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Ferrocene Compounds. XXXVII.* Reactions of 1,1'-Ferrocenylenebis(carbinyl acetates) and Derived Quaternary Ammonium Iodides with Methyl Salicylate

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Key words
• α,α'-(1,1'-ferrocenylene)biscarbinols
• α,α'-(1,1'-ferrocenylene)bis(carbinyl acetates) and derived quaternary iodides
• *O*- and *C*-ferrocylation
• methyl salicylate
• *ab initio*
• DFT

Acetates **1** were prepared from appropriate biscarbinols according to described procedures. Iodides **3** were obtained by quaternization of appropriate amines **2** with methyl iodide in acetone. A solution of reagents **1a** (**3a**) in an excess of methyl salicylate containing 6 moles of sodium was refluxed for 2 hours, giving **4a** [8 (14) %] and **5a** [10 (15) %]. Under similar conditions, **1b** (**3b**) gave **4b** [10 (3) %] and **5b** [4 (9) %], followed by elimination products **7** and **8**. Similarly, acetate **1c** was transformed into **4c** (8 %), **5c** (15 %) and **6c** (6 %). The structure of heteroannularly substituted unsymmetrical ferrocene derivatives **4**–**8** was undoubtedly confirmed on the basis of elemental and spectroscopic analyses, and the reaction mechanisms of their formation were proposed. *Ab initio* MO calculations of the ground states were performed to elucidate the character of hydrogen bonding and the stability of disubstituted ferrocene compounds **4**–**6**.

INTRODUCTION

In continuation of our programme on the chemistry of ferrocene heteroaliphatic acids and their derived α- and β-ferrocenyl-carbenium ions,[2–4] we have prepared a new type of ferrocenyloxaaliphatic acid esters, $FcCHROCHR'CO_2Me$ (R = H, Me, Ph; R' = H, Me),[3] by reaction of methyl glycolate and lactate-derived alkoxides with *N,N,N*-trimethylferrocylammonium iodides (ferrocyl = ferrocenylmethyl) or ferrocenylcarbinyl acetates. Oligomeric by-products, $FcCHR(OCHR'CO)_nOMe$ and methyl ethers, FcCHROMe, were also isolated. Under the same conditions, heteroannular bisacetate **1b** and bisquaternary salt **3b** gave:

$Fn(CHMeOMe)CH{=}CH_2$ (8–22 %),
$Fn(CHMeOCHRCO_2Me)CH{=}CH_2$ (2–18 %) and
$Fn(CHMeOCHRCO_2Me)CHMeOMe$ (6–15 %), (Fn = 1,1'-ferrocenylene, $C_{10}H_8Fe$; R = H,Me).[5]

The results obtained from a study of the reactions with methyl salicylate[6] have prompted us to investigate the analogous transformations of ferrocene bisacetates **1** or bisquaternary salts **3**. In addition, the anticipated 1,1'-ferrocenylenebissalicylates **4**, **5** and **6** could be of considerable interest as a new type of chiral polydentate ligands.

RESULTS AND DISCUSSION

According to the procedure for the synthesis of ferrocenyloxaaliphatic esters,[3] sodium (9 mmol) was dissolved in a large excess of methyl salicylate and heated

* For Part XXXVI, see Ref. 1.

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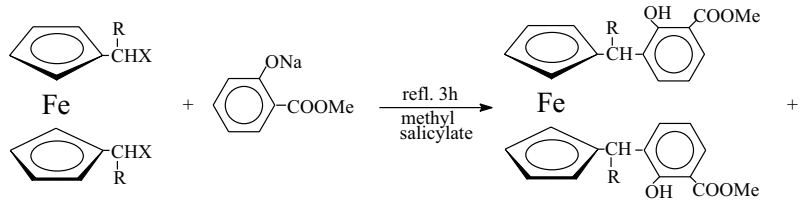
under reflux with $FcCHRNMe_3I$ (3 mmol, R = H, Me, Ph) for 2–3 hours, to give a mixture of the *o*-substituted product [methyl 3-ferrocylsalicylates (12–20 %)] and the *p*-substituted product [methyl 5-ferrocylsalicylates (10–23 %)]. Along with these *ortho*- and *para*-products, the reaction of the quaternary salt (R = Me) also yielded 20 % of vinylferrocene and 6 % of 1-ferrocenylethyl methyl ether. The origin of this ether was rationalized by AC1-cleavage of an oxonium species initially formed by *O*-ferrocylation of the substrate methoxy group. The overall yields of *para*- and *ortho*-salicylates were significantly higher (43 %) in conversions of $FcCHRNMe_3I$ (R = Ph) than in those of the salt (R = H) (27 %), presumably owing to the relative stability of the corresponding carbocations ($FcCHPh^+ > FcCH_2^+$). The *ortho-para* ratio for R = H and R = Me was similar, probably because of the competition from an elimination to $FcCH{=}CH_2$ or formation of a methyl ether in the latter case.[6] Similar results were obtained with acetates **1** or quaternary salts **3** in a large excess of methyl salicylate using a 6-fold molar excess of sodium (Scheme 1).

