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^{57}Fe NMR CHEMICAL SHIFTS AND ^{57}Fe, ^{13}C COUPLING CONSTANTS IN α-FERROCENYL CARBOCATIONS. DIRECT METAL PARTICIPATION IN THE STABILIZATION OF METALLOCENYL CARBOCATIONS

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Summary

The $^{13}C\{^{57}Fe\}$ double resonance method has been used to investigate ^{57}Fe-enriched samples of ferrocene derivatives, α-ferrocenyl carbocations and carbonyl complexes with various σ- and π-hydrocarbon ligands. In the α-ferrocenyl carbocations the ^{57}Fe resonances span a 1200 ppm range, being a sensitive tool of direct iron participation in the stabilization. The ^{57}Fe resonances in the carbocations $[FcCH_2][HSO_4]$ (I), $[FcCHMe][HSO_4]$ (II), $[FcCHPh][HSO_4]$ (III), $[FcCHC_5H_4Mn(CO)_3][CF_3CO_2]$ (IV), $[(Fc)_2CH][BF_4]$ (V), $[FcCHC_5H_4RuC_5H_5][BF_4]$ (VI) and $[FcCMe_2][HSO_4]$ (VII), −523.6, −219.3, 221.0, 368.7, 699.0, 405.0 and 288.5 ppm, respectively, relative to ferrocene, are interpreted in terms of rehybridization of the iron non-bonding *d* orbitals (shielding effect) and the electron withdrawing effect of the substituent in the cyclic ligand (deshielding effect). The role of rehybridization of non-bonding iron orbitals in the low-frequency shift of the ^{57}Fe resonances, in addition to that in the previously investigated complex $[(C_5H_5)_2FeH][BF_3OH]$ (−1109.3 ppm), has been demonstrated for bridge-substituted [3]ferrocenophanes, whose ring tilting induces a low-frequency shift of up to 340 ppm relative to their unbridged analogues.

The ^{13}C NMR spectra of carbocations V and VI reveal a temperature dependence due to the rotation around the C(1)–C_α exocyclic bonds. In carbocation VI the ruthenium atom effectively competes with the iron atom to bond with C_α whereas in carbocation V two equivalent metal atoms possess the same ability for such bonding; as a result, complex V has a more pronounced “carbenium ion” nature than IV and VI, as indicated by the relative positions of the $^{13}C_\alpha$ resonances in carbocations IV, V and VI: δ 122.4, 147.2 and 116.9 ppm, respectively.

The values of ^{57}Fe, ^{13}C coupling constants for α-ferrocenyl carbocations exclude Fe–C_α σ-bonding and support a structure in which the iron atom is π-bonded with six carbon atoms of a fulvenoid ligand. According to the data on ^{57}Fe resonances and ^{57}Fe,^{13}C coupling constants in α-ferrocenyl carbocations the strength of Fe–C_α bonding is markedly influenced by the electronic effect of the substituent at C_α, being even lower in carbocation I than that of Fe–cyclopentadienyl carbon atoms.

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Introduction

The reasons for the unusual stability of α-ferrocenyl carbocations have been discussed for a long time [1–3]. The data on ^1H and ^{13}C NMR spectra [4a,b; 5a–f] do not give an unequivocal answer to the question of whether the enhanced stability of α-ferrocenyl carbocations and related cationic complexes is the consequence of resonance stabilization [6a,b], or direct metal participation [1,2,7]. Two extended Hückel s.c.c. calculations for the carbocation $[FcCH_2]^+$ (Fc = ferrocenyl) have been performed. According to Gleiter and Seeger [7] the minimum-energy structure is that where the exocyclic bond is displaced by 40° (regarded as perhaps an overestimate) from the five-membered ring plane towards the iron atom. Schmitt et al. [8] found, however, that the displacement of the above bond must be only 6°.

One might expect that the data from X-ray diffraction investigation of α-ferrocenyl carbocations and related systems would help to resolve this problem. Investigation of bis(α-cyclobutadienyltricarbonyliron)phenyl carbocation tetrafluoroborate did not reveal any substantial interaction of iron with the exocyclic carbon atom: $Fe \cdots C_\alpha$ distances are 2.85 and 2.94 Å [9]. In diferrocenyl carbocation tetrafluoroborate the $Fe \cdots C_\alpha$ distances are similar, 2.71 and 2.85 Å, but in this case the C_α atom is displaced from the planes of the cyclopentadienyl rings: the exocyclic bond is tilted by 19.9° to one of the iron atoms and by 17.7° to the other iron atom [10a,b]. The same distortion has been found in the carbocation $[\{Fe(\eta\text{-}C_5H_5)(CO)_2\}_2(CH_2CHCH_2)]^+$ in which the $Fe \cdots CH^+$ distances are 2.59 and 2.72 Å; the authors assume that the differences in the two $Fe \cdots CH^+$ distances are probably caused by crystal packing effects [11]. In ferrocenyldiphenylcyclopropenium tetrafluoroborate, which contains an aromatic three-membered cycle, the $Fe \cdots C_\alpha$ distance is 2.96 Å [12]. Recently, the crystal structure of the BF_4^- salt of α-ferrocenyldiphenyl carbocation has been determined; in this cation the tilt of the "exocyclic fulvene double bond" is 20.7° with a $Fe \cdots C_\alpha$ distance of 2.715 Å, which substantially exceeds the average distance of Fe–cyclopentadienyl carbon atoms (2.056 Å) [13].

