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DIRECT OBSERVATION OF ^{57}Fe CHEMICAL SHIFTS IN DIAMAGNETIC ORGANOIRON COMPLEXES

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Summary

^{57}Fe NMR spectra of 35 organoiron complexes predominantly of the type $[Fe(CO)_3(diene)]$ have been measured by direct detection at 2.9 MHz and at natural isotope abundance (2.2%). The ^{57}Fe chemical shift range so far observed is 3000 ppm, corresponding to about 9 KHz. The majority of the resonances are at higher frequency than that of $Fe(CO)_5$, which is proposed as a secondary standard. The ^{57}Fe resonance frequencies are also reported as ratios relative to the ^{73}Ge frequency of $GeCl_4$.

The ^{57}Fe shielding is discussed qualitatively in terms of charge distribution in the complexes, very large deshielding effects being observed for cationic olefinic ligands. For η^4-diene complexes, the shielding also depends upon ligand geometry and decreases with increasing ring size or CCC bond angle. Two types of ferrocenylcarbenium ions may be distinguished, indicated by high- or low-frequency shifts relative to ferrocene. For a number of $[Fe(CO)_3(olefin)]$ complexes $^1J(^{57}Fe, ^{13}C)$ coupling constants involving the carbonyl carbon are also reported.

Introduction

The detection of NMR signals of transition metal nuclei with very small magnetic moments and low natural isotope abundance, i.e., with low magnetic receptivity, has become feasible by a combination of suitable pulse-FT-techniques with large diameter sample tubes and, possibly, high magnetic field strengths. Because of the wide distribution of iron in organometallic and

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biological complexes, NMR studies of the ^{57}Fe nucleus ($I = 1/2$, 2.2% abundance) present an interesting challenge to the structural chemist [1]. At a given field strength, however, the receptivity of the ^{57}Fe isotope to NMR detection is only 0.4% of the ^{13}C receptivity. An additional handicap is the very long relaxation times, which means that the widths of the recorded NMR lines are governed by the unavoidable inhomogeneity of B_0 and not by the transverse relaxation time T_2, which gives rise to inhomogeneously broadened NMR lines and a considerable loss of NMR signal intensity. By special steady-state pulse techniques [2], the NMR lines can be broadened to any desired width, and a loss of NMR signal due to the inhomogeneity of the field B_0 can be avoided without addition of paramagnetic reagents to the sample, a technique with well known disadvantages. One of the authors has previously shown [3,4] that the ^{57}Fe resonances of $Fe(CO)_5$ and ferrocene can be detected in the pure liquid or a concentrated solution using steady-state free precession and the Quadriga Fourier Transform technique [5].

A further disadvantage of long relaxation times is the influence of any chemical exchange in the complex under investigation on the transverse relaxation time T_2, as pointed out by Meiboom [6] and by Allerhand and Gutowsky [7]. In this way T_2 of the ^{57}Fe resonance may be shortened by orders of magnitude. For any measuring technique, the ^{57}Fe NMR signal intensity is reduced at least by the factor $(T_2/T_1)^{1/2}$ and, therefore, the ^{57}Fe NMR signal will be too weak to be detectable.

An alternative mode of detection of this very weak resonance is given by heteronuclear double resonance which requires spin coupling of ^{57}Fe to a more sensitive nucleus, for example ^{13}C. Koridze et al. [8,9] have used such ^{13}C-$\{^{57}$Fe$\}$ double resonance experiments on ^{57}Fe enriched samples (80—90%) to obtain chemical shifts of substituted ferrocenes.

We have now initiated an investigation of organoiron complexes with a large variety of ligands by direct observation of the ^{57}Fe nucleus, in order to establish the ^{57}Fe chemical shift scale and to examine the significance of this parameter for structural studies.

Experimental

The ^{57}Fe measurements were performed with a pulse spectrometer, especially developed for investigations of weak NMR signals in the frequency range 1—4.5 MHz [2]. The static field $B_0 = 2.114$ T (corresponding to a 90 MHz proton Larmor frequency) was achieved by a Bruker B-E 45 electromagnet and externally locked on a proton signal by the Bruker NMR stabilizer B-SN 15. The spatial homogeneity of $|\Delta B_0| \leqslant 10^{-6}$ T in the range of the relatively large sample (20 mm inner diameter, 40 mm filling height) was achieved by 12 gradient electric shims. The temperature of the samples was stabilized to (300 ± 1) K by a thermostate.

