. The magnitude of this upfield shift (0.018 ppm; 0.45 Hz at 25.2 MHz) agrees well with the magnitude observed earlier for one-bond <sup>13</sup>C—<sup>13</sup>C(<sup>12</sup>C) isotope shifts [4] and with the values obtained from AB-analysis of the <sup>13</sup>C—<sup>13</sup>C satellite spectra for II (Table 2). No similar isotope shift could be observed from the spectrum of the ring carbons of III which shows slightly broader lines. Isotopic shifts due to <sup>54</sup>Fe and/or <sup>57</sup>Fe were not observed for any of the compounds as would be expected from the recently reported very small magnitude (0.009 ppm) for a <sup>13</sup>C—<sup>34</sup>S(<sup>32</sup>S) isotope shift [4].

The <sup>13</sup>C spectrum of 1,1'-dimethylferrocene (II) shows the presence of some impurities in the spectral regions for the quaternary ring carbon C1 (Fig. 2) and for the protonated ring carbons C2 and C3 (Fig. 3); the spectral region for the methyl carbon (not shown) also shows one impurity peak. Only to a minor degree these impurities disturbed the measurements of the satellite spectra for II and, furthermore, they could be identified as arising from monomethylferrocene (IV) (peak marked C1<sub>IV</sub> in Fig. 2: C1 for IV; peaks marked C2<sub>IV</sub>, C3<sub>IV</sub>, and C1'<sub>IV</sub> in Fig. 3: C2, C3, and cyclopentadienyl carbons for IV) and ferrocene (I) (peak marked C1<sub>I</sub> in Fig. 3). In the satellite spectrum for II (Fig. 2 and 3; methyl region not shown) it was possible to unambiguously assign the lines arising from six out of the total of seven possible <sup>13</sup>C—<sup>13</sup>C AB satellite spectra involving one-, two-, and three-bond <sup>13</sup>C—<sup>13</sup>C coupling constants

