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Structural characterization of open, half-open, and closed ferrocenes in solution by ^{57}Fe and ^{13}C NMR spectroscopy

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Abstract

Substituted open, half-open and closed ferrocene derivatives have been characterized by ^{13}C and ^{57}Fe NMR spectroscopy. Unsymmetrical substitution of the open pentadienyl moiety, as in (2,3-dimethyl-C_5H_5), leads to the presence of two diastereoisomers, as confirmed by variable temperature ^{13}C NMR spectra or directly by ^{57}Fe NMR spectroscopy at $T = 300$ K. On going from the corresponding closed via the half-open to the open ferrocenes there is a deshielding of the iron nucleus by about 700 and 1100 ppm. This can be rationalized in terms of the $1/\Delta E$ dependence of the paramagnetic shielding term.

Introduction

Recently the area of transition metal pentadienyl chemistry has received growing attention [1,2] and one interesting aspect involves comparing structural data for related open and closed ferrocenes. To date, the structural elucidation of pentadienyl complexes has mainly rested on high resolution ^{1}H and ^{13}C NMR spectroscopy and X-ray analysis [1]. For structural comparisons of open and closed ferrocenes, theoretical calculations such as molecular orbital studies [3,4] as well as photoelectron spectroscopy [3,4], cyclic voltammetry [5], ESR measurements [5], and X-ray structure analysis [1,2] have been employed. In this paper ^{57}Fe NMR data [6] for open, half-open, and closed ferrocenes are presented, and an assessment made of the extent to which they can function as probes for structural properties. Complementary ^{13}C spectroscopic results for these organoiron complexes are also described.

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Results and discussion

The closed ferrocene compounds $(\eta^5\text{-}C_5H_5)_2Fe$ (**1**), $[\eta^5\text{-}C_5H_4(\text{n-butenyl})]_2Fe$ (**2**), $[(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5H_5)]Fe$ (**3**), and $(\eta^5\text{-indenyl})_2Fe$ (**4**) [7 *] as well as of the half-open ferrocene $[(\eta^5\text{-}C_5H_5)(\eta^5\text{-2,4-dimethyl-}C_5H_5)]Fe$ (**5**) [8] were identified by use of ^{13}C and ^1H NMR spectroscopy. The relatively low shielding of the central pentadienyl proton in **5** indicates that, just as in the crystal, the C_7H_{11} ligand possesses the "U" configuration. There is good evidence that in the open ferrocenes the relative orientations of the ligands with respect to rotation around the coordination axis differ by 60°. In particular the X-ray study of the open ferrocene $(\eta^5\text{-2,4-dimethyl-}C_5H_5)_2Fe$ (**6**) showed that in the solid state this complex adopts the *gauche*-eclipsed form (conformation angle 59.7°). The variable temperature ^{13}C NMR spectra indicate that the solution structure of **6** is similar. Because of the symmetric substitution of its pentadienyl ligand, **6** possesses an element of symmetry and both the $\eta^5\text{-dimethyl-}C_5H_5$ moieties are equivalent, leading to a total of seven carbon signals in the low temperature ^{13}C NMR spectrum. This definitely rules out a *syn*- or an *anti*-eclipsed structure which would be favored on the basis of theoretical calculations [3].

A more complex situation is met in $(\eta^5\text{-2,3-dimethyl-}C_5H_5)_2Fe$ (**7**). As a consequence of the presence of the methyl substituents in the 2 and 3 positions and