For all ^{57}Fe investigations, equal, periodic, and coherent rf pulses were applied with a repetition rate of 83 Hz. The pulse spacing T was chosen $T \ll T_2^*$ (the time constant, describing the decay of the transverse magnetization due to the inhomogeneity of B_0) in order to avoid any loss of NMR signal due to this inhomogeneity, cf. p. 381 in ref. 5. To search for the unknown ^{57}Fe

NMR signals in the widespread frequency range 2.910—2.925 MHz, the Quadriga technique [5] was used; the flip angle of the rf pulses was chosen ~60° (this is the optimum value for the ratio $T_1/T_2 = 2$). As all the ^{57}Fe NMR spectra consisted of one single NMR line, an accurate determination of the resonance frequency ν_L was achieved in a single steady-state free precession experiment, with the irradiation frequency ν_E fulfilling the condition $\nu_L - \nu_E = (n + 1/2)/T = (n + 1/2) \times 83$ Hz (n = integer number), and with the optimum flip angle [10] resulting from the estimated ratio T_1/T_2. Depending on the concentration of the samples (3—0.1 M) and the ratio T_1/T_2, measuring times from 2 hours up to 4 days were necessary to achieve a signal-to-noise ratio of at least 10.

Thus it is not advisable to refer the ^{57}Fe resonance frequencies to that of a ^{57}Fe standard. The ^{73}Ge NMR frequency of $GeCl_4$ (~3.139 MHz), which is independent of temperature, and which is referred to the Larmor frequency of ^{2}H in D_2O with high accuracy [4], was used as standard; the spectrometer can be tuned to the ^{73}Ge resonance frequency within less than 5 minutes. To determine the ratios of the Larmor frequencies $\nu(Fe)/\nu(Ge)$, the sample replacement technique was used; for each sample at least 8 frequency ratios were determined.

The following compounds were obtained from commercial sources: $Fe(CO)_5$, $Fe_3(CO)_{12}$ and ferrocene (Fluka), [$Fe(CO)_3$(cyclobutadiene)], [$Fe(CO)_3$-(1,3-cyclohexadiene)], [$Fe(CO)_3$(butadiene)], [$Fe(CO)_2(C_2H_5)]_2$ (Strem Chemicals, Inc.), [Fe(CO))butadiene)$_2$] (Emser Werke). Gifts of samples of [$Fe_2(CO)_6$(tetracyclopropylbutatriene)] (Prof. S. Sarel, Hebrew University, Jerusalem), acetylferrocene and benzoylferrocene (Dr. F. Köhler, Technische Universität, München), triferrocenylcyclopropenium tetrafluoroborate (Prof. I. Agranat, Hebrew University, Jerusalem) and diferrocenylmethylium tetrafluoroborate (Prof. M. Cais, Technion, Haifa) are gratefully acknowledged.

All other complexes were synthesized by literature procedures, the relevant references being given in Tables 1 and 2. Slight modifications are described in ref. 11.

The compounds were dissolved under an inert gas atmosphere in the appropriate solvent and filtered directly into the sample tube (Pyrex ampoule, 22 mm o.d., 20 mm i.d.) through alumina, silicagel or microcrystalline cellulose. Afterwards, the samples were degassed by several freeze-thaw cycles and sealed.

Results

The iron complexes investigated may be divided into derivatives of pentacarbonyliron of the general type [$Fe(CO)_{5-n}(en)_n$] and complexes containing cyclopentadienyl ligands. In some cases the olefinic ligand exhibits cyclic π-electron delocalisation, as for example in [$Fe(CO)_3$(cyclobutadiene), [$Fe(CO)_3$(tropone)], [$Fe(CO)_3$(6,6-diphenylfulvene)], and in the ferrocene derivatives. Octahedral iron(II) complexes were also investigated, but only in the case of $K_4[Fe(CN)_6]$ was a signal observed.