Thus, X-ray diffraction data have yielded much useful information on the structures of α-ferrocenyl carbocations and related systems in the crystalline state and implied the existence of direct $Fe \cdots C_\alpha$ bonding [10b,13]. However, it remains unclear how important the packing effects are in the deviation of the exocyclic bond from the plane of cyclopentadienyl ring, and to what extent the structural parameters found in the crystalline state are retained in solution. Also, there are no X-ray diffraction data on the primary carbocation $[FcCH_2]^+$, in which one would expect the strongest $Fe–C_\alpha$ interaction; finally, and this is especially important, the question arises to what extent the $Fe \cdots C_\alpha$ distances found in the crystal, covering the wide range from 2.59 to 2.94 Å, should be considered as "bonding" interactions.

In 1978 we published the results of an investigation of the iron-57 (2.2% natural abundance, $I = (1/2)$ enriched carbocations, $[FcCH_2][HSO_4]$ (I) and $[FcCHMe][HSO_4]$ (II) by the $^{13}C\{^{57}Fe\}$ heteronuclear double resonance technique [14a]. It was found that whereas electron-withdrawing substitutents in ferrocene, such as acyl groups lead to a substantial shift of the ^{57}Fe resonance to the high-frequency region, in carbocations I and II and ^{57}Fe resonances are observed in the opposite, low-frequency side of ferrocene. A very strong shift to the low-frequency region (– 1109.3 ppm) was also observed for the metal-protonated ferrocene $[(C_5H_5)_2FeH][BF_3OH]$.

This result along with the ^{57}Fe,^{13}C coupling constants for I and II allowed us to conclude that rehybridization of the iron non-bonding orbitals (hybridized dz^2, $dx^2–y^2$ and dxy orbitals) takes place on going from ferrocene derivatives to α-ferrocenyl carbocations, with the purpose of realizing the interaction with C_α atom. As we pointed out in the conclusion of our paper, "in α-ferrocenylcarbenium ions one of the cyclopentadienyl ligands of ferrocene derivatives is replaced by a fulvenoid ligand, which is bonded to the metal by all the six carbon atoms. Consequently, the mechanism of stabilization of α-ferrocenylcarbenium ions should include not only the resonance interaction [ref.] but also the direct involvement of the iron atom [ref]. The difference between the iron chemical shifts in primary and secondary α-ferrocenylcarbenium ions possibly reflects the degree of its involvement" [14b].

Our interest in transition metal-substituted carbocations prompted us to follow variations in the ^{57}Fe resonances as a function of the substituents at the C_α carbon atom. It was interesting to elucidate whether it is possible to select such substituents at the C_α atom which would exclude the necessity of direct Fe–C_α interaction, i.e., to obtain evidence for the presence in solution of true three-coordinated carbenium ions. With this purpose we investigated the ^{57}Fe-enriched carbocations $[FcCHPh][HSO_4]$ (III), $[FcCHC_5H_4Mn(CO)_3][CF_3CO_2]$ (IV), $[(Fc)_2CH][BF_4]$ (V), $[FcCHC_5H_4RuC_5H_5][BF_4]$ (VI) and $[FcCMe_2][HSO_4]$ (VII). Then, in connection with the interpretation of the low-frequency shift of the ^{57}Fe resonances in carbocations I and II, as well as in protonated ferrocene, it seemed desirable to find additional evidence for the effect of rehybridization of the iron non-bonding orbitals in ferrocene on the ^{57}Fe shielding. Such evidence was obtained during the study of [3]ferrocenophanes, in which the above rehybridization is conditioned by ring tilting.

As will be shown, the results of the present work completely confirm the earlier conclusion concerning direct metal participation in the stabilization of α-ferrocenyl carbocations; they also confirm the supposition that the ^{57}Fe resonance is a sensitive tool of such participation [14a]. Preliminary results have been published [15a] and reported [15b].

Experimental

Iron-57-enriched (about 90%) samples of organoiron complexes were synthesized by conventional procedures from $^{57}Fe(C_5H_5)_2$ or $^{57}Fe(CO)_5$. Carbinol C_5H_5-$^{57}FeC_5H_4CH(OH)C_5H_4RuC_5H_5$, m.p. 160–164°C (dec.), was obtained by reduction of enriched ferrocenyl ruthenocenyl ketone with lithium aluminium hydride. Anal.found: C, 56.37, H, 4.46. Calcd.for $C_{21}H_{21}{}^{57}FeORu$: C, 56.50, H, 4.48%. The salt $[C_5H_5{}^{57}FeC_5H_4CHC_5H_4RuC_5H_5][BF_4]$ was obtained upon treatment of the above carbinol solution in acetic anhydride with aqueous HBF_4. Anal.found: C, 48,64, H, 3.75. Calcd.for $C_{21}H_{19}BF_4{}^{57}FeRu$: C, 48,84, H, 3.68%.

The $^{13}C\{^1H_{noise}, ^{57}Fe\}$ NMR spectra were recorded under conditions reported earlier [16]. The ^{57}Fe NMR chemical shifts (ppm) were measured relative to external ferrocene in CS_2 solution.