One can see that in contrast to more or less successful transformations of ferrocene mono- or bis-acetates and quaternary salts with hydroxyaliphatic esters to ferrocene-containing oxaaliphatic esters, the reaction with methyl salicylate gave products reminiscent of those from aromatic electrophilic substitutions. Since the Friedel-Crafts type processes nearly always require an acid catalyst,[7] we decided to explore the role of solvent and the anionic species in the formation of new products. Prolonged heating of ferrocene reagents with methyl salicylate in 1,2-dichloroethane or dimethyl sulfoxide, either with or without sodium, yielded only the starting material, traces of 1,1'-ferrocenylenebiscarbinols,[8] bridged saturated[4] or unsaturated ethers, and some so far unidentified decomposition products. Similar results were obtained upon heating with a large excess of methyl salicylate without sodium. It is therefore possible that the α-ferrocenyl carbenium ion was formed from the attacking ferrocene reagent and phenoxide; this cation may exist as a tight ion pair with phenoxide. It seems that a specific catalysis by the conjugate base of the solvent and solvation characteristics of such a buffer-like reaction system are involved in a fundamental way in the mechanism.

A possible mechanism is depicted in Scheme 2 (one ring is shown for simplicity).

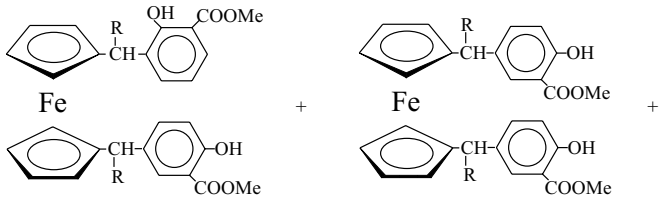
Initial formation of a solvated carbenium ion **A** by solvolysis of substrates **1** or **3** is assumed. The electrophilic substitution on phenoxide (**B**) occurred in the *para*-(**C**) or *ortho*-position (**D**) (path *i*). The alternative in-



1a X = OAc, R = H
1b X = OAc, R = Me
1c X = OAc, R = Ph

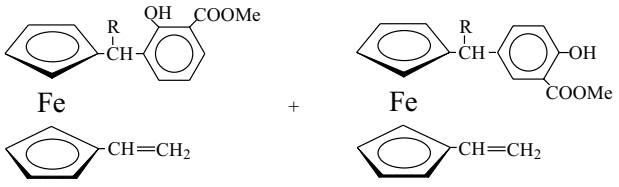
3a X = NMe_3I, R = H
3b X = NMe_3I, R = Me

4a R = H
4b R = Me
4c R = Ph



5a R = H
5b R = Me
5c R = Ph

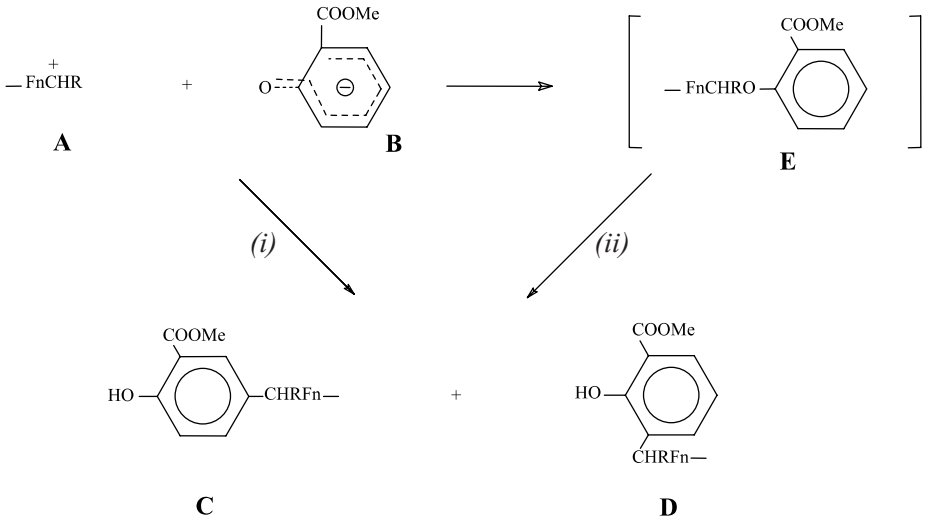
6a R = H
6b R = Me
6c R = Ph



7 R = Me

8 R = Me

Scheme 1. *Note:* Compounds **6a** and **6b** were not obtained and are presented for the purpose of theoretical calculation.