The chemical shift data observed so far span a range of about 3000 ppm, corresponding to 9 kHz in a field of 2.114 Tesla. $K_4[Fe(CN)_6]$ has the highest resonance frequency so far detected, whereas that of [$Fe(CO)_3$(cyclobuta-

(Continued on p. 216)

TABLE 1

^{57}Fe CHEMICAL SHIFTS OF IRON CARBONYL COMPLEXES

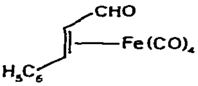
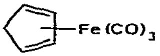
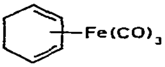
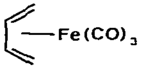
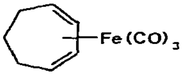
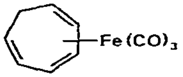
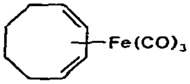
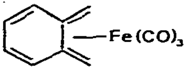
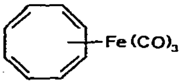
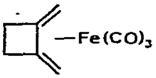
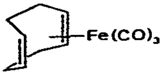
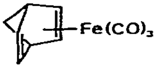
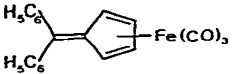
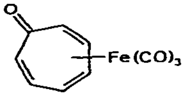
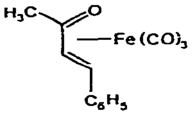
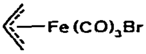
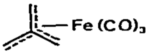
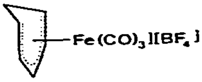
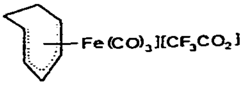
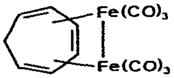
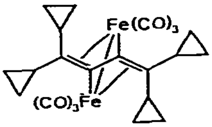
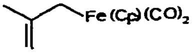
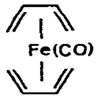
Compound	Ref. a)	Solv., Conc. (*M*)	ν(Fe)/ν(Ge) b)	δ(Fe)(ppm)
$Fe(CO)_5$	c)	neat CS_2, 2.5 CS_2	0.928 155 42(15) 0.928 173 3 (3)	0 +19.3 ± 0.3 +19.2 d)
$Fe_3(CO)_{12}$	c)	CH_2Cl_2, 0.08	e)	
$Fe(NO)_2(CO)_2$	13	C_6H_6, 1.1	e)	
	14	CH_2Cl_2, 0.4	0.928 164(4)	+9.2 ± 4
	c)	C_6H_6, 0.7	0.927 614 1 (15)	—583.2 ± 1.5
	15	C_6H_6, 0.51	0.928 327 4 (18)	±185.3 ± 2
	c)	C_6D_6, 3.0 CS_2	0.928 087 8 (4)	—72.9 ± 0.4 —43.2 d)
	c)	C_6H_6, 2.9 C_6D_6, 2.9 C_6H_6, 0.35 CH_2Cl_2, 0.35	0.928 155 95(40) 0.928 155 4 (4) 0.928 154 3 (15) 0.928 151 2 (14)	+0.6 ± 0.4 0.0 ± 0.4 —1.2 ± 1.5 —4.5 ± 1.4
	16	C_6H_6, 0.52	0.928 235 6 (9)	+86.4 ± 1
	16	C_6H_6, 0.83	0.928 312 8 (10)	+169.6 ± 1
	17	C_6H_6, 0.52	0.928 312 7 (40)	+169.4 ± 4
	18	C_6H_6, 0.47	0.928 427 5 (10)	+293.2 ± 1
	19	C_6H_6, 0.67	0.928 434 3 (9)	+300.5 ± 1
	20	C_6H_6, 1.5	0.928 459 0 (15)	+327.1 ± 1.5

TABLE 1 (continued)