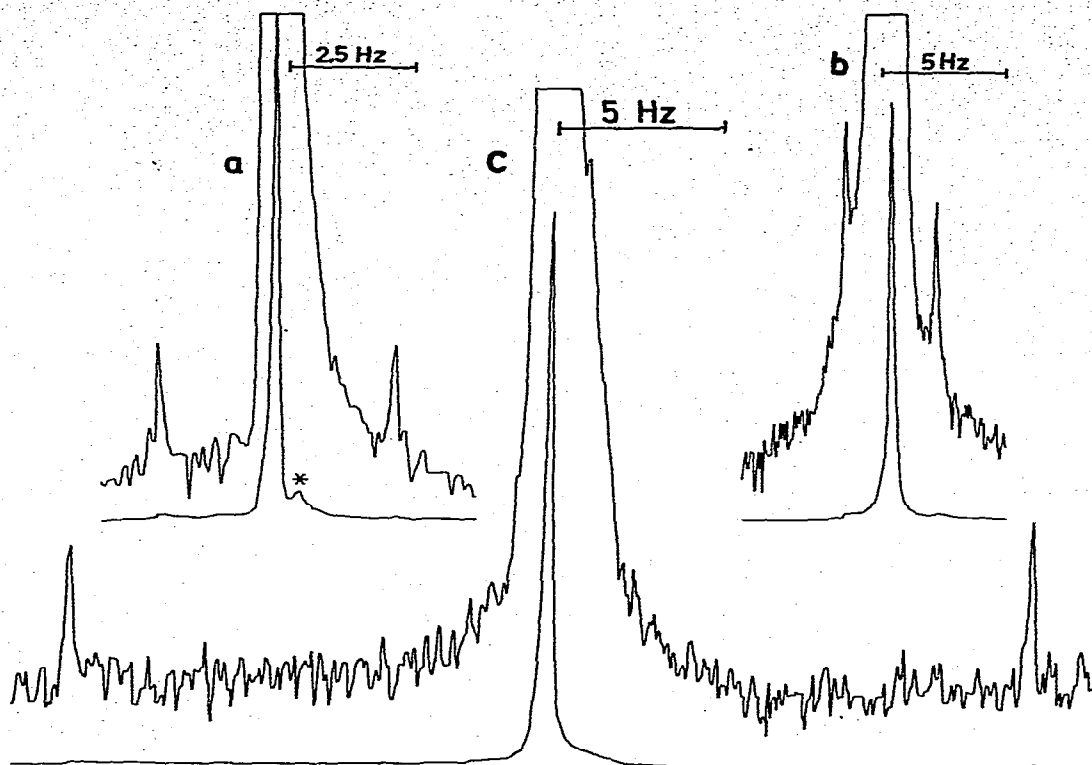


Fig. 1.  $^{13}\text{C}$  FT NMR spectra showing the  $^{13}\text{C}$ - $^{57}\text{Fe}$  satellites obtained for: (a) ferrocene (I), the peak marked with an asterisk (\*) is the one-bond  $^{13}\text{C}$ - $^{13}\text{C}$  ( $^{12}\text{C}$ ) isotope shifted  $^{13}\text{C}$ - $^{13}\text{C}$  satellite spectrum ( $A_2$  spectrum); (b) the ring carbons, and (c) the carbonyl carbons in cyclobutadieneiron tricarbonyl (III).

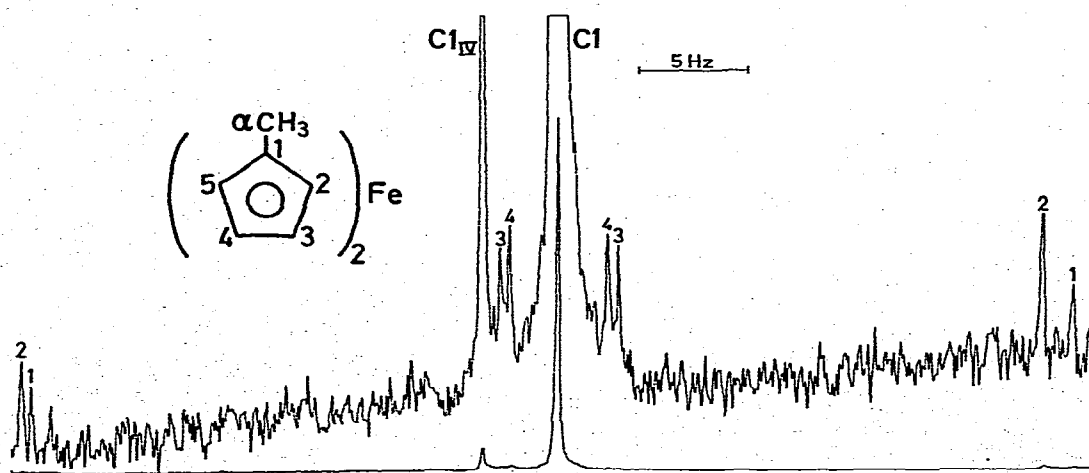


Fig. 2.  $^{13}\text{C}$ - $^{57}\text{Fe}$  and  $^{13}\text{C}$ - $^{13}\text{C}$  satellite spectra for the C1 carbon in 1,1'-dimethylferrocene (II). The numbering of the satellite spectra corresponds to: 1:  $^{13}\text{C}_1$ - $^{13}\text{C}_\alpha$  one-bond satellites; 2:  $^{13}\text{C}_1$ - $^{13}\text{C}_2$  one-bond satellites; 3:  $^{13}\text{C}_1$ - $^{13}\text{C}_3$  two-bond satellites; 4:  $^{13}\text{C}_1$ - $^{57}\text{Fe}$  one-bond satellites. An impurity peak from monomethylferrocene (IV) is marked C1<sub>IV</sub>.