Results and discussion

The ^{57}Fe,^{13}C coupling constants of numerous ferrocene derivatives and α-ferrocenyl carbocations $[FcCH_2][HSO_4]$ (I) and $[FcCHMe][HSO_4]$ (II) were discussed by us earlier [14a]. For this reason we include in Table 1 the results for a small number

(Continued on p. 350)

TABLE 1

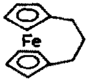
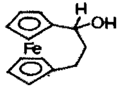
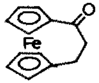
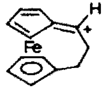
^{57}Fe,^{13}C COUPLING CONSTANTS

Compound	^{13}C chemical shifts (ppm)/^{57}Fe,^{13}C Coupling constant (Hz)	Solvent	References
Ferrocene	67.7/4.80 ± 0.12	CH_2Cl_2	16
Iodoferrocene	39.9/4.4 (C(1)), 74.6/4.4 (C(2,5)), 69.1/5.2 (C(3,4)) 71.1/4.4	CH_2Cl_2	
Formylferrocene	79.2/4.94 (C(1), 68.0/4.40 (C(2,5)), 72.6/4.40(C(3,4) 192.2 (CHO), 69.4/4.64 (C_5H_5)	$(CH_2Cl)_2$	14a
$[FcCH_2][HSO_4]$	110.6/2.8 (C(1)),84.6/4.4 (C(2,5)),94.4/2.5 (C(3,4)) 87.7/0.8 [a](CH_2),82.3/4.1 (C_5H_5)	H_2SO_4	14a
$[Fe(\eta\text{-}C_6H_6)(\eta\text{-}C_5H_5)][BF_4]$	88.4/3.30 (C_6H_6),76.9/4.76 (C_5H_5)	CH_2Cl_2	
$Fe(\eta\text{-}C_6H_7)(\eta\text{-}C_5H_5)$ [b]	22.1/5.8 (C(1,5)), 79.8/4.0 (C(2,4)),79.5/4.0 (C(3)), 25.7/1.4 (C(6)), 72.7/4.0 (C_5H_5)	CH_2Cl_2	17
$[Fe(\eta\text{-}C_6H_7)(CO)_3][BF_4]$ [b,c]	65.0/2.8 (C(1,5)),102.8/2.7 (C(2,4)),89.4/2.7 (C(3)) 24.2 (C(6)),200.8/25.7 (CO)	CF_3COOH	14a
$Fe(\eta\text{-}C_6H_8)(CO)_3$ [d]	61.1/3.66 (C(1,4)),84.3/2.81 (C(2,3)),26.8(C(5,6)) 212.7/27.95 (CO)	CS_2	14a
$[Fe(\eta\text{-}C_5H_5)(CO)_2(\eta\text{-}CH_2{=}CMe_2)][BF_4]$	54.0/4.41(CH_2=),122.9/1.48(=CMe_2),28.6(CH_3), 89.7/2.94(C_5H_5), 211.1/27.93 (CO)	CH_3NO_2	14a
$Fe(\eta\text{-}C_5H_5)(CO)_2(\sigma\text{-}CH_2C(Me){=}CH_2)$	10.3/8.82 ($FeCH_2$),155.2 (*C*(Me)=),107.3 (=CH_2), 24.7 (CH_3), 87.4/2.32 (C_5H_5)	CS_2	14a
$Fe(\eta\text{-}C_5H_5)(CO)_2(\sigma\text{-}C{\equiv}CPh)$	89.8/19.5 (FeC≡),116.3/3.0 (≡CPh),131.2,128.1 125.3 (C_6H_5), 85.6/2.3 (C_5H_5),213.0/27.8 (CO)	CH_2Cl_2	

[a] According to line-width this coupling constant must be more than 0.8 Hz ($\leqslant$ 1.45 Hz). [b] η-C_6H_7 is a cyclohexadienyl ligand. [c] At −75°C in SO_2 solution this complex displays two resonances of the CO groups with a relative intensities of 1:2 at 208.4/28.7 and 198.8/25.7, respectively [14a]. [d] η-C_6H_8 is a 1,3-cyclohexadiene ligand.

TABLE 2

^{57}Fe CHEMICAL SHIFTS AND ^{57}Fe,^{13}C COUPLING CONSTANTS IN [3]FERROCENOPHANES

Compound	$\delta(^{57}Fe)$ [a] (ppm)	^{13}C chemical shifts (ppm)/^{57}Fe,^{13}C coupling constants (Hz)								
		C(1)	C(2,5)	C(3,4)	C(6)	C(7)	C(8)	C(1′)	C(2′,5′)	C(3′,4′)
 (VIII)	−275.5	85.6/4.8	68.2/4.4	69.5/4.8	24.6	35.4	24.6	85.6/4.8	68.2/4.4	69.5/4.8
 (IX)	−227.2	87.5/4.8	70.1/4.5 69.3/4.6	68.9/4.4 68.8/5.0	68.1	21.9	43.6	87.0/3.6	86.7/4.7 68.6/4.9	67.9/5.0 67.1/4.9
 (X)	123.0	74.4/5.6	70.3/4.6	72.4/4.2	211.1	44.3	31.7	88.3/5.6	70.3/4.7	69.4/4.8
 (XI)	−161.0	124.3/2.2	82.7/4.0 83.4/4.4	93.1/1.8 93.4/1.8	121.8/2.7	42.1	31.5	106.3/2.2	79.5/4.9 79.6/4.9	80.6/3.7 80.6/3.3

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[a] Measured at 30°C in CH_2Cl_2 solution (VIII–X) and concentrated H_2SO_4 (XI).

of ferrocene derivatives only, mostly the data on the organoiron complexes with various σ- and π-hydrocarbon ligands, which are related with the problem discussed here are included. Data on [3]ferrocenophanes are listed in Table 2.