Compound	Ref. [a]	Solv., Conc. (M)	ν(Fe)/ν(Ge) [b]	δ(Fe)(ppm)
	17	C_6H_6, 0.58	0.928 508 5 (12)	+380.4 ± 1.5
	21	C_6H_6, 0.60	0.928 510 0 (10)	+382.0 ± 1
	22	C_6H_6, 0.6	0.928 702 3 (20)	+589.2 ± 2
	23	C_6H_6, 1.0	0.928 943 7 (15)	+849.3 ± 1.5
	24	C_6H_6, 0.6	0.929 604 8 (15)	+1561.6 ± 1.5
	25	C_6H_6, 0.55	0.929 574(3)	±1528 ± 3
	26	C_6H_6, 1.3	0.928 084 2 (8)	−76.7 ± 0.8
		CF_3COOH		+1127.8 [d]
	22	CF_3COOH, 0.8	0.929 014 5 (7)	+925.6 ± 0.7
	27	CH_2Cl_2, 0.16	0.928 367 3 (25)	+228.3 ± 2.5
	28	C_6H_6, 0.21	0.928 600 6 (8)	+479.6 ± 0.8
		CS_2		+959.1 [d]
[Fe(Cp)(CO)$_2$]$_2$	c)	CH_2Cl_2, 0.3	e)	
	c)	C_6H_6, 0.75	0.929 465 7 (5)	+1411.7 ± 0.5

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[a] References refer to the synthesis of the complexes. [b] The reported uncertainties correspond to the threefold standard deviation. [c] Commercially available. [d] Reported in refs. 8 and 9 and recalculated relative to Fe(CO)$_5$ with the aid of the formula

$$\delta(Fe(CO)_5) = \delta(\text{Ferrocene}) \times 1.00156 + (1560.06 \pm 0.4)\ \text{ppm}$$

These chemical shifts were not obtained at the standard temperature of 300 K. [e] A signal could not be observed.

diene)] lies at the low frequency end of the scale. The ^{57}Fe resonances are expected to extend beyond the range so far observed, but the ^{59}Co data suggest that the chemical shifts of higher oxidation states of iron will lie on the high frequency side of $[Fe(CN)_6]^{4-}$. For this reason, we chose $Fe(CO)_5$ as a secondary reference, since this leads to positive values for the majority of chemical shifts. $Fe(CO)_5$ can be measured as a neat liquid, thus avoiding uncertainties due to medium effects. The temperature coefficient has been shown previously to be very small [3], amounting to ca. +0.5 ppm/K. Our data are referred to a temperature of 300 K. On the other hand, the literature data on substituted ferrocenes [8,9] are reported relative to ferrocene dissolved in CS_2. These authors have also reported the iron Larmor frequency of their standard relative to the deuterium frequency of D_2O ($\nu(Fe)/\nu(D) = 0.2113157$). This result, however, is in disagreement with the frequency ratio obtained by our direct measurement ($\nu(Fe)/\nu(D) = 0.21125713(8)$) of ferrocene in CS_2. The chemical shifts as referred to $Fe(CO)_5$ as a standard are collected in Tables 1 and 2.

Because of the variable solubility of the complexes and the experimental requirements of relatively high concentrations, we used benzene and methylene chloride as solvents. The medium effect for these two solvents has been investigated in the case of $[Fe(CO)_3(butadiene)]$, as well as the concentration dependence in the range of 0.35 to 3.0 *M*. Whereas the concentration dependence

TABLE 2

^{57}Fe CHEMICAL SHIFTS OF FERROCENE DERIVATIVES

Compound	Ref. [a]	Solv., Conc. (*M*)	$\nu(Fe)/\nu(Ge)$ [b]	$\delta(Fe)$(ppm)
Ferrocene	[c]	THF, 1.0	0.929 580 3(6)	+1535.2 ± 0.6
		CS_2	0.929 603 4(4)	+1560.1 ± 0.4
		C_6H_6	0.929 577 7(8)	+1532.4 ± 0.8
1-Acetylferrocene	29	THF, 1.0	0.929 785 4(7)	+1756.1 ± 0.7
		CH_2Cl_2		+1775.9 [d]
1-Benzoylferrocene	30	THF, 0.5	0.929 833 6(7)	+1808.1 ± 0.7
1,1'-Diacetylferrocene		CH_2Cl_2		+1986.4 [d]
[Triferrocenylcyclopropenium][BF_4]	31	CH_2Cl_2 0.32	0.929 920 0(14)	+1901.2 ± 1.4
$[(Fc)_2CH][BF_4]$ [f]	32	CH_2Cl_2, 0.08	0.930 266 6(25)	+2274.6 ± 2.5
$[FcCHCH_3][HSO_4]$		H_2SO_4		+1340.5 [d]
$[FcCH_2][HSO_4]$		H_2SO_4		+1035.7 [d]
$[Fe(Cp)_2(H)][BF_3OH]$		$BF_3 \cdot H_2O$		+459.5 [d]
$K_4[Fe(CN)_6]$	[c]	H_2O(pH 12.6), 1.0 [g]	0.930 473 0(10)	+2497.0 ± 1
$[Fe(H_2O)_6][SO_4]$	[c]	H_2O(pH 1.0), 1.0	[e]	
$Na_2[Fe(CN)_5(NO)]$	[c]	H_2O, 1.3	[e]	