Fn = 1,1'-ferrocenylene

Scheme 2. *Note*: Reactions on only one cyclopentadienyl ring are shown.

volves *O*-alkylation into an intermediate **E**, which can undergo rearrangement into **C** and **D** (path *ii*). In these reactions, *o,o*-, *o,p*- and *p,p*-substitution products (in relation to the OH group) were obtained, due to the activating and *o,p*-directing effect of hydroxyl and the concurrent deactivating and *m*-directing influence of methoxycarbonyl group. Unsaturated products **7** and **8** were formed by the elimination process. Support for the intermediate being something like an ion pair is provided by the fact that the reaction led to the formation of not inconsiderable amounts of the alkenes that could be formed by the loss of a proton.

In a previous work we showed that reactions of ferrocyl substrates FcCHRX (X = good leaving group) with *O*- and *S*-nucleophiles mainly followed the unimolecular pathway.[9] Ferrocene is an excellent stabilizer of an adjacent positive charge involving a resonance contributor wherein substantial positive charge is localized on iron.[10] The rates and overall yields of the reactions were clearly dependent on the relative stability of carbocations $FcCHPh^+ > FcCHMe^+ > FcCH_2^+$. The yields of *o*- and *p*-products resulting from **1b** (*i.e.*, **4b**, **5b**, **7** and **8**) were appreciably higher (60 %) than those from **1a** (18 % of **4a** and **5a**) but only moderate yields were obtained in conversion of **1c** (29 % of **4c**, **5c** and **6c**). The greater overall yields in transformation of **1b** compared to **1a** can be explained in terms of the mentioned difference in stability of cationic intermediates. In the case of **1c**, the expected greatest reactivity was not reached despite favorable electronic factors: combination of this overcrowded substrate with two molecules of sterically demanding salicylate was inhibited, resulting in lower yields. There is little doubt that the decreasing proportion of the *ortho*-product in series **a**, **b**, **c** stems from increasing crowding of the bulky groups. This is supported by an exceptional formation of a *p,p*-disubstituted product **6**. In this context it is worth mentioning that *p*-substitution of phenol is kinetically and thermodynamically preferred over the *o*-substitution, because of the bulk effects and unfavorable electrostatic interactions of some substituents in this position; *e.g.*, bromination gives only *p*-bromophenol, and in nitration the *p*-position is almost two times more reactive than the *o*-position. Furthermore, acid catalyzed reactions of methyl salicylate with benzyl chloride[7a] or styrene[11] mostly gave the products of *p*-substitution. Nevertheless, we found almost equal amounts of *o*- and *p*-isomers in the reaction of FcCHRX with methyl salicylate.[6] Similar results were obtained in the present study. Reactions of methyl salicylate with **1a** and **1b** yielded nearly equal quantities of *o,o*- (8–14 %) and *o,p*-positional isomers (4–15 %); in the case of **1c**, *p*-substitution was slightly improved (8 % *o,o*, 15 % *o,p*, and 6 % *p,p*).

New salicylates underwent hydrolysis into the corresponding acids in good yields (60–70 %) and without noticeable decomposition of the molecules.

The structure of new compounds was unambiguously determined by spectral data. The IR spectra show absorptions in the 3170–3184 and 1675–1681 cm^{-1} regions characteristic of intramolecular hydrogen-bonded salicylate CO···HO groups. ^1H NMR signals for phenolic protons appear in the range δ 10.59–11.19 ppm. The double bond in esters **7** and **8** is characterized by an IR band at ~ 1620 cm^{-1}, a typical ^1H NMR-pattern H_α at 6.41–6.45, H_β at ~ 5.32–5.34 and H_γ at ~ 5.05 ppm, and methine and methylene ^{13}C NMR signals at 130.76 and 135.51 ppm. ^1H NMR spectra of **5b** and **5c** exhibit discrete signals that are consistent with a mixture of *threo*-

and *erythro*-forms in the product. *E.g.,* two discrete signals at 5.48 and 5.51 ppm corresponding to methine protons were found in the spectrum of **5c/ 5c'**. The differences in the spectra of *o,o*-, *o,p*- and *p,p*-substituted salicylates were obvious, clearly demonstrating assignment of these positional isomers. Aromatic protons in *o,o*-isomers (H-6, H-4 and H-5) were registered at ~ 7.68–7.65 (d), 7.21–7.12 (d) and 6.76–6.73 (dd or t); two vicinal and one isolated proton in *p,p*-compound (H-4, H-3 and H-6) gave signals at 7.08 (d), 6.90 (d) and 7.63 (s) ppm.