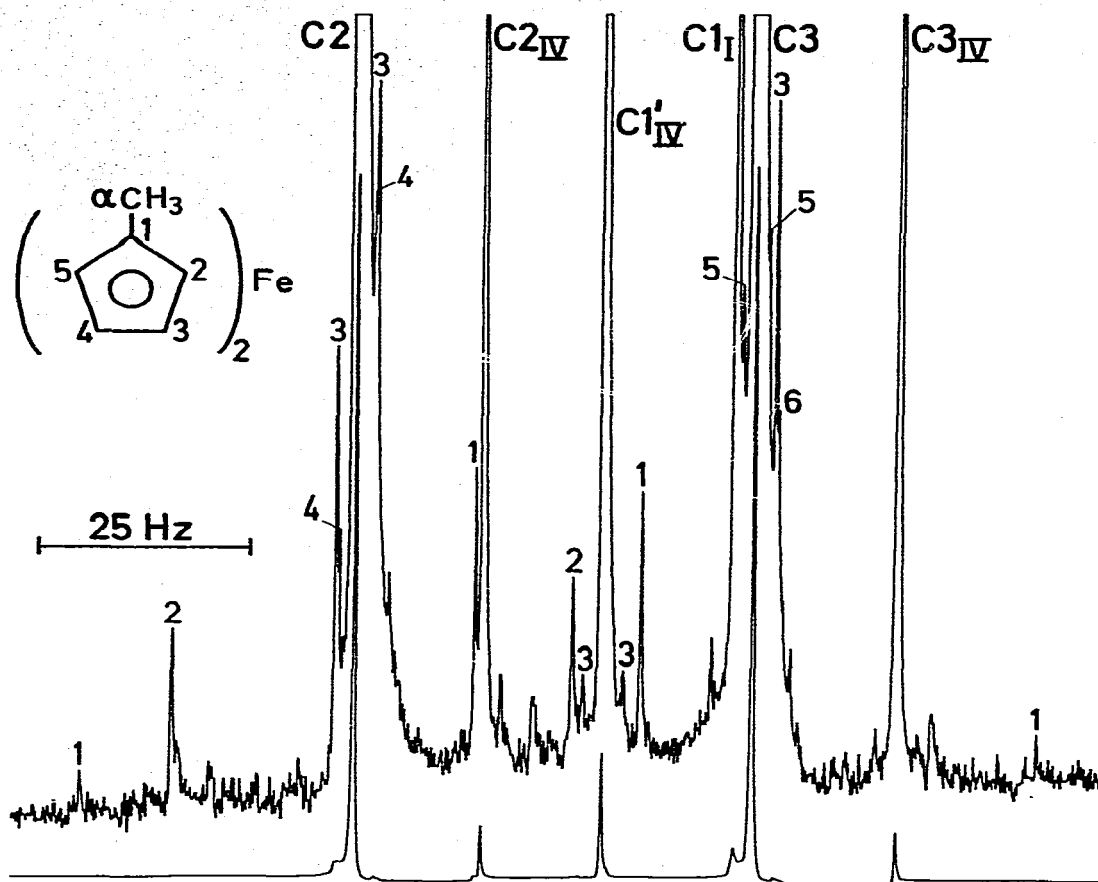


Fig. 3.  $^{13}\text{C}$ - $^{57}\text{Fe}$  and  $^{13}\text{C}$ - $^{13}\text{C}$  satellite spectra for the C2 and C3 carbons in 1,1'-dimethylferrocene (II). The numbering of the satellite spectra corresponds to: 1:  $^{13}\text{C}2$ - $^{13}\text{C}3$  one-bond satellites; 2:  $^{13}\text{C}2$ - $^{13}\text{C}1$  one-bond satellites (only half of the spectrum); 3:  $^{13}\text{C}$ - $^{57}\text{Fe}$  one-bond satellites; 4:  $^{13}\text{C}2$ - $^{13}\text{C}\alpha$  two-bond satellites (half of the spectrum); 5:  $^{13}\text{C}3$ - $^{13}\text{C}\alpha$  three-bond satellites (half of the spectrum); 6:  $^{13}\text{C}3$ - $^{13}\text{Cl}$  two-bond satellite line (only one line is observed due to the impurity peak from ferrocene; see also Fig. 2). Impurity peaks from monomethylferrocene (IV) are C2<sub>IV</sub>, C3<sub>IV</sub>, and C1<sub>IV</sub> and from ferrocene C1<sub>I</sub>.

along with three sets of  $^{13}\text{C}$ - $^{57}\text{Fe}$  satellites for C1, C2, and C3. Only lines for the C2-C4 spectrum (two-bond coupling) could not be unambiguously assigned. Due to the almost similar intensities for the  $^{13}\text{C}$ - $^{13}\text{C}$  and  $^{13}\text{C}$ - $^{57}\text{Fe}$  satellites, an unequivocal assignment of the  $^{13}\text{C}$ - $^{57}\text{Fe}$  coupling constants was only possible after analyses of the  $^{13}\text{C}$ - $^{13}\text{C}$  satellite spectra were complete. The AB analyses of these spectra yielded the  $^{13}\text{C}$ - $^{13}\text{C}$  coupling constants and one- and two-bond  $^{13}\text{C}$ - $^{13}\text{C}$  ( $^{12}\text{C}$ ) isotopic shifts shown in Table 2.