As we pointed out previously, the main differences in the ^{57}Fe,^{13}C coupling constants between the ferrocene derivatives and the α-ferrocenyl carbocations are as follows. The value of the constants depends only slightly on the nature of substituent and position of the carbon atom in the cyclopentadienyl ring, being usually equal to 4.1–5.2 Hz; the resonance of the exocyclic carbon atom is observed as a narrow singlet. In contrast, in the carbocations I and II the ^{57}Fe,^{13}C coupling constants obviously differ for various carbons of the substituted ring, being twice as small for the C(3,4) carbons as for the other cyclopentadienyl carbon atoms; the resonances of the C_α atom are either broadened or, at sufficient resolution, are split into a doublet. Thus in the present work we observed a splitting of C_α carbon resonance of 0.8 Hz in carbocation I. However, the NMR linewidth implies that in reality the above constant must be somewhat higher (~ 1.45 Hz). For [3]ferrocenophane-6-yl cation the ^{57}Fe,^{13}C coupling constant has the value of 2.7 Hz, i.e. a higher value than that of C(3,4) carbons of the neighbouring cyclopentadienyl ring (Table 2). The broadening of the C_α resonances was also noted for other α-ferrocenyl carbocations and even in carbocation [$FcCHC_5H_4RuC_5H_5$][BF_4] (VI), a fact which will be discussed later.

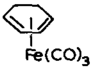
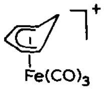
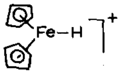
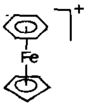
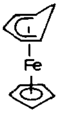
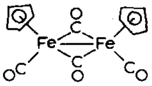
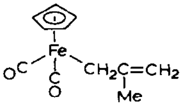
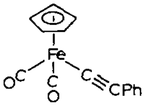
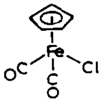
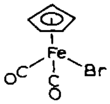
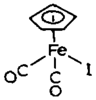
The data on ^{57}Fe,^{13}C(6) coupling constants suggest rehybridization of iron non-bonding orbitals on going from ferrocene derivatives to α-ferrocenyl carbocations, with the aim of extending interaction with the C_α atom [14]. Evidently, this interaction does not involve σ-bond formation between the iron atom and C_α carbon, as follows from comparison with the spectrum of the complex Fe(η-C_5H_5)$(CO)_2${σ-$CH_2C(Me){=}CH_2$} in which the σ-bonded carbon resonance is split into a doublet with a coupling constant of 8.8 Hz. The splitting value of C_α resonances in α-ferrocenyl carbocations is close to that of η-ethylene or -diene carbons in the complexes [Fe(η-C_5H_5)$(CO)_2$(η-$CH_2{=}CMe_2$)][BF_4] and Fe(η-C_6H_8)$(CO)_3$ (1.48–4.41 Hz) [14].

Presumably the splitting (broadening) of C_α resonances observed in the ^{13}C{^{1}H} NMR spectra of the α-ferrocenyl carbocations is the result of two-bonded ^{57}Fe, C(1), ^{13}C spin-spin coupling but not of one-bonded spin-spin coupling. A two-bonded ^{57}Fe,^{13}C coupling constant has been observed for two complexes. In the complex Fe(η-C_6H_7)(η-C_5H_5), where this is favoured by the geometry of the cyclohexadienyl ligand, the resonance of the methylene carbon is split into a doublet with a coupling constant of 1.4 Hz [17]. In the σ-acetylene derivative of iron, Fe(η-C_5H_5)$(CO)_2$(σ-C-≡CPh), acetylenic carbons are split into doublets with coupling constants of 19.5 and 3.0 Hz. These examples, however, are more or less in agreement with direct Fe–C_α interaction in α-ferrocenyl carbocations.

More substantial differences were found in the ^{57}Fe resonances of ferrocene derivatives and α-ferrocenyl carbocations. It is known that ^{57}Fe and ^{187}Os nuclei are the least sensitive ones among the 1/2 nuclear spin isotopes; 7.39×10^{-7} and 2.00×10^{-7}, respectively, relative to proton receptivity [18]. Consequently, and also to its low natural abundance and long relaxation time, the ^{57}Fe nucleus is very inconvenient for direct NMR study [19a–c]. Our alternative approach to the study of this nucleus based on isotopic enrichment combined with the use of ^{13}C{^{57}Fe} double resonance has allowed us to reduce substantially the measurement time from several days to 1–2 hours. Thus, it appeared possible to apply ^{57}Fe NMR spectros-

TABLE 3

^{57}Fe CHEMICAL SHIFTS IN ORGANOIRON COMPOUNDS

Compound	Solvent	Temp.(°C)	δ(^{57}Fe)(ppm)	Ref.
$Fe(CO)_5$	CS_2	30	− 1538.5	14a
	CS_2	27	− 1538.6	21
$Fe_3(CO)_{12}$	CH_2Cl_2	30	− 1206.8	
	CS_2	30	− 1600.8	14a
	CF_3COOH	30	−431.6	14a
	$BF_3 \cdot H_2O$	30	− 1109.3	16
	CH_2Cl_2	30	32.9	17
	CH_2Cl_2	30	735.1	17
	CH_2Cl_2	−85	− 1179.1	22
	CS_2	−30	−600.1	14a
	CH_2Cl_2	30	−515.7	
	CH_2Cl_2	30	1263.4	22
	CH_2Cl_2	30	962.8	22
	CH_2Cl_2	30	304.8	22

copy to resolve some chemical problems [14,17].