In ^{13}C NMR spectra, differences between *o*- and *p*-positions were shown in *o,p*-compounds **5**. *E.g.*, aromatic methyne C-atoms in compound **5a** (C-5, C-6, C-4), which corresponded to *o*-isomer were registered at 118.53, 127.64 and 135.41, whereas *p*-methyne C-atoms (C-3, C-6, C-4) were found at 117.28, 129.09 and 136.01 ppm. Also, aromatic quaternary C-atoms (C-1, C-3, C-2) in *o*-position gave signals at 111.64, 130.39 and 159.20, and those in *p*-position (C-1, C-5, C-2) were registered at 111.77, 132.35 and 159.86 ppm.

The characteristic differences in IR and ^{1}H NMR spectra of mono *o*- and *p*-isomers[6] permitted quite straightforward differentiation between them. The *para*-derivatives showed IR bands at 1680–1682 and 3206–3221 cm^{-1}, similar to those of the parent methyl salicylate (1682 and 3200 cm^{-1}), whereas the *ortho*-isomers exhibited a distinct shift to lower frequencies (1677–1678 and 3162–3195 cm^{-1}). ^{1}H NMR spectra of *p*-isomers show phenolic protons at 10.58–10.76 ppm, while *o*-isomers exhibit a downfield shift ($\Delta\delta$ *ca.* 0.6 ppm), allowing for magnetic anisotropy contributions to the proton NMR shielding. The local deshielding effect clearly depends on the distance between the ferrocene ring and the resonating proton (4 bonds in *o*- *vs.* 6 bonds in *p*-isomer). A similar situation is encountered in the spectra of *o,o*- (**4a**–**4c**), unsaturated *o*- (**7**) and *p*-compounds (**8**). The fine differences in IR spectra revealed the strengthening of »salicylic« hydrogen bond in *o*-isomers in comparison with methyl salicylate and *p*-substituted compounds. This fact could be explained in terms of sterical forcing of CO···HO groups by the bulky *o*-ferrocyl groups to stronger interaction.

There is an interesting observation that both **6c** and the related phenyl substituted derivative **5c** show an IR band at 3463 and 3448 cm^{-1} (ν (OH)), respectively, which is significantly different from the corresponding salicylate band (3200 cm^{-1}).