As a result of the  $^{13}\text{C}$ - $^{13}\text{C}$  satellite analyses of II it turns out that the earlier proposed [1] chemical shift assignment for C2(5) and C3(4) in IV must be reversed. The assignment for II is based on the fact that only C2(5) can give rise to two different one-bond  $^{13}\text{C}$ - $^{13}\text{C}$  satellite AB patterns, whereas only one such pattern may be observed for C3(4). The revised assignment was also confirmed using the technique [6] of residual splittings of long-range  $^{13}\text{C}$ - $^1\text{H}$

TABLE 1

EXPERIMENTAL AND CALCULATED  $^{13}\text{C}$ - $^{57}\text{Fe}$  COUPLING CONSTANTS AND  $^{13}\text{C}$  CHEMICAL SHIFTS FOR SOME ORGANOIRON COMPOUNDS <sup>a</sup>

	$(\text{C}_5\text{H}_5)_2\text{Fe}$ (I)	$(\text{CH}_3\text{C}_5\text{H}_4)_2\text{-Fe}$ (II)	$(\text{C}_4\text{H}_4)\text{-Fe}(\text{CO})_3$ (III)	$(\text{CH}_3\text{C}_5\text{H}_4)\text{-Fe}(\text{C}_5\text{H}_5)$ (IV)	$(\text{C}_9\text{H}_7)_2\text{Fe}$ (V)	$\text{Fe}(\text{CO})_5$
$\delta(\text{C1})$	68.20	83.34	65.16	83.47	87.00	
$\delta(\text{C1}')$	68.11 <sup>b</sup>		215.58	68.73		211.9 <sup>d</sup>
$\delta(\text{C2})$		69.89		69.29	61.84	
$\delta(\text{C3})$		68.02		67.35	69.90	
$\delta(\text{C}\alpha)$		14.39		14.78	126.55 <sup>c</sup>	
$\delta(\text{C}\beta)$					122.75 <sup>c</sup>	
$^1J(^{13}\text{C1}-^{57}\text{Fe})$	4.70 (5.24 <sup>e</sup> , 2.06 <sup>f</sup> )	4.56	3.62			
$^1J(^{13}\text{C2}-^{57}\text{Fe})$		4.68				
$^1J(^{13}\text{C3}-^{57}\text{Fe})$		4.83				
$^1J(^{13}\text{C1}'-^{57}\text{Fe})$			28.73	4.70		23.4 <sup>d</sup> (19.2) <sup>g</sup>

<sup>a</sup> Chemical shifts are in ppm downfield from internal TMS with errors within  $\pm 0.01$  ppm; however, the chemical shifts for V were determined relative to internal  $\text{C}_6\text{D}_6$  and converted to the TMS scale using  $\delta(\text{C}_6\text{D}_6)$  127.96 ppm. Coupling constants are in Hz with errors within  $\pm 0.05$  to 0.10 Hz; calculated  $^{13}\text{C}$ - $^{57}\text{Fe}$  coupling constants are given in parentheses. <sup>b</sup> As an impurity in the sample of II. <sup>c</sup> Assignment may be reversed. <sup>d</sup> From ref. 2. <sup>e</sup> Using the MO's of Shustorovich and Dyatkina [18]. <sup>f</sup> Using the MO's of Dahl and Ballhausen [17]. <sup>g</sup> From ref. 19.

coupling constants obtained by off-resonance irradiation. Thus selective decoupling in the region for the ring protons causes larger residual 1 : 3 : 3 : 1 quartet splittings for the C2(5) than for the C3(4) carbons ( $|^3J(\text{C2}-\text{CH}_3)| > |^4J(\text{C3}-\text{CH}_3)|$  [6]). The  $^{13}\text{C}$  chemical shifts for IV were assigned in accordance with those for I and II.

Diindenyliron (V) was found to be only marginally soluble in a number of solvents from which benzene- $d_6$  was finally chosen; consequently only the  $^{13}\text{C}$  chemical shifts were determined for this compound.

Tables 1 and 2 summarize the  $^{13}\text{C}$ - $^{57}\text{Fe}$  and  $^{13}\text{C}$ - $^{13}\text{C}$  coupling constants,  $^{13}\text{C}$  chemical shifts, and  $^{13}\text{C}$ - $^{13}\text{C}$  ( $^{12}\text{C}$ ) isotopic shifts obtained from the  $^{13}\text{C}$  NMR spectra reported here.

### (b). $^{13}\text{C}$ - $^{57}\text{Fe}$ coupling constants

The  $^{13}\text{C}$ - $^{57}\text{Fe}$  coupling constants obtained so far (Table 1) fall into three ranges: (i)  $^1J(^{13}\text{C}-^{57}\text{Fe})$  involving the  $\sigma$ -bonded carbonyl carbons of fluxionally averaged CO groups [7] is approximately 25 Hz, (ii)  $^1J(^{13}\text{C}-^{57}\text{Fe})$  couplings involving  $sp^2$  hybridized carbons in  $\pi$ -complexed ligands lie in the range 3-5 Hz, and (iii) long-range  $^nJ(^{13}\text{C}-^{57}\text{Fe})$  couplings involving side-chain carbons of a  $\pi$ -complexed ligand appear to be too small to be observable ( $< 2$  Hz).