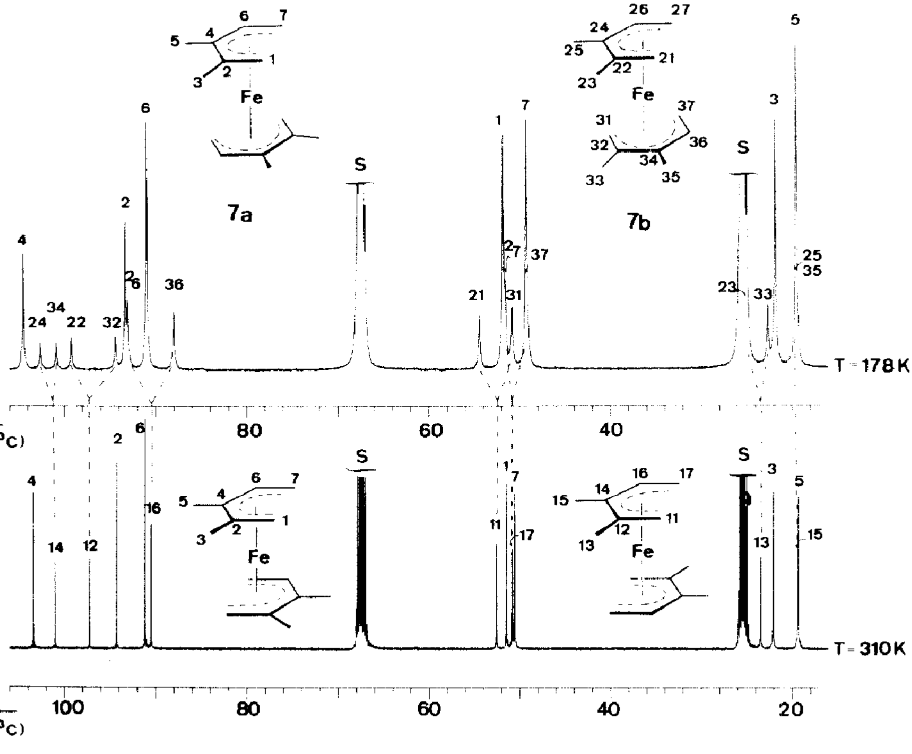

Fig. 1. 100.6 MHz ^{13}C NMR spectra of **7a** and **7b** at $T = 310$ and $T = 178$ K. In the low temperature spectrum the assignment of the signals to individual carbons of one of two ligands of the minor isomer is tentative.

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* Reference number with asterisk indicates a note in the list of references.

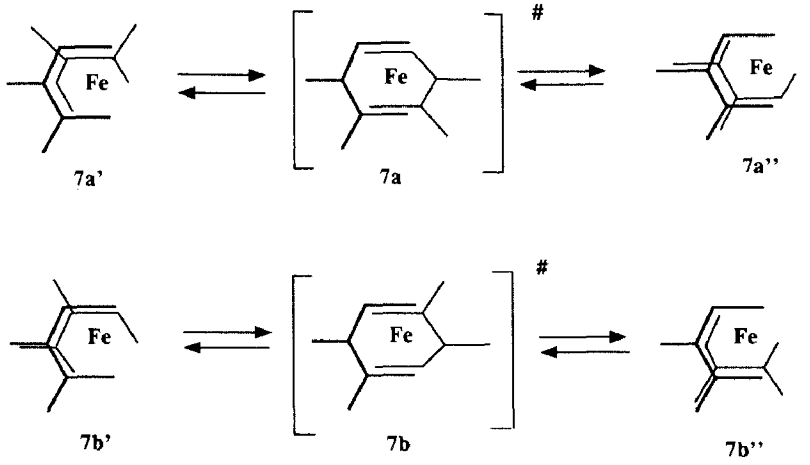
pentadienyl ligand no longer has an element of symmetry and even in presence of fast dynamic processes such as ligand oscillations diastereoisomers may be formed. Thus the 310 K ^{13}C NMR spectrum (cf. Fig. 1) shows that the two isomers **7a** and **7b** are present in the ratio 2/1. Under these conditions each of these isomers yields a set of seven signals with the expected multiplicity and one-bond C,H coupling constants.

When the temperature is lowered the seven resonances of the minor isomer **7b** broaden, and finally at $T = 178$ K a total of fourteen signals is observed. At the same time the signals of the major isomer **7a** remain unaffected except for insignificant shift changes of less than ±1.6 ppm. These findings can be attributed to a slowing down of the ligand oscillations. Since the activation barrier for this process is not much dependent on the number and position of the methyl substituents and the relative orientation of the dienyl ligands [1] it can be assumed that at $T = 178$ K both **7a** and **7b** are within the slow exchange limit. Consequently, in the ground state the major isomer **7a** must possess an element of symmetry, whereas the minor component **7b** adopts a structure in which the two pentadienyl ligands are inequivalent.