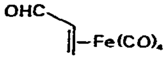
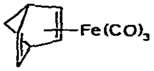
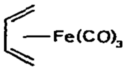
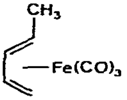
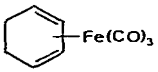
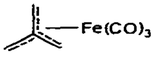
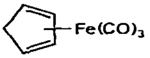
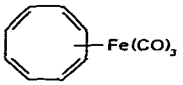
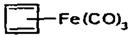
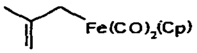
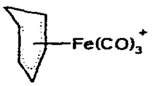
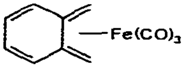
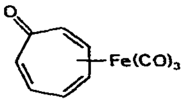
[a] References refer to the synthesis of the complexes. [b] The reported uncertainties correspond to the threefold standard deviation. [c] Commercially available. [d] Reported in refs. 8 and 9 and recalculated relative to $Fe(CO)_5$ with the aid of the formula

$$\delta(Fe(CO)_5) = \delta(Ferrocene) \times 1.00156 + (1560.06 \pm 0.4)\ ppm$$

These chemical shifts were not obtained at the standard temperature of 300 K. [e] A signal could not be observed. [f] Fc = ferrocenyl. [g] Measured at 318 K.

TABLE 3

^{57}Fe, ^{13}C COUPLING CONSTANTS

Compound	^1J (Hz)	δ(CO) (ppm)	Temp. (K)	Solvent	Ref.
$Fe(CO)_5$	23.31 23.4 ± 0.4	211.5 211.9	303 —	CS_2 C_6F_6	9 33
	23.0 ± 0.2	207.6	258	$CHFCl_2$	
	26.4 ± 0.1	216.7	253	CD_2Cl_2	
	27.7 ± 0.3	212.9	300	C_6D_6	34
	27.9 ± 0.5	213.3	300	C_6D_6	34
	28.0 ± 0.5 27.95	212.7 212.7	300 303	C_6D_6 CS_2	34 9
	28.5 ± 0.1	212.2	245	CD_2Cl_2	
	28.6 ± 0.1	212.3	280	C_6D_6	
	28.6 ± 0.2	212.6	300	C_6D_6	
	28.73 ± 0.1	215.6	—	C_6D_6	35
	30.15	223.1	243	CS_2	9
	28.69 [a] 25.73 [b]	200.8 [c]	198	CF_3CO_2H	9
	32.0 ± 0.2 [a] 26.8 ± 0.2 [b]	217.1 208.0	204	CD_2Cl_2	
	31.5 ± 0.2 [a] 24.5 ± 0.2 [b] 24.5 ± 0.2 [b]	214.3 205.4 204.2	213	CD_2Cl_2	

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[a] Apical ligand with respect to the tetragonal pyramidal structure. [b] Basal ligand. [c] Only averaged value reported.

was found to be within the experimental error of the chemical shift determination (±1 ppm), the solvent effect $\Delta\delta_{C_6H_6}^{CH_2Cl_2}$ is about —3 ppm. Even larger solvent effects were observed for the iron resonance of ferrocene measured in C_6H_6, THF and CS_2, $\Delta\delta_{C_6H_6}^{CS_2} = +28$ ppm, $\Delta\delta_{C_6H_6}^{THF} = +3$ ppm, respectively. Temperature effects on the chemical shifts depend, as expected, on the nature of the solvent and, for ferrocene, were found to be +0.5 ppm/K (CS_2), +0.6 ppm/K (THF) and +0.9 ppm/K (C_6H_6). A larger effect was observed for $K_4[Fe(CN)_6]$ in water (1.9 ppm/K). The solvent isotope effect for $[Fe(CO)_3(butadiene)]$ in C_6H_6 and C_6D_6 respectively, is less than 1 ppm.