The observation for the  $^{13}\text{C}$ - $^{57}\text{Fe}$  couplings of case (iii) seems reasonable in view of the analysis for the reported proton  $^{13}\text{C}$ - $^1\text{H}$  inner satellite spectra for I [8] and III [9]. Apparently the related  $^1\text{H}$ - $^{57}\text{Fe}$  coupling constants for I and III are also too small to be discernible in these spectra. Thus based on the Karabatsos relationships [10] which are known to work quite well for  $^nJ(^{13}\text{C}-^1\text{H})/{}^nJ(^1\text{H}-^1\text{H})$  couplings [11] e.g.  ${}^nJ(^{13}\text{C}-^1\text{H}) = 0.3 \times {}^nJ(^1\text{H}-^1\text{H})$  for

TABLE 2  
 $^{13}\text{C}$ - $^{13}\text{C}$  COUPLING CONSTANTS AND  $^{13}\text{C}$ - $^{13}\text{C}(^{12}\text{C})$  ISOTOPIC SHIFTS OBTAINED FROM ANALYSIS OF THE  $^{13}\text{C}$ - $^{13}\text{C}$  SATELLITE SPECTRA FOR 1,1'-DIMETHYLFERROCENE (II) <sup>a</sup>

Effect on carbon	Coupling constants <sup>b</sup> and isotopic shifts <sup>c</sup>	Effect from carbon CX			
		C1	C2	C3	C $\alpha$
C(1)	$J(^{13}\text{C}(1)-^{13}\text{CX})$ $\delta(^{13}\text{C}(1)-^{13}\text{C}(^{12}\text{C})\text{X})$		47.20 0.51	5.42 0.09	48.11 0.12
C(2)	$J(^{13}\text{C}(2)-^{13}\text{CX})$ $\delta(^{13}\text{C}(2)-^{13}\text{C}(^{12}\text{C})\text{X})$	47.20 0.45		46.58 0.49	3.97 0.07
C(3)	$J(^{13}\text{C}(3)-^{13}\text{CX})$ $\delta(^{13}\text{C}(3)-^{13}\text{C}(^{12}\text{C})\text{X})$	5.42 0.06	46.58 0.23		3.00 <0.03
C( $\alpha$ )	$J(^{13}\text{C}(\alpha)-^{13}\text{CX})$ $\delta(^{13}\text{C}(\alpha)-^{13}\text{C}(^{12}\text{C})\text{X})$	48.11 0.14	3.97 0.07	3.00 <0.03	

<sup>a</sup> Obtained at 25.16 MHz. Both coupling constants and isotopic shifts are in Hz with errors within  $\pm 0.05$  and  $\pm 0.15$  Hz, respectively. The isotopic shifts are all to lower frequency (high-field) from the main peaks.

<sup>b</sup> The coupling constant  $^2J(^{13}\text{C}2-^{13}\text{C}4)$  could not be unambiguously assigned from the spectra. <sup>c</sup> For comparison, a value of  $0.45 \pm 0.10$  Hz was obtained for the one-bond  $^{13}\text{C}-^{13}\text{C}(^{12}\text{C})$  isotopic shift in ferrocene (see text).

a  $sp^3$  carbon) and also for other  $^nJ(^{13}\text{C}-\text{X})/^nJ(^1\text{H}-\text{X})$  couplings [12] in related model compounds, it is expected that the magnitude of  $^nJ(^{13}\text{C}-^{57}\text{Fe})$  should be even smaller than of  $^nJ(^1\text{H}-^{57}\text{Fe})$ . A related  $^1\text{H}-^{103}\text{Rh}$  coupling constant of 1.0 Hz has been reported for the  $\pi$ -cyclopentadienyl ligand of  $(\text{C}_5\text{H}_5)_2\text{RhCl}$  [13] ( $^{103}\text{Rh}$ : 100% natural abundant,  $I = \frac{1}{2}$ ). However, for the  $(\text{C}_5\text{H}_5)\text{Rh}(\text{C}_2\text{H}_4)_2$  complex the  $^{13}\text{C}-^{103}\text{Rh}$  coupling constant was unresolved for the cyclopentadienyl carbons whereas  $^1J(^{13}\text{C}-^{103}\text{Rh}) = 10$  Hz for the carbons of the ethylene ligands [14]. Similarly,  $^1J(^{13}\text{C}-^{103}\text{Rh})$  was claimed unobservable for the cyclopentadienyl carbons for related cyclopentadienylrhodium complexes [14].