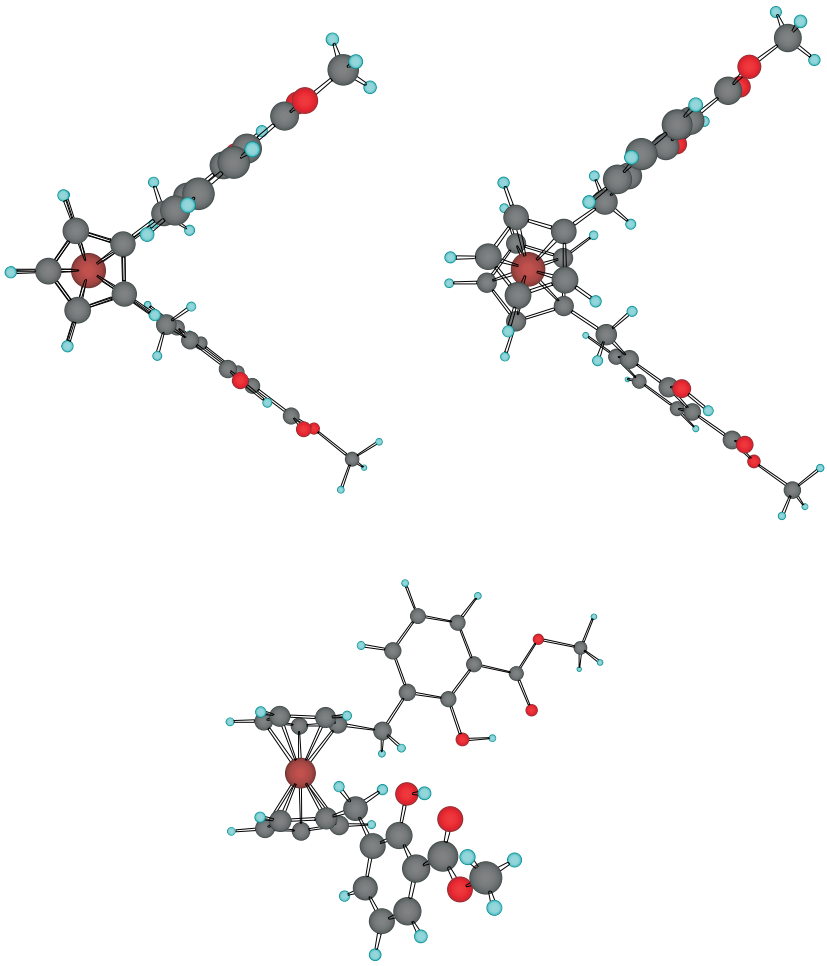


Figure 1.

In conclusion, it could be stated that the obtained *o,o*-, *o,p*- and *p,p*-1,1'-ferrocenylenebis(salicylates) represent interesting substrates exerting the various types and strengths of intramolecular hydrogen bonds.

To elucidate the character of the hydrogen bonding and stability of disubstituted ferrocene compounds **4–6**, *ab initio* calculations of the ground states were performed (Table I). All calculations were carried out on the DFT[12] pBN/DN** and pBN/DN* levels with the SPARTAN[13] program. The total energies including hydrogen bonds are presented in Table I. As an example, conformation of ferrocene salicylate **4a** obtained by DFT calculation is shown on Figure 1.

In a series of methylene-containing compounds, **6a** is more stable than **5a** and **4a** by 0.00304 and 0.00661

TABLE I. DFT pBN/DN** and pBN/DN* total energies and the calculated hydrogen bond lengths for salicylates 4–6

Molecule	E_{TOT} / a.u.	d_{Hbond} / Å
4a	$E_{pBN/DN**}$ = –2798.63946	1.628
4b	$E_{pBN/DN**}$ = –2877.29465	1.638
4c	$E_{pBN/DN*}$ = –3260.76998	1.658
5a	$E_{pBN/DN**}$ = –2798.64303	1.628_o; 1.641_p
5b	$E_{pBN/DN**}$ = –2877.29412	1.632_o; 1.664_p
5c	$E_{pBN/DN*}$ = –3260.77528	1.663_o; 1.681_p
6a	$E_{pBN/DN**}$ = –2798.64607	1.655
6b	$E_{pBN/DN**}$ = –2877.28951	1.673
6c	$E_{pBN/DN*}$ = –3260.77474	1.679

TABLE II. Physical constants and IR spectral data for Fn[CH(R)-3-C_6H_3(OH)COOMe]$_2$ (**4**), Fn[CH(R)-3/5-C_6H_3(OH)COOMe]$_2$ (**5**), Fn[CH(Ph)-5-C_6H_3(OH)COOMe]$_2$ (**6c**), Fn[CH(Me)-3-C_6H_3(OH)COOMe]CH=CH_2 (**7**), Fn[CH(Me)-5-C_6H_3(OH)COOMe]CH=CH_2 (**8**)

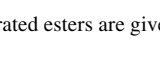
Compd. No.	R	Formula (M_r)	Analysis calcd. (found)/% C	Analysis calcd. (found)/% H	Yield[a] %	M.p. °C	IR / cm^{-1} ν(CH) arom.	ν(CH) aliph.	ν(C=O)	ν(OH)
4a	H	$C_{28}H_{26}FeO_6$ (514.4)	65.38 (65.59)	5.09 (4.91)	8 (14)	113.1–114.0	3084 w	3013 w 2955 m 2855 w	1675 s	3184 b
4b	CH_3	$C_{30}H_{30}FeO_6$ (542.4)	66.43 (66.67)	5.57 (5.32)	10 (13)	resin	3093 w	2977 s 2933 w 2866 s	1676 s	3175 b
4c	C_6H_5	$C_{40}H_{34}FeO_6$ (666.6)	72.07 (71.87)	5.14 (5.21)	8	227.5–228.0	3079 w	3028 w 2950 m 2853 w	1677 s	3163 b
5a	H	$C_{28}H_{26}FeO_6$ (514.4)	65.38 (65.55)	5.09 (4.87)	10 (15)	91.2–92.8	3084 w	3011 w 2952 m 2843 w	1677 s	3189 b
5b	CH_3	$C_{30}H_{30}FeO_6$ (542.4)	66.43 (66.69)	5.57 (5.29)	4 (9)	resin	3091 w	2974 s 2932 w 2866 w	1681 s	3210 b
5c	C_6H_5	$C_{40}H_{34}FeO_6$ (666.6)	72.07 (71.90)	5.14 (5.01)	15	resin	3086 w	3027 m 2955 m 2847 w	1679 s	3448 b
6c	–	$C_{40}H_{34}FeO_6$ (666.6)	72.07 (71.89)	5.14 (5.00)	6	89.0–89.5	3084 w	3021 m 2956 m 2853 w	1681 s	3463 b
7	–	$C_{22}H_{22}FeO_3$ (390.3)	67.70 (67.45)	5.68 (5.89)	11 (4)	resin	3096 w	2977 s 2932 w 2866 m	1677 s	3177 b
8	–	$C_{22}H_{22}FeO_3$ (390.3)	67.70 (67.49)	5.68 (5.92)	35 (17)	resin	3083 w	3003 w 2953 s 2840 w	1680 s	3170 b