If it is assumed that the *gauche*-eclipsed arrangement of the dienyl ligands is also favored in solution, the duplication of the signals for **7b** then can be rationalized as arising from interconversion between the two enantiomers **7b′** and **7b″**. This process can proceed by ligand oscillations in 120° steps involving the *anti*-eclipsed structure **7b** as an intermediate. The barrier for the ligand oscillations, as calculated from the coalescence temperatures and the splittings of the corresponding lines, is 9.1 kcal/mol. This is in good agreement with those found for the corresponding unsubstituted, 3-methyl and 2,4-dimethyl substituted open ferrocenes [1].

The situation for the symmetrical major complex **7a** is still more complex, since for this compound, owing to symmetry considerations, any pair of rotamers will exist diastereomers, each of which possesses an element of symmetry which makes the pentadienyl ligands equivalent. Therefore for each individual diastereoisomer seven distinct ^{13}C resonances are expected. However, at $T = 178$ K, where the ligand oscillations can be assumed to be slow (relative to the NMR time scale), only one set of seven signals for **7a** is observed, (cf. Fig. 1). Careful studies at $B_0 = 9.4$ T down to $T = 168$ K have not revealed any hint of the presence of another diastereoisomer. It can be assumed that the major isomer is **7a′**, and that it adopts the *gauche*-eclipsed conformation with a conformation angle of around 60°. Probably steric repulsions between the methyl groups in the second diastereoisomer **7a″** lead to its destabilization.

The chemical shifts and $^1J(C, H)$ coupling constants for **7a** and **7b** are indicative of the ligand to metal bonding. The highest carbon shieldings are observed for the terminal pentadienyl carbon atoms. These findings are in line with charge density considerations resulting from simple MO pictures and more sophisticated theoretical calculations [3,4]. Selective $^{13}C\text{-}\{^1H\}$ double resonance experiments confirm that at both terminal pentadienyl carbon atoms the $^1J(C, H_{syn})$ coupling constants differ significantly from the $^1J(C, H_{anti})$ couplings (cf. Table 1). As in the case of the simple transition metal η^3-allyl complexes [9], this can be attributed to a partial sp^3 rehybridization of the terminal carbon atoms in order to improve metal–ligand overlap, leading to a tilting of the *anti* protons away from the metal. For the 1- and 5-positions of the pentadienyl ligands, the substituents directed away from one



Scheme 1

another ("*syn*") bend 15–20° down toward the metal atom, while those directed toward each other ("*anti*") bend ca. 45–50° away from the metal [2]. It is noteworthy that the different spatial environment in e.g. bis(η^3-allyl)nickel [9b] leads to less and different bending; thus, in the latter complex the *anti* protons are directed towards the metal by ca. 30° while the *syn* protons are located 6° above the carbon plane. When there are substituents attached at the terminal carbon atoms still more pronounced effects are observed.

Scheme 2 shows the ^{57}Fe shifts for the complexes **1**–**7**. As observed previously for ferrocenes [10] substituents with +I (inductive) effects produce a moderate ^{57}Fe shift to high field; evidently in ferrocene the deshielding per alkyl substituent is about 30 ppm. In contrast, replacement of the two cyclopentadienyl rings by two indenyl residues leads to a deshielding of iron by more than 1000 ppm. In cobalt and rhodium half sandwich complexes a 400 ppm deshielding has been observed upon replacement of one (η^5-C_5H_5) moiety by an (η^5-indenyl) residue [11]. This can understood in terms of the weaker complexation of the indenyl ligand.