In order to rationalize the magnitude obtained for  $^1J(^{13}\text{C}-^{57}\text{Fe})$  in ferrocene (I) (case ii) we have calculated the Fermi contact contribution, normally considered to be the predominant part [15], to the  $^{13}\text{C}-^{57}\text{Fe}$  coupling in I using the molecular orbital expression [16] given by eq. 1.

$$^1J(\text{C}-\text{Fe}) = (2\pi\hbar)^{-1} \sum_i^{\text{occ}} \sum_j^{\text{unocc}} (16\pi\mu_B\hbar/3)^2 \gamma_C\gamma_{\text{Fe}} \Phi_C^2(0)\Phi_{\text{Fe}}^2(0) \times c_{i\text{Fe}}c_{i\text{C}}c_{j\text{Fe}}c_{j\text{C}}(E_i - E_j)^{-1} \quad (1)$$

where  $\mu_B$  is the Bohr magneton,  $\gamma_X$  is the magnetogyric ratio,  $\Phi_X^2(0)$  is the electron density at the X-nucleus, the  $c$ 's are the LCAO-MO coefficients, and the  $E$ 's are the corresponding energies.  $^1J(^{13}\text{C}-^{57}\text{Fe})$  was calculated for two different sets of wave functions reported for ferrocene [17,18]. These result from MO-calculations [17,18] which differ by the choice of atomic orbitals for the iron atom. The two calculated  $^1J(^{13}\text{C}-^{57}\text{Fe})$  couplings obtained for ferrocene (I) are given in Table 1. The calculated value based on the MO's of Shustorovich and Dyatkina [18] ( $^1J(^{13}\text{C}-^{57}\text{Fe})$  5.24 Hz) is ca. 12% larger than the experimental coupling ( $^1J(^{13}\text{C}-^{57}\text{Fe})$  4.70 Hz) whereas the value based on the MO's of Dahl and Ballhausen [17] is ca. 56% smaller in magnitude.

Introducing a number of approximations into eq. 1, a value of  ${}^1J({}^{13}\text{C}-{}^{57}\text{Fe})$  19.2 Hz has recently been calculated for iron pentacarbonyl [19]; this value is 17% smaller than the experimental value ( ${}^1J({}^{13}\text{C}-{}^{57}\text{Fe})$  23.2 Hz) [2] which is of about the same magnitude as observed for the coupling involving the carbonyl carbons in III. The agreements between the calculated and observed coupling constants for both ferrocene and iron pentacarbonyl are surprisingly good especially when compared to the results usually obtained for calculated carbon-metal coupling constants [19]. With the assumption that the Fermi contact term constitutes the dominant contribution to the  ${}^{13}\text{C}-{}^{57}\text{Fe}$  coupling constant, the calculated values for I indicate that the ferrocene MO's of Shustorovich and Dyatkina [18] give a better approximation to the states containing iron 4s contribution (only these states contribute to the Fermi contact term) than those of Dahl and Ballhausen [17]. However, a reverse indication (at least for some of the other states) is favoured by other types of experimental results [20].

The methyl group substituent effects on the  ${}^{13}\text{C}-{}^{57}\text{Fe}$  coupling in I, as obtained from the experimental results for II, are small ( $<0.2$  Hz) (Table 1). This is consistent with the observations that methyl group substituent effects on coupling constants are in general small for aromatic and heteroaromatic compounds and that substituent effects on  ${}^1\text{H}-{}^1\text{H}$  ring couplings in substituted ferrocenes [21] are small also.

### (c). ${}^{13}\text{C}-{}^{13}\text{C}$ coupling constants

The  ${}^{13}\text{C}-{}^{13}\text{C}$  coupling constants obtained for II (Table 2) appear to be the first report of such couplings in  $\pi$ -cyclopentadienyl ligands. Although the cyclopentadienyl rings in ferrocenes are aromatic in nature [22], the magnitudes for the one-bond ring  ${}^{13}\text{C}-{}^{13}\text{C}$  coupling constants as well as for  ${}^3J({}^1\text{H}-{}^1\text{H})$  [8] differ significantly from the values for other aromatic and heteroaromatic compounds. The magnitudes of the two observable  ${}^1J({}^{13}\text{C}-{}^{13}\text{C})$  couplings for II are about 47 Hz and are the smallest reported so far for aromatic ring carbons. For monosubstituted benzenes [23,24] and five- and six-membered heteroaromatic compounds [23] the one-bond  ${}^{13}\text{C}(sp^2)-{}^{13}\text{C}(sp^2)$  couplings fall in the range 54-70 Hz with the largest magnitudes being observed for  ${}^1J(\text{C}2-\text{C}3)$  in the five-membered heteroaromatics and the smallest for  ${}^1J(\text{C}2-\text{C}3)$  (= 53.8 Hz) in pyridine [23].