Since chemical shift calculation for heavier nuclei is a very difficult matter the interpretation of chemical shifts is essentially of correlative nature [20]. Thus, identification of the factors affecting the shielding of heavier nuclei requires data for various types of complexes. Table 3 lists data on ^{57}Fe resonances of various organoiron compounds. Here we give only brief comments of these data; a more detailed discussion of the factors affecting the ^{57}Fe shielding will be presented elsewhere. Strong deshielding of the iron atom on going from the complex Fe(η-C_6H_8)(CO)$_3$ (-1600.8 ppm) to the cationic complex [Fe(η-C_6H_7)(CO)$_3$][BF$_4$] (-431.6 ppm) may be ascribed to the positive charge on the metal atom in the latter. At the same time comparison of the ^{57}Fe resonances in the three sandwich complexes, ferrocene (0.0 ppm), [Fe(η-C_6H_6)(η-C_5H_5)][BF$_4$] (32.9 ppm) and Fe(η-C_6H_7)(η-C_5H_5) (735.1 ppm) indicates that the charge is not the only factor strongly affecting iron shielding. The same can be said about the (formal) oxidation state of the metal. For example, the difference of 1538.5 ppm between the resonances in ferrocene and iron pentacarbonyl was considered to be the consequence of the difference in oxidation states of iron in these complexes, Fe^{II} and Fe^{0} respectively [21]. However, in the iron-protonated ferrocene [$(C_5H_5)_2$FeH][BF$_3$OH] the ^{57}Fe resonance is observed in a very low frequency region, -1109.3 ppm. These results indicate that for the ^{57}Fe nucleus, as well as for other heavier nuclei, magnetic shielding is determined by many factors of which local electron density is not the most important. As for the halogen effect, it has been shown for the complexes Fe(η-C_5H_5)(CO)$_2$X (X = Cl, Br and I) that ^{57}Fe nuclei display "normal" dependence [22].

As expected, ^{57}Fe shielding is very sensitive to the substituents in ferrocene (Table 4). Alkyl groups cause comparatively poor deshielding of the ^{57}Fe nucleus ($\leqslant 45$ ppm). One should note the additivity of substituent effects. For example, in acetyl and 1,1′-diacetylferrocene the ^{57}Fe resonances are observed at 215.5 and 425.6 ppm, respectively [14]. Recently, the same additivity was found for alkyl substituents [23]. In the case of iodo- and 1,1′-diiodoferrocene, where the substituent has $-$I and $+$M electronic effects, no additivity is observed. This may be due to a comparatively weak effect of the substituent on ^{57}Fe resonance. It is not excluded, however, that the ^{57}Fe resonances in these compounds are also influenced by steric interactions of the bulky iodine atom with the iron. Such steric interactions evidently take place in the polychloroferrocenes as follows from the Mössbauer spectral data [24].

In ferrocenyl ketones FcCOR (R = Me,Fc,Ph and cymantrenyl) the ^{57}Fe resonances exhibit an order corresponding to the electronic effect of the R group in neutral molecules in the ground state: 215.5, 238.5, 269.0 and 271.9 ppm, respectively. The electronic effect in the benzene ring of these groups is in the same order as follows from the ^{19}F NMR data of *m*- and *p*-fluorophenyl derivatives RC$_6$H$_4$F-*m*(-*p*) [25]. Incidentally, according to the same data the ferrocenyl substituent does not possess exceptional electron-donating capacity in neutral molecules in the ground-state, being in this respect similar to the alkyl substituents: an additional fact supporting the idea that the ability of the $C_5H_5FeC_5H_4$ group to stabilize a α-cationic carbon is due to direct metal participation.

From the consideration of ^{57}Fe resonances data in the other ferrocene derivatives one can conclude that the substituent effect is of a more complex nature. For example, relative ^{57}Fe shielding in cyanoferrocene (113.1 ppm) and in phenylferrocene (188.2 ppm) does not agree with the conventional view on the electronic effects of the corresponding groups as substituents. Possible reasons for this discrepancy will be discussed elsewhere.

In the light of the substitutional deshielding of ^{57}Fe in acylferrocenes and other ferrocene derivatives with substituents of −M electronic effects, the strong low-frequency shift of ^{57}Fe resonances in α-ferrocenyl carbocations I (−523.6 ppm) and II (−219.3 ppm) was interpreted as the result of rehybridization of the iron nonbonding *d* orbitals, in accordance with the data on ^{57}Fe,^{13}C coupling constants [14]. This interpretation was also based on the fact that in the complex $[(C_5H_5)_2FeH][BF_3OH]$, where the above rehybridization does take place [26,27], the ^{57}Fe resonance was observed also in the low-frequency region (−1109.3 ppm). If the low-frequency shift of the ^{57}Fe resonance in carbocations I and II, as well as in $[(C_5H_5)_2FeH][BF_3OH]$ results from rehybridization of the iron non-bonding orbitals, a shift in the same direction would be expected in [*m*]ferrocenophanes with a sufficiently short bridge ($m \leqslant 3$). It is well recognized that ring tilting in these compounds is accompanied by rehybridization of the above orbitals [27,28a,b]. Accordingly we have measured the ^{57}Fe resonances in [3]ferrocenophanes (Table 2). As can be seen, in [3]ferrocenophane (VIII), [3]ferrocenophane-6-ol (IX), [3]ferrocenophane-6-one (X) and [3]ferrocenophane-6-yl cation (XI) the ^{57}Fe resonances are observed at −275.5, −277.2, 123.0 and −161.0 ppm, respectively, i.e. at positions substantially shifted to the low-frequency region compared with these of the unbridged analogues. It is known that in ketone X there is a ring tilt of 8.8° [29]. An even greater tilt, 13.8°, was found in the cation-radical salt of [3]ferrocenophane, $[Fe(C_5H_5)_2(CH_2)_3{}^+][(TCNQ)_2{}^-]$ (TCNQ = 7,7,8,8-tetracyano-*p*-chinodimethane) which is considered to be due to oxidation of [3]ferrocenophane [30]. The ^{57}Fe resonance data suggest, however, that in non-oxidized [3]ferrocenophane ring tilting would exceed 8.8°. Thus, the data on ^{57}Fe resonances both in protonated ferrocene and in [3]ferrocenophane unequivocally prove that rehybridization of iron non-bonding *d* orbitals results in a low-frequency shift of the ^{57}Fe resonances [15].