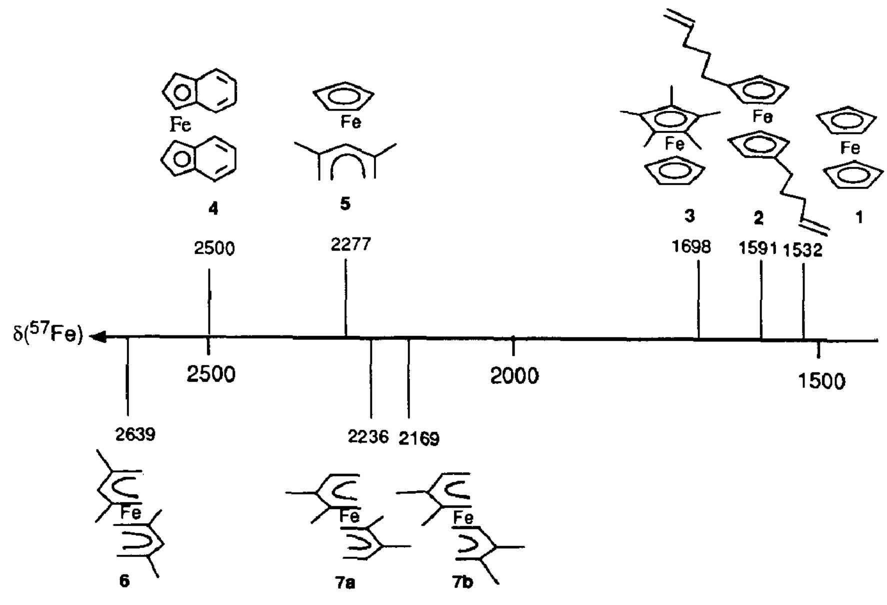
Of particular interest is a comparison of the iron shieldings in **1**, **5** and **6**. Upon replacement of one cyclopentadienyl ring by the corresponding open dienyl ligands

Table 1

^{1}H and ^{13}C NMR data for **7a** and **7b**, dissolved in THF-d_8 at T = 300 K

		1		2	3	4	5	6	7	
7a	$\delta(^1H)$	−1.40 [a]	1.35 [b]		1.76		1.90	3.96	1.54 [a]	3.81 [b]
7b	$\delta(^1H)$	−0.27 [a]	2.44 [b]		1.80		1.90	3.92	0.35 [a]	2.73 [b]
7a	$\delta(^{13}C)$	51.5		94.2	22.0	103.4	19.3	91.1	50.5	
	^1J(C, H)	162 [a]	149 [b]		126		126	157	165 [a]	151 [b]
7b	$\delta(^{13}C)$	52.6		97.2	23.4	101.0	19.3	90.5	50.8	
	^1J(C, H)	162 [a]	150 [b]		126		126	157	165 [a]	154 [b]
7a	$\delta(^{13}C)$ [c]	51.8		93.3	21.8	104.4	19.5	90.9	49.2	
7b	$\delta(^{13}C)$ [c]	54.4		99.1	24.9	102.6	19.5	93.0	51.6	
		51.6		94.4	22.6	100.8	19.5	88.0	49.2	

[a] *anti*-Proton. [b] *syn*-Proton. [c] T = 178 K; for numbering of atoms cf. Fig. 1.



Scheme 2

there is a deshielding of iron by about 700 and 1000 ppm, respectively. It can be assumed that the shift of iron is dominated by the paramagnetic shielding contribution, which according to Ramsey [12] can be expressed as:

$$\delta \sim -\sigma_{para} = \langle r^{-3}\rangle_{d} P_{\mu}/\Delta E$$

To a very rough first approximation it is assumed that both the bond order term P_{μ} as well as the charge density term $\langle r^{3}\rangle_{d}$ do not vary much within the series **1**, **5**, and **6**. In fact INDO-type calculations for **1** and the unsubstituted bis(pentadienyl)iron compound have shown that the net charge at iron is ca. +0.416 and +0.436, respectively [3]. According to these calculations the most prominent feature is the strong destabilization of the HOMO due to ring opening in **5** and **6**. In parallel with the results for the isolated anions, theoretical studies also indicate that **6** has a lower LUMO than **1** [1,3] Thus there is good evidence that the HOMO/LUMO separation deceases on going from ferrocene (**1**) via the half open ferrocenes e.g. **5** to the open dienyl compound e.g. **6**. In line with these results the open ferrocenes have been found to undergo electrochemical oxidation more readily than ferrocene [5]. The redox potential decreases from 0.49 via 0.29 to 0.11 for the series **1**, **5**, and **6**, respectively. Consequently it is concluded that the ^{57}Fe deshielding in the open ferrocenes is essentially governed by the $1/\Delta E$ dependence of the paramagnetic shielding contribution. Although the redox data fit nicely with $\delta(^{57}\mathrm{Fe})$ in **1**, **5**, and **6** a simple quantitative correlation cannot be established [13*].