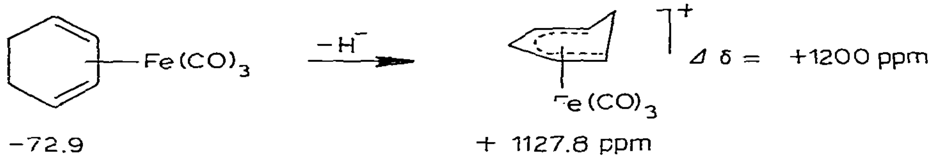
In the following cases we were not successful in observing ^{57}Fe signals: $Fe_3(CO)_{12}$, $[Fe(CO)_2(NO)_2]$, $[Fe(CO)_2(C_5H_5)]_2$, $[Fe(H_2O)_6][SO_4]$, and $Na_2[Fe(CN)_5NO]$. These negative results are probably due to unfavourable T_2/T_1 ratios. As mentioned above, T_2 may be drastically reduced by chemical exchange processes, which are known to occur for the first two species given above. ^{57}Fe signals considerably weaker than expected from the iron concentration were observed for $[Fe(CO)_4(cinnamic\ aldehyde)]$ and $K_4[Fe(CN)_6]$. For the first complex an exchange process has been reported [12] whereas the iron(II) in $K_4[Fe(CN)_6]$ may be involved in a redox equilibrium with traces of iron(III). A very small flip angle (~10°) was required in this experiment and hence it can be concluded that in this case also a small T_2/T_1 ratio is responsible for the weak signal. The redox-equilibrium argument can also be advanced to explain the missing signal in the cases of $[Fe(H_2O)_6][SO_4]$ and $Na_2[Fe(CN)_5NO]$.

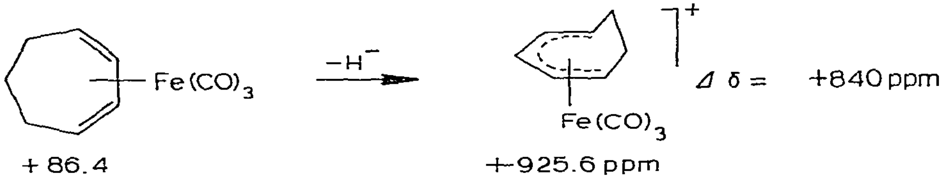
The spin quantum number of the ^{57}Fe isotope ($I = 1/2$) allows the determination of scalar coupling constants to other nuclei, e.g., ^{13}C. Such data can in principle be obtained from the ^{13}C spectrum, but without ^{57}Fe labelling the observation is confined to large one-bond interactions as observed for σ-bonded ligands. If labelled substrates are available, small interactions can also be detected, for example coupling to π-bonded carbon atoms [8,9]. ^{57}Fe, ^{13}C coupling constants between iron and σ-bonded CO are summarized in Table 3.

Discussion

In the discussion of ^{57}Fe chemical shifts in iron carbonyl complexes, $Fe(CO)_5$ constitutes a convenient starting point, since, at least formally, the five CO groups can be successively replaced by olefinic ligands. Such substitutions lead to very small changes in the chemical shift for $[Fe(CO)_4(cinnamic\ aldehyde)]$ (+9.4 ppm) and $[Fe(CO)_3(butadiene)]$ (0.0 ppm). Within the large class of complexed 1,3-diene hydrocarbons, however, there is a considerable spread of the chemical shifts over a range of several hundred ppm which indicates a substantial perturbation of the electronic structure of the metal by the structure of the ligand. Even larger effects on the ^{57}Fe shift occur if the ligand serves as a strong electron acceptor. Typical examples are $[Fe(CO)_3(tropone)]$ (+849 ppm) and $[Fe(CO)_3(1\text{-phenylbuten-2-one})]$ (+1562 ppm). A special type of electron acceptor is the cyclopentadienyl ligand, which tends to achieve the aromatic 6π electron structure of the cyclopentadienyl anion. The resonances of $Fe(C_5H_5)$ systems are generally observed above 1000 ppm.