We will now discuss the ^{57}Fe resonances in α-ferrocenyl carbocations. From the data summarized in Table 5 one can see that in the α-ferrocenyl carbocations, $[FcCHR]^+$, the ^{57}Fe resonances are successively shifted (excluding diferrocenyl carbocation V) to the high-frequency region with increasing ability of the substituent at C_α to delocalize a positive charge: in $[FcCH_2][HSO_4]$ (I), $[FcCHMe][HSO_4]$ (II), $[FcCHPh][HSO_4]$ (III), $[FcCHC_5H_4Mn(CO)_3][CF_3CO_2]$ (IV), $[(Fc)_2CH][BF_4]$ (V) and $[FcCHC_5H_4RuC_5H_5][BF_4]$ (VI) the ^{57}Fe resonances are observed at −523.6, −219.3, 220.0, 368.7, 699.0 and 405.0 ppm, respectively. Beginning with carbocation III there is deshielding of the ^{57}Fe compared to ferrocene, although the ^{57}Fe resonance for III is observed in a lower frequency region than in benzoylferrocene (269.0 ppm). It was desirable to measure the ^{57}Fe resonances in the common solvent. Unfortunately, this was not carried out because carbocations V and VI decompose slowly in acidic media, and the $BF_4{}^-$ and $PF_6{}^-$ salts of the other carbocations are insufficiently stable to measure their ^{57}Fe resonances by the $^{13}C\{^{57}Fe\}$ double resonance technique.

Recently it was suggested that deshielding of the ^{13}C resonances in α-ferrocenyl carbocations may be at least partly due to acid complexation with metallocene substrate [31]. Comparison of the ^{13}C resonances of the α-ferrocenyl carbocation III in concentrated sulfuric acid and of the $PF_6{}^-$ salt of the same cation, $[FcCHPh][PF_6]$,

TABLE 4

^{57}Fe CHEMICAL SHIFTS OF FERROCENE DERIVATIVES

Compound[a]	Solvent	$\delta(^{57}\text{Fe})_{(\text{ppm})}$	Ref.
Ferrocene	CS_2	0.0	14a
	MeCN	−2.1	
	CH_2Cl_2	−13.0	
	THF	−26.0	
	C_6H_6	−30.5	
FcMe	CS_2	44.5	14a
FcEt	CH_2Cl_2	36.7	14a
	$CDCl_3$	35.5	23
Fć(Et)$_2$	$CDCl_3$	69.1	23
Fc(i-Pr)	CS_2	28.4	14a
Fc(t-Bu)	CS_2	34.9	14a
$FcCH_2CMe_3$	CS_2	3.1	
$FcCH_2NMe_2$	$CDCl_3$	0.5	23
FcPh	$CDCl_3$	188.2	23
$FcCH_2OH$	CS_2	11.3	14a
	$CDCl_3$	−1.2	23
FcCH(OH)Me	CH_2Cl_2	0.0	14a
	$CDCl_3$	7.0	23
FcCH(OH)Ph	CH_2Cl_2	−22.9	
$FcCH(OH)C_5H_4Mn(CO)_3$	CH_2Cl_2	−32.6	
FcCHO	CS_2	217.2	14a
	CH_2Cl_2	210.0	14a
	$CDCl_3$	232.5	23
FcCOMe	CH_2Cl_2	215.5	14a
	$CDCl_3$	234.2	23
Fć(COMe)$_2$	CH_2Cl_2	425.6	14a
	$CDCl_3$	437.2	23
FcCO(t-Bu)	CS_2	257.3	14a
Fć{CO(t-Bu)}$_2$	$CDCl_3$	526.1	23
FcCOPh	CH_2Cl_2	269.0	14a
$FcCOC_5H_4Mn(CO)_3$	CH_2Cl_2	271.9	
FcCOFc	CH_2Cl_2	238.5	
$FcCO_2Me$	$CDCl_3$	194.7	23
Fć(CO$_2$Me)$_2$	$CDCl_3$	379.9	23
FcCN	CS_2	113.1	14a
	$CDCl_3$	121.1	23
FcI	CH_2Cl_2	−20.5	
Fć(J)$_2$	CH_2Cl_2	6.2	

[a] Fc-ferrocenyl, Fć = 1,1′-ferrocenylene.

in a methylene chloride solution reveals, however, that they do not differ significantly. Of course, considering the wide range of the ^{57}Fe chemical shifts (approximately 3600 ppm for the compounds investigated at present) one would expect the solvent effect to be in this case more substantial. As can be seen from Table 4, even for ferrocene in common solvents the ^{57}Fe resonances vary by up to 30.5 ppm. We believe, however, that the data on ^{57}Fe resonances (Table 5) correctly reflect the order of relative shielding in carbocations I–VII. This is confirmed by the data obtained in concentrated sulfuric acid on carbocations I–III and VII, and also the known data on the relative ability of the phenyl, cymantrenyl, ferrocenyl and ruthenocenyl substituents to stabilize the α-cationic centre.