[a] Given yields were obtained after purification by preparative thin layer chromatography. First values refer to reactions with acetates **1**, and the second values in brackets to the yields obtained in reactions with quaternary salts **3**.

TABLE III. ^{1}H NMR spectral data (δ/ ppm) for Fn[CH(R)-3-C_6H_3(OH)COOMe]$_2$ (**4**), Fn[CH(R)-3/5-C_6H_3(OH)COOMe]$_2$ (**5**),[a] Fn[CH(Ph)-5-C_6H_3(OH)COOMe]$_2$ (**6c**), Fn[CH(Me)-3-C_6H_3(OH)COOMe]CH=CH_2 (**7**),[b] Fn[CH(Me)-5-C_6H_3(OH)COOMe]CH=CH_2 (**8**)[b]

Compd. No.	R	Benzene (salicylate) protons[c] [e]				Ferrocene protons		Aliphatic protons [e]			COOMe	OH	Ph
		H-6 *H-6'*	**H-4** *H-4'*	**H-3** *H-3'*	**H-5**[f] *H-5'*			CH	CH_2	CH_3			
4a	H	***7.67*** ***(2, d)***	***7.21*** ***(2, d)***	–	***6.75*** ***(2, t)***	4.12 (4, m)	4.08 (4, m)	–	3.71 (4, s)	–	3.93 (6, s)	11.08 (2, s)	–
4b	CH_3	***7.65*** ***(2, d)***	***7.12*** ***(2, d)***	–	***6.73*** ***(2, t)***	4.25 m (8)	4.14 m	3.81 (2, q)	–	1.52 (6, d)	3.93 (6, s)	11.16 (2, s)	–
4c	C_6H_5	***7.68*** ***(2, dd)***	(d)	–	***6.76*** ***(2, dd)***	4.02 (4, m)	3.96 (4, m)	5.45 (2, s)	–	–	3.91 (6, s)	11.12 (2, s)	7.18 [d] (12, m)
5a	H	***7.80*** ***(2, d)***	**7.19** (**1**, **d**) *7.30 (1, d)*	*6.88 (1, d)*	**6.75** (**1**, **t**)	4.13 (8, bm)		–	3.68 (2, s) 3.59 (2, s)	–	3.93 s 3.92 s (6)	11.11 (1, s) 10.61 (1, s)	–
5b	CH_3	***7.78*** ***(2, id)***	***7.45*** ***(2, m)***	***6.97*** ***(2, m)***		4.19 m (8)	4.09 m	~3.8 (2, m)	–	1.51 d 1.45 d (6)	3.89 s 3.88 s (6)	11.19 (1, s) 10.59 (1, s)	–
5b'	CH_3	***7.99*** ***(2, id)***	***7.65*** ***(2, d)***	*6.89 (1, m)*	**6.73** (**1**, **t**)	4.20 m (8)	4.08 m	3.85 (2, m)	–	1.55 d 1.52 d (6)	3.94 s 3.92 s (6)	11.19 (1, s) 10.60 (1, s)	–
5c	C_6H_5	**7.69** (**1**, **id**) *7.58 (1, dd)*	***7.01*** ***(2, d)***	*6.83 (1, dd)*	**6.75** (**1**, **m**)	4.02 (4, m)	3.92 (4, m)	5.48 (1, s) 4.78 (1, s)	–	–	3.85 (6, s)	11.14 (1, s) 10.65 (1, s)	7.18 (10, m)
5c'	C_6H_5	**7.69** (**1**, **id**) *7.58 (1, dd)*	***7.01*** ***(2, d)***	*6.83 (1, dd)*	**6.75** (**1**, **m**)	4.02 (4, m)	3.92 (4, m)	5.51 (1, s) 4.78 (1, s)	–	–	3.87 (6, s)	11.15 (1, s) 10.65 (1, s)	7.18 (10, m)
6c	–	***7.63*** ***(2, s)***	***7.08*** ***(2, d)***	***6.90*** ***(2, d)***	–	4.05 (4, m)	3.93 (4, m)	4.86 (2, s)	–	–	3.89 (6, s)	10.69 (2, s)	7.19 (10, m)
7	–	**7.65** (**1**, **d**)	**7.09** (**1**, **d**)	–	**6.72** (**1**, **t**)	4.33 m (8)	4.21 m	4.05 (1, q)	–	1.55 (3, d)	3.94 (3, s)	11.18 (1, s)	–
8	–	**7.63** (**1**, **s**)	**7.23** (**1**, **d**)	**6.87** (**1**, **d**)	–	4.31 m (8)	4.18 m	3.80 (1, q)	–	1.53 (3, d)	3.93 (3, s)	10.59 (1, s)	–