There is also a clearly defined resonance range for substituted ferrocenes (+1535 to 1986 ppm) and again, substitution of the Cp ring by electronegative groups leads to deshielding affects of the iron nucleus, e.g., ferrocene (+1535 ppm), 1-acetylferrocene (+1756 ppm, $\Delta\delta$ = +221 ppm), 1,1-diacetylferrocene (+1986 ppm, $\Delta\delta$ = +431 ppm [9]). For the resonance of the triferrocenylcyclopropenium cation (+1901 ppm) a similar effect is observed, and the diferrocenylmethylium cation is even further deshielded (+2275 ppm). These findings suggest a correlation with the positive atomic charge of the iron atom, which is further substantiated by the deshielding of 1200 ppm and 840 ppm upon formation of the cations from the 1,3-cyclohexadiene and 1,3-cycloheptadiene complexes:





Finally, a typical Fe^{2+} species, $K_4[Fe(CN)_6]$, shows the most strongly deshielded iron resonance in our chemical shift table (+2497 ppm). The fact that changes in the iron atomic charge appear to be responsible for the large chemical shift effects within our series of organoiron complexes is reminiscent of the results obtained from ^{59}Co NMR studies on a large number of cobalt complexes (cf. [1], p. 225 ff.).

On the other hand, it can be expected that the extent of $p\pi$—$d\pi$ overlap between ligand and metal orbitals will affect the ^{57}Fe shielding constants. This effect appears to govern the detailed shielding of the iron nucleus in the large family of $[Fe(CO)_3(\text{diene})]$ complexes where the shielding constant increases with a decrease in the ring size of the diene, or with a decrease in the CCC bond angle of the s-*cis* diene system: 1,2-Bis(exomethylen)-cyclobutane (+327.1), 1,3-cyclooctadiene (+169.4), 1,3-cycloheptadiene (+86.4), 1,3-cyclohexadiene (—72.9), cyclobutadiene (—583.2 ppm) (Table 1). Whether the high shielding value of the iron complexing the four-membered ring in tricarbonyl(cyclobutadiene)iron can be attributed solely to this effect cannot be decided at present, since there is no reliable information available about the π-electron charge distribution between ligand and metal in this compound *. On the other hand, the observed chemical shifts of $[Fe(CO)_3(\text{cyclooctatetraene})]$ (+300.5 ppm), $[Fe(CO)_3(\text{1,2-bis-exomethylene-cyclohexadiene})]$ (+293.2 ppm), and $[Fe(CO)_3(\text{cycloheptatriene})]$ (+169.6 ppm) illustrate that additional, formally

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* Ab initio SCF-MO and extended CNDO/2 calculations [36] indicated a positive charge on the metal and a negative charge on the diene ligand.

conjugated double bonds cause a decrease in the ^{57}Fe shielding. A further increase in the ^{57}Fe resonance frequencies occurs when the Fe(CO)$_3$ moiety has to bridge a 1,4- or 1,5-diene system, e.g., in [Fe(CO)$_3$(norbornadiene)] (+382.0 ppm) and [Fe(CO)$_3$(1,5-cyclooctadiene)] (+380.4 ppm). The ring-size effect has also been observed recently in the ^{59}Co and ^{103}Rh chemical shifts of similar diene complexes [37] and, therefore, appears to be a general shielding phenomenon in this class of transition metal complexes *.

[Fe(CO)(butadiene)$_2$] may be formally derived from Fe(CO)$_5$ in the same way as [Fe(CO)$_3$(butadiene)], its ^{57}Fe chemical shift, however, is not observed in the expected range but exhibits a deshielding effect of 1412 ppm relative to Fe(CO)$_5$ and [Fe(CO)$_3$(butadiene)]. This result cannot be rationalized on the basis of a simple successive ligand substitution and so has been discussed in terms of another model for the binding between conjugated dienes and transition metals [11].