Thus, as for the relative effects of phenyl and cymantrenyl groups in α-carbocations, it is known that α-acetoxybenzylcymantrene undergoes solvolysis in absolute ethanol faster than benzhydryl acetate [32a]. This result and other data [32b] also indicate that the cymantrenyl group is more effective in stabilizing a cationic centre than is the phenyl one. The solvolytic rate data also indicate that the ferrocenyl group is much more effective than the cymantrenyl and phenyl ones in stabilizing a cationic centre and ruthenocenyl exceeds ferrocenyl in this respect [1–3].

While considering the ^{57}Fe resonances in α-ferrocenyl carbocations it becomes evident that two opposite factors influence the shielding of the ^{57}Fe nucleus in these carbocations: transformation of the substituted cyclopentadienyl ligand into a fulvenoid one with concomitant Fe–C_α bond formation (rehybridization of the iron non-bonding *d* orbitals) leads to shielding, and the presence of electron-withdrawing substituents (positive charge) on the ring leads to deshielding of the iron. With increasing ability of the substituent at C_α to delocalize a positive charge, the strength of the Fe–C_α bond weakens and the ^{57}Fe resonance shifts to the high-frequency region [14,17].

The ^{13}C NMR spectra of carbocations $[(Fc)_2CH][BF_4]$ (V) and $[FcCHC_5H_4RuC_5H_5][BF_4]$ (VI) reveal a temperature dependence due to rotation about the exocyclic bonds (dependence of the ^{1}H NMR spectrum of V on the temperature has been mentioned earlier [10a]).

The data on the ^{13}C resonances in carbocation VI indicate that the ruthenocenyl group is more effective than the ferrocenyl one in charge delocalization. Thus ^{13}C resonances of the ruthenocenyl group experience much stronger deshielding than the ferrocenyl one, in comparison with the ^{13}C resonances in the parent metallocenes, δ 70.4 and 67.7 ppm, respectively. Moreover, in the temperature range 30 to −65°C the ^{13}C resonance of the ruthenocenyl substituent undergoes only small alterations in contrast to those of the ferrocenyl substituent. At −65°C all the carbon atoms of the substituted cyclopentadienyl rings are seen as distinct resonances, indicating that the rotation about the exocyclic bonds has stopped. It is interesting that the resonance of the C_α atom is obviously broadened. Although ruthenium has two magnetic isotopes, ^{99}Ru ($I = 3/2$, 12.72%) and ^{101}Ru ($I = 5/2$, 17.07%), in the ^{13}C NMR spectra of ruthenocene and its derivatives we observed no splitting owing to these ruthenium isotopes. Therefore, we assume that the broadening of the C_α resonance in carbocation VI may be due to ^{57}Fe,^{13}C spin-spin coupling. Such spin-spin coupling would be favoured by the transoid structure, similar to that found in the crystalline state for $[(Fc)_2CH][BF_4]$ [10], in which the C_α atom is bonded simultaneously both with the ruthenium and, to a lesser extent, with the iron atom.

Upon cooling from 30 down to −65°C the ^{57}Fe resonance of cabocation VI is shifted to the low-frequency region from 405.0 to 377.8 ppm. Thus, the temperature coefficient is 0.3 ppm/°C, close to that of ferrocene.

In the ^{13}C NMR spectra of diferrocenyl carbocation V at 30°C only two resonances are observed from the C(2,5) and C(3,4) carbons of the substituted rings, at δ 74.9 and 84.2 ppm, respectively, and the intensity of the first resonance is approximately 2.5 times less than that of the second one. At −70°C resonances of the C(2), C(5) and C(3,4) carbons are observed as three signals with a relative intensities of 1 : 1 : 2, at δ 77.8, 70.4 and 83.3 ppm, respectively. Evidently, the rotational barrier about the exocyclic bond in carbocation V is lower than in carbocation VI.

(Continued on p. 358)

TABLE 5

^{57}Fe CHEMICAL SHIFTS AND ^{57}Fe,^{13}C COUPLING CONSTANTS IN FERROCENYL CARBOCATIONS

Compound	Solvent	Temp. (°C)	$\delta(^{57}Fe)$ (ppm)	^{13}C chem.shifts (ppm)/^{57}Fe,^{13}C coupling const. (Hz)					
				C_α	C(1)	C(2,5)	C(3,4)	C_5H_5Fe	other carbons
[FeCH$_2$][HSO$_4$] (I)	H_2SO_4	5 0	−523.6 −524.9	87.7/0.8	110.6/3.1	84.6/4.4	94.4/2.5	82.3/4.1	
[FcCHMe][HSO$_4$] (II)	H_2SO_4	15	−219.3	117.3/^{b}	104.7/3.5	80.9/4.8 80.0/4.3	93.3/2.5 93.0/2.6	81.5/4.3	19.0(CH$_3$)
[FcCHPh][HSO$_4$] (III)	H_2SO_4	0	221.0	121.5/^{b}	101.2/3.7	81.8/4.1 79.5/4.0	93.7/2.5 92.8/2.7	82.6/4.3	133.7(C*i*) 130.2 (C*o*,*m*) 133.4(C*p*)
[FcCHPh][PF$_6$]	CH_2Cl_2	0		122.2	101.7	82.4 89.0	94.2 93.3	83.0	134.4, 130.6 133.4
[FcCHC$_5$H$_4$Mn(CO)$_3$][CF$_3$CO$_2$] (IV)	CH_2Cl_2/ /CF_3CO_2H ~ 7/1	15	368.7	122.4/^{b}	97.7/3.9	80.8/4.4 77.6/4.1	92.9/2.7 92.2/2.7	81.8/4.4	89.3(C(1′)) 92.2, 88.4, 85.6, 83.9 (C(2′–5′)),222.0 (C≡O)