[a] Due to the presence of two chiral centers, compounds **5b** and **5c** exist in the form of the corresponding stereoisomers **5b**, **5b'**, and **5c**, **5c'**.

[b] Vinyl protons of unsaturated esters are given in sequence α, β, γ  : **7**: 6.45 (1, dd), 5.34 (1, d), 5.05 (1, d); **8**: 6.41 (1, dd), 5.32 (1, d), 5.05 (1, d) ppm; the following coupling constants were measured: $^3J_{H\alpha,\ H\beta}$ ~ 17, $^3J_{H\alpha,\ H\gamma}$ ~ 10 and $^4J_{H\beta,\ H\gamma}$ ~ 0 Hz.

[c] Chemical shifts of protons of the benzene substituting the first cyclopentadiene ring are bolded and those belonging to the benzene placed on the second cyclopentadiene ring are italicized. Protons of both benzene moities registered at the same chemical shifts are bolded and italicized.

[d] Signals are included in the multiplet belonging to the phenyl group.

[e] The following coupling constants were measured: for CH–CH_3 ^3J ~ 7 Hz; for *o*-substituted salicylate protons $^3J_{H\text{-}4,\ H\text{-}5}$ ~ 7.5, $^3J_{H\text{-}5,\ H\text{-}6}$ ~ 7.65, $^4J_{H\text{-}4,\ H\text{-}6}$ ~ 1.5 Hz; for *p*-substituted salicylate protons $^3J_{H\text{-}3,\ H\text{-}4}$ ~ 8.7 Hz.

[f] The observed triplets arose due to the simultaneous spin-spin coupling of H-5 with H-4 and H-6 $^3J_{H\text{-}5,\ (H\text{-}4,H\text{-}6)}$ ~ 7.65 Hz.

atomic units, respectively. In the case of methyl substituted derivatives **b** one can notice the reverse order of stability, **4b** > **5b** > **6b**, with differences by 0.00053 and 0.00514 atomic units. Furthermore, the pBN/DN* results for **c**-series show a non-monotonous change of stability: **5c** > **6c** > **4c** (differences are 0.00530 and 0.00054 atomic units).

The average hydrogen bond lengths in **a**-series are: 1.628 for **4a**, 1.628 and 1.641 for **5a**, 1.655 for **6a**, in methyl-substituted compounds: 1.638 for **4b**, 1.632 and 1.664 for **5b**, 1673 for **6b** and in phenyl-derivatives: 1.658 for **4c**, 1.663 and 1.681 for **5c**, 1.679 Å for **6c**. From these results one can see that the hydrogen bonds in the corresponding series (**a**, **b** or **c**) are longer for *p*-than for *o*-substituted salicylates, indicating a strengthening of these bonds in the reverse order. Furthermore, it is interesting to note that phenyl substituted derivatives **c** contain the largest hydrogen bonds while compounds **a** the shortest and strongest ones. These facts are in agreement with the above described spectral analysis.

EXPERIMENTAL

Melting points were determined with a Buechi apparatus. The IR spectra were recorded for KBr pellets or CCl_4 solutions with a Bomem MB100 Mid FT IR spectrophotometer. The ^1H and ^{13}C NMR spectra of $CDCl_3$ and acetone solutions were recorded on a Varian EM 360 or Varian Gemini 300 spectrometer with tetramethylsilane as internal standard. Products were purified by preparative thin layer chromatography on silica gel (Merck, Kieselgel 60 HF_{254}) and by recrystallization from (aqueous) ethanol.