An unexpected shielding effect of the ^{57}Fe resonance has been reported [8,9] for the ferrocenylcarbenium ions [FcCH$_2$][HSO$_4$] (+1036 ppm) and [FcCHCH$_3$][HSO$_4$] (+1341 ppm) which are observed on the low-frequency side of ferrocene, in contrast to the diferrocenylmethylium ion [(Fc)$_2$CH]-[BF$_4$] (+2275 ppm) which appears on the high-frequency side of ferrocene (+1535 ppm). The structure of the [(Fc)$_2$CH]$^+$ ion has been investigated by X-ray, Mössbauer spectroscopy and ESCA, and the result compared with extended Hückel calculations (cf. refs. 38, 39). The observed ^{57}Fe chemical shift suggests that we are dealing with a ferrocene structure in which the carbenium ion acts predominantly as an electronegative substituent. X-ray diffraction has shown [32,38] that the crystal structure of the [(Fc)$_2$CH]$^+$ ion has a pseudo-twofold symmetry axis bisecting the C(α)—CH—C(α') carbon atoms. The two ferrocene units are *trans*-oriented with a slight bending of the carbenium carbon out of the plane of the Cp ring towards the Fe atoms and with different Fe, CH distances of 287 and 269 pm. Since, however, proton spectra clearly show rapid rotation at room temperature of the ferrocene units about the two C(α)—CH bonds, the observation of only one ^{57}Fe resonance is to be expected.

The large shielding effects observed in going from ferrocene to the cations [FcCH$_2$]$^+$ ($\Delta\delta$ = —500 ppm) and [FcCHCH$_3$]$^+$ ($\Delta\delta$ = —194 ppm) cannot be explained on the basis of substituent effects. They could be a direct consequence of the transformation of one cyclopentadienyl ring into a fulvene-type ligand (cf. Table 1) [39] with a concomittant increase in the bending of the carbenium carbon towards the iron atoms. This was predicted by Herbstein et al. [32] for monoferrocenylcarbenium ions, and is actually observed in the case of tricarbonyl(diphenylfulvene)chromium [40]. Thus, the ^{57}Fe chemical shift data seem to allow a differentiation between two types of ferrocenyl carbenium ions.

The very large chemical shift range observed in ^{57}Fe NMR of olefinic complexes sharply contrasts with the rather small effects which have been observed for the isomer shifts in Mössbauer spectra [41,42]. This applies both to neu-

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* [Fe(CO)$_3$(cyclopentadiene)] (+185.3 ppm) appears to be an exception, since the Fe resonance would be expected at negative δ-values (corresponding to higher shielding).

tral and cationic species, and it thus appears that in this class of organometallic compounds ^{57}Fe shielding constants are more sensitive to metal—ligand bonding effects.

One-bond ^{57}Fe, ^{13}C coupling constants are expected to reflect the type of bonding between iron and carbon. In fact, the observed values for predominantly σ-bonded carbon ligands are considerably larger than those for π-bonded ligands. The coupling constants for Fe—CO bonds lie in the range of 23—32 Hz whereas those to π-bonded carbons are found below 6 Hz [9]. Because of the dynamic nature of the iron carbonyl complexes the data obtained for the Fe—CO bond (Table 3) are averaged values. These data exhibit only a very small variation and structural dependence. Individual ^1J(Fe, C) values have been determined at low temperature for [$Fe(CO)_3$(tropone)] and [$Fe(CO)_3$(1,2-bis-exomethylene-cyclohexadiene)]. The assignment of the Fe—CO resonances can be derived from chemical shift and intensity arguments, and consequently the larger coupling constants (>30 Hz) can be attributed to the interaction of iron with the apical CO ligand. In the case of the tropone complex we observe a value of 31.5 Hz for the apical CO, whereas the two non-equivalent basal CO ligands yield the same coupling constant within experimental error (24.5 Hz). However, an attempt to correlate these data with Fe—CO bond distances (177.1 and 174.9 ppm for basal CO and 175.7 for apical CO) as obtained from X-ray analysis [43] was unsuccessful. A similar observation has been made for the coupling between iron and π-bonded diene carbons in [$Fe(CO)_3$(1,3-cyclohexadiene)] [9], in which the more distant * terminal carbon atoms show a larger coupling constant (3.7 Hz) than the central carbon atoms (2.8 Hz). These observations illustrate the fact that nuclear spin coupling constants are sensitive to small variations in the type of bonding between two nuclei, and the results have also been rationalized in terms of a new bonding model for [$Fe(CO)_3$-(diene)] complexes [11].

Acknowledgement

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* From a number of X-ray structure determinations it is known that the interatomic distance between the iron and the terminal carbon is always significantly longer [44].

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