Similar changes of the iron shielding are also observed in related complexes. In [(η^5-C_5H_5)(η^5-cyclohexadienyl)]iron the metal shift is found at 2267 [6,14], and thus much as for **5** (relative to **1**), there is a deshielding $\Delta\delta$ of roughly 700 ppm. In the quasi-tetrahedral ionic $[(CO)_3FeL]^+BF_4^-$ complexes a regular increase in the deshielding of iron was observed in going from L = cyclopentadienyl ($\delta(^{57}\mathrm{Fe}) = 686$) via L = cyclohexadienyl ($\delta(^{57}\mathrm{Fe}) = 1018$ ppm, $\Delta\delta \sim 350$) to L = η^5-(1-methyl)$_{syn}$-C_5H_6 ($\delta(^{57}\mathrm{Fe}) = 1125$ ppm $\Delta\delta \sim 450$) [15].

The ^{57}Fe NMR spectrum of **7** directly indicates the presence of two isomers. Their shift difference of more than 70 ppm indicates a significant structural difference. This was also judged to be the case from symmetry considerations on the basis of the temperature dependent ^{13}C spectra. Since it was argued above that in both of these compounds the pentadienyl ligands adopt the *gauche*-eclipsed orientation, at the first glance it is striking that in the bis(pentadienyl)iron complexes **6** and **7** the metal chemical shifts vary by more than 400 ppm. The only structural difference between these two complexes results from the position of the methyl substituents. Qualitatively there may be two reasons for the larger shielding of iron in **7a** and **7b**. First, from comprehensive MO calculations and PE spectra it has been concluded that the HOMO in **6** is lower in energy than in 7. Thus in 7 ΔE probably is larger than in **6** and thus in the former complexes there is a higher shielding of iron. Secondly, in an open pentadienyl ligand the electronic charge is essentially centered at positions 1, 3, and 5. Consequently, from charge density considerations one would expect that methyl substitution in the 3 position would produce a higher metal shielding, as is observed for **7a** and **7b**. On the other hand, substitution in the 2 and 4 positions should produce only insignificant metal shift changes.

Although many more ^{57}Fe data have to be collected in order to provide a full understanding of the factors which govern the iron chemical shifts, the data presented here indicate that $\delta(^{57}\text{Fe})$ values sensitively reflect the electronic surroundings of the metal centers in open, half-open, and closed η^5-bonded dienyl iron complexes.

Experimental

Preparation and characterization of the compounds

Standard procedures were employed for the preparation of complexes **1**, **2**, and **4**. The preparations of the complexes **5**, **6**, and **7** are described in Ref. 8. Compound **3** was synthesized by treating $(\eta^5\text{-C}_5\text{H}_5)\text{FeI(THF)}_x$ with pentamethyllithium [16]. ^{13}C NMR: **2** $\delta = 69.0$ (d, 173 Hz, $I = 2$), 68.3 (d, 175 Hz, $I = 2$), 89.1 (s), 29.3 (t, 127 Hz), 31.0 (t, 128 Hz), 34.0 (t, 126 Hz), 138.9 (d, 152 Hz), 114.9 (t, 155 Hz); **3** $\delta = 71.8$ (d), 80.5 (s) and 11.6 (q); **4** $\delta = 70.3$ (d, 175 Hz, $I = 1$), 62.3 (d, 176 Hz, $I = 2$), 87.6 (s, $I = 2$), 123.2 (d, 159 Hz, $I = 2$), 127.1 (d, 163 Hz, $I = 2$).

NMR details

All spectra were recorded on a modified Bruker WH 400 spectrometer. Proton and carbon spectra were obtained by use of conventional pulse techniques. The ^{57}Fe NMR spectra were recorded using a special low frequency (10–20 MHz at $B_0 = 9.4$ T) 10 mm probe head. The 90° iron pulse length was 40 μs. Continuous pulsing with small flip angles was employed. Typical recording times for saturated samples were in the order of 20 h. All iron shifts are shown as δ values relative to $\delta(^{57}\text{Fe(CO)}_5) = 0$ [6,11] as external standard.

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