$[(Fc)_2CH][BF_4]$ (V)	CH_2Cl_2	30	699.0	147.2/[b]	86.5/3.8	74.9[a]/4.4	84.2/2.2	75.9/4.4	
		−70		(?)	85.3	77.8 70.4	83.3	75.1	
$[FcCHC_5H_4RuC_5H_5][BF_4]$ (IV)	CH_2Cl_2	30	405.0	117.6	79.9	70.7	76.0	72.0	95.9(C(1')), 88.4 (C(3',4')), 81.1 (C(2',5')), 82.8 (C_5H_5Ru)
		0	394.0	116.0	79.4		75.4	71.6	95.9(C(1')), 88.4 (C(3',4')), 81.1 (C(2',5')), 82.8 (C_5H_5Ru).
		−65	377.8	112.2/[b]	78.3/4.4	74.4/[c]	73.7/[c]	70.6/4.1	95.9(C(1')), 88.6
						64.8/[c]	73.5/[c]		88.1 (C(3',4')), 81.4 80.8 (C(2',5'), 82.8 (C_5H_5Ru).
$[FcCMe_2][HSO_4]$ (VII)	H_2SO_4	30	288.5	156.0/[b]	100.0/3.9	78.7/4.1	93.4/2.5	81.9/4.3	27.6 (CH_3)

[a] The intensity of the signal is much lower than that of the C(3,4) carbons. [b] The signal is broadened. [c] The $^{57}Fe,^{13}C$ coupling constant was not measured.

To understand the strong deshielding of the ^{57}Fe nucleus in carbocation V it is necessary to compare the $^{13}C_\alpha$ resonances in binuclear carbocations IV, V and VI. The resonances for the $^{13}C_\alpha$ carbon in these carbocations are observed at δ 122.4, 147.2 and 116.9 ppm, respectively. The broadening of the C_α carbon resonances due to ^{57}Fe,^{13}C spin-spin coupling, as well as their relative positions imply direct metal–C_α atom interaction. Thus, in diphenyl carbocation $(C_6H_5)_2\overset{+}{C}H$ the resonance of the exocyclic carbon is observed in the much lower frequency region of 200.2 ppm [33], and even in the rigid diferrocenyl carbocation generated by hydride abstraction from [1,1]ferrocenophane the resonance of the cationic C_α carbon atom is observed at δ 162.3 ppm [34] (in this ion the bridging CH_2 group effectively eliminates twisting and rotation).

The ^{57}Fe resonances in carbocation IV and VI differ very little, despite the fact that in the former the positive charge is delocalized mainly on the ferrocene substituent, whereas in the latter mostly on the ruthenocenyl one. As we pointed out above, in α-ferrocenyl carbocations the shielding of iron is influenced by the balance of two opposite effects. Thus, in carbocation IV the ferrocenyl substituent makes a greater contribution to the stabilization than the cymantrenyl one does, and this is accompanied by rehybridization of the iron non-bonding *d* orbitals (shielding of ^{57}Fe nucleus). In carbocation VI the extent of such rehybridization must be substantially lower because the ruthenium atom interacts more strongly with the C_α carbon than the iron atom does; as a result, we observe a decrease in the electron-withdrawing $-M$ effect of the substituent relative to ferrocene or, in other words, the role of the factor responsible for iron deshielding diminishes.

A somewhat different situation occurs in carbocation V. The most stable conformation here will be a transoid one, too, found in the crystalline state [10a,b]. In this conformation both ferrocenyl substituents participate equally in the stabilization of the cationic centre, and meanwhile each iron atom experiences a lesser degree of rehybridization of the non-bonding *d* orbitals; for this reason the role of the shielding factor will be less. At the same time such a structure of carbocation V should facilitate positive charge delocalization through the π-system of the substituted cyclopentadienyl ring (deshielding of the ^{57}Fe nucleus). Both these factors must result in stronger deshielding of the ^{57}Fe nucleus in carbocation V as compared to that in carbocations IV and VI. Thus, the relative deshielding of the ^{13}C resonance in carbocation V in comparison with the two other binuclear carbocations is, apparently, explained by enhanced charge delocalization through the π-system of the cyclic ligands.

Thus, in all the α-ferrocenyl carbocations investigated in the present work there is direct Fe-C_α interaction irrespective of the substituent at the C_α atom, both in the secondary ions III and IV and the tertiary one VII. Only in the case of carbocation VI may there be absence of direct Fe–C_α interaction (see, however, the discussion of C_α resonance broadening), evidently due to effective competition of the ruthenium atom to bond with the C_α carbon. The data on the ^{57}Fe resonances give a good indication of the weakening of the iron–C_α bonding as the substituent at C_α increases its ability to delocalize the positive charge [14]. Therefore, one may expect that when the C_α atom has other substituents containing, for instance, O,N and other heteroatoms, the direct metal participation becomes unnecessary. So, it has been claimed that the relative contributions of olefin and allyl structures to cationic carbonyliron complexes depend on the nature of the substituent at the C_α atom [35].

Finally, we hope that the results of investigating ^{57}Fe-enriched organoiron complexes by $^{13}C\{^{57}Fe\}$ NMR spectroscopy have convincingly proved the presence of direct Fe–C_α interaction in α-ferrocenyl carbocations. Our results obtained for solutions of α-ferrocenyl carbocations confirm the assumption that the structural distortions found in the crystals of the salts of these and related carbocations are due to the bonding interaction between the metal atom and the "cationic centre". Therefore, the exceptional stability of α-metallocenyl carbocations and related ions has been experimentally explained.

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