Although no regular trend has been observed for the effect of substituents on  ${}^1J({}^{13}\text{C}-{}^{13}\text{C})$  in aromatic compounds (probably due to somewhat erratic values) [23], it is tempting to propose that the low  ${}^1J({}^{13}\text{C}-{}^{13}\text{C})$  values in II originate from the electropositive iron atom and the resulting negative charge density on the cyclopentadienyl ring carbons [25]. Thus phenyllithium has been compared with pyridine (with which it is isoelectronic) in terms of electronegativity effects, since the lithium substituent causes the *ortho*- ${}^1\text{H}-{}^1\text{H}$  coupling ( ${}^3J(\text{H}2-\text{H}3)$ ) to decrease markedly as has also been observed for pyridine [26]. Similarly low  ${}^3J({}^1\text{H}-{}^1\text{H})$  couplings have also been obtained for ferrocene [8] and its derivatives [21]. If the above qualitative comparisons hold, one would predict  ${}^1J({}^{13}\text{C}2-{}^{13}\text{C}3)$  in phenyllithium to be at the low extreme of the range for  ${}^1J(\text{C}2-\text{C}3)$  in monosubstituted benzenes; unfortunately no  ${}^{13}\text{C}-{}^{13}\text{C}$  couplings have been reported for phenyllithium so far.



However, it may also be argued that the magnitudes of the one-bond  $^{13}\text{C}-^{13}\text{C}$  and  $^{13}\text{C}-^1\text{H}$  coupling constants in ferrocenes bear a close relation to the size of the cyclopentadienyl rings. For a number of cyclic compounds these one-bond couplings have been observed to vary systematically with ring size. In this dependence  $^1J(^{13}\text{C}-^{13}\text{C})$  and  $^1J(^{13}\text{C}-^1\text{H})$  show an increasing and decreasing trend, respectively, with an increase in ring size [23]. This effect is observed for the cyclopentadienyl ring carbons in ferrocenes when compared with the data for benzene (benzene:  $^1J(^{13}\text{C}-^{13}\text{C}) = 57.0$  Hz [23] and  $^1J(^{13}\text{C}-^1\text{H}) = 157.5$  Hz [11]; ferrocenes:  $^1J(^{13}\text{C}-^{13}\text{C}) \approx 47$  Hz and  $^1J(^{13}\text{C}-^1\text{H}) = 174.9$  Hz [8,29]). Furthermore, this view may find support in the magnitude observed for the one-bond  $^{13}\text{C}-^{13}\text{C}$  coupling between the ring and the side-chain methyl carbon,  $^1J(^{13}\text{C}_1-^{13}\text{C}_\alpha) = 48.11$  Hz, which is of about 4 Hz larger magnitude than the corresponding coupling in toluene [24] and some of its derivatives [27].

Two-bond  $^{13}\text{C}-^{13}\text{C}$  coupling constants between aromatic ring carbons are smaller than the corresponding  $^3J(^{13}\text{C}-^{13}\text{C})$  couplings in six-membered rings [23]. So far magnitudes of  $^2J(^{13}\text{C}-^{13}\text{C})$  in the series of aromatic and heteroaromatic compounds have been reported for only  $^{13}\text{C}$ -enriched toluene [24] and pyrene [28]. In both studies  $^2J(^{13}\text{C}-^{13}\text{C})$  values less than 2 Hz were reported. For the cyclopentadienyl ring in II  $|^2J(\text{C}_1-\text{C}_3)| = 5.42$  Hz whereas an unambiguous assignment for  $^2J(\text{C}_2-\text{C}_4)$  could not be obtained from the present spectra. The magnitudes of the two- and three-bond couplings between the ring and methyl carbons,  $|^2J(\text{C}_2-\text{C}_\alpha)| = 3.97$  Hz and  $|^3J(\text{C}_3-\text{C}_\alpha)| = 3.00$  Hz, have lower values than the corresponding  $^{13}\text{C}-^1\text{H}$  couplings,  $^2J(^{13}\text{C}_2-^1\text{H}_1) = 6.35$  Hz and  $^3J(^{13}\text{C}_3-^1\text{H}_1) = 7.27$  Hz, obtained for ferrocene (I) from analysis of proton coupled  $^{13}\text{C}$  spectra [29] and proton  $^{13}\text{C}-^1\text{H}$  satellite spectra [8]. The smaller magnitudes of the  $^{13}\text{C}-^{13}\text{C}$  long-range couplings may be accounted for using the Karabatsos relationship [10] although strict application of the Karabatsos proportionality constant (0.3) for  $sp^3$  hybridized carbons yields calculated  $^{13}\text{C}-^{13}\text{C}$  couplings which are slightly too small.

More detailed discussion of the  $^{13}\text{C}-^{13}\text{C}$  coupling constants obtained for II is not warranted because of the inadequacy of the experimental data and will have to await further experimental and theoretical results for these and related molecules.

#### (d). $^{13}\text{C}$ chemical shifts

Apart from the  $^{13}\text{C}$  chemical shifts for II and from reversal of the earlier proposed assignments for the C2 and C3 carbons in IV [1], the  $^{13}\text{C}$  chemical shifts (Table 1) are almost identical to those reported and discussed elsewhere [1]. It should be noted (see Table 1) that the methyl group substituent effects on the protonated ring carbon chemical shifts in IV (I→IV) are additive in predicting the chemical shifts for II. Finally, the relative order of the five-membered ring carbon (C2 and C3) shifts for V is similar to the order for the five-membered ring carbons in azulene but opposite to that expected from substituent effects in aromatic hydrocarbons [30].

#### (e). $^{13}\text{C}-^{13}\text{C}(^{12}\text{C})$ isotope shifts

AB spectral analysis of the  $^{13}\text{C}-^{13}\text{C}$  satellites for II showed that the  $^{13}\text{C}$

atoms separated by one and two bonds consistently exert small mutual high-field (low-frequency)  $^{13}\text{C}$ — $^{13}\text{C}$  ( $^{12}\text{C}$ ) isotope shifts (Table 2). As mentioned earlier (a), a similar one-bond isotope shift was also observed in the  $A_2$   $^{13}\text{C}$ — $^{13}\text{C}$  ( $^{12}\text{C}$ ) satellite spectrum of I. Very few data have been reported for this kind of isotope effect and so far only for the  $^{13}\text{C}$ — $^{13}\text{C}$  ( $^{12}\text{C}$ ) isotope shift through one bond [4]. Although little, if anything, is known about the effect of substituents on these shifts, a value of about 0.02 ppm (0.4–0.5 Hz at 25.2 MHz) appears to be the generally encountered shift through one bond for  $sp^2$ -hybridized ring carbons in aromatic molecules (Table 2 and ref. 4). Apparently the one-bond shift is somewhat smaller for a carbon pair involving an  $\alpha$ -methyl side-chain carbon and its contiguous ring carbon as observed for the  $^{13}\text{C}\alpha(sp^3)$ — $^{13}\text{C}1(sp^2)$  bond in II (Table 2).

The  $^{13}\text{C}$ — $^{13}\text{C}$  ( $^{12}\text{C}$ ) isotope shifts through two bonds, obtained from the analysis and shown in Table 2, are the first report of this kind of isotope shift. Despite their extremely small magnitudes (ca. 0.003 ppm; 0.06–0.09 Hz at 25.2 MHz; i.e. within error limits), it is believed that these shifts are real on the basis of the consistency, the nature of their directional change (high-field shifts), and from the values estimated [4] for two-bond  $^{13}\text{C}$ — $^{13}\text{C}$  ( $^{12}\text{C}$ ) shifts (ca. 0.003 ppm) from a comparison with two-bond  $^{19}\text{F}$ — $^{13}\text{C}$  ( $^{12}\text{C}$ ) isotope shifts (ca. 0.015 ppm) [31]. Finally, it is noteworthy that no isotope shifts were obtained from analysis of the three-bond  $^{13}\text{C}$ — $^{13}\text{C}$  satellite spectra, as would be expected.

## Conclusions

The magnitudes of  $^{13}\text{C}$ — $^{57}\text{Fe}$  spin coupling constants in organoiron  $\pi$ -complexes have been determined from natural abundance  $^{13}\text{C}$  FT NMR spectra. This parameter as well as the  $^{13}\text{C}$ — $^{13}\text{C}$  coupling constants, which may often be obtained simultaneously from the same experimental spectra, appear to be extremely useful in studies of the electronic and geometric structures for such molecules.

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