Acetates **1** were prepared by reactions of the corresponding biscarbinols with glacial acetic acid in benzene abs.[19] or with acetic anhydride in pyridine.[20]

Iodides **3** were prepared by quaternization of the corresponding amines **2** (Ref. 21) with methyl iodide in acetone.[3]

2a: yellow-brown oil, 87 %;

IR (CCl_4) ν_{max}/cm^{-1}: 3092 w $(CH)_{arom.}$, 2940 m, 2856 w, 2815 m, 2769 s $(CH)_{aliph.}$; ^1H NMR ($CDCl_3$) δ/ppm: 4.08 (m, 8H, Fn), 3.26 (s, 4H, CH_2), 2.16 (s, 12H, NMe_2).

2b: red-brown oil, 70 %;

IR (CCl_4) ν_{max}/cm^{-1}: 3093 m $(CH)_{arom.}$, 2937 s, 2858 m, 2820 s, 2780 s $(CH)_{aliph.}$; ^1H NMR ($CDCl_3$) δ/ppm: 4.07 (m, 8H, Fn), 3.61 (q, 2H, CH), 1.45 (d, 6H, CH_3), 2.08 (m, 12H, NMe_2).

*1,1'-Ferrocenylenebis(salicylates) **4–8***

Sodium (115 mg, 6 mmol) was added under mechanical stirring to methyl salicylate (17.61 g, 0.12 mol). After formation of sodium phenoxide, quaternary salts **3** or acetates **1** (1 mmol) were added and the reaction mixture was refluxed for 2 h, whereby the yellow color changed to brown. The mixture was cooled to room temperature, poured into 5 % aqueous solution of sodium hydroxide (10 ml) and extracted with diethyl ether. The ethereal layer was thoroughly washed with saturated aqueous solution of sodium chloride, dried over Na_2SO_4 and evaporated to dryness. Products **4–8** were separated by preparative thin layer chromatography using the mixture petroleum ether/ benzene (3:2) as eluents (Tables II, III and IV).

TABLE IV. ^{13}C NMR spectral data (δ/ ppm) for Fn[CH(R)-3-C_6H_3(OH)COOMe]$_2$ (**4**), Fn[CH(R)-3/5-C_6H_3(OH)COOMe]$_2$ (**5**), Fn[CH(Ph)-5-C_6H_3(OH)COOMe]$_2$ (**6c**), Fn[CH(Me)-3-C_6H_3(OH)COOMe]CH=CH_2 (**7**), Fn[CH(Me)-5-C_6H_3(OH)COOMe]CH=CH_2 (**8**)

Compd. No.	R	Ferrocene C-atoms		Salicylate C-atoms		Methine C-atoms		Methylene C-atoms		Methyl C-atoms		*C*OO
		CH	C	CH	C	*C*HR	*C*H=CH_2	*C*HR	CH=*C*H_2	$CHCH_3$	$COOCH_3$	
4a	H	68.23, 69.64 (4+4)	86.96 (2)	118.48 (2)	111.62 (2)	–	–	28.87 (2)	–	–	52.05 (2)	171.03 (2)
				127.60 (2)	130.50 (2)							
				135.47 (2)	159.23 (2)							
4b	Me	67.98–70.58 (8)	91.76 (2)	119.17 (2)	112.57 (2)	32.26 (2)	–	–	–	20.96 (2)	52.98 (2)	171.99 (2)
				128.31 (2)	137.29 (2)							
				134.77 (2)	159.32 (2)							

TABLE IV. contd.

Compd. No.	R	Ferrocene C-atoms		Salicylate C-atoms		Methine C-atoms		Methylene C-atoms		Methyl C-atoms		*C*OO
		CH	C	CH	C	*C*HR	*C*H=CH_2	*C*HR	CH=*C*H_2	$CHCH_3$	$COOCH_3$	
4c [a]	Ph	68.79–70.23 (8)	91.69 (2)	118.31 (2) 127.77 (2+2)	111.72, 111.79 (1+1) 133.90 (2) 158.57 (2)	43.19 (2)	–	–	–	–	52.09 (2)	170.99 (2)
5a	H	68.13–69.56 (8)	86.89 (1) 88.04 (1)	117.28, 118.53 (1+1) 127.64, 129.09 (1+1) 135.41, 136.01 (1+1)	111.64, 111.77 (1+1) 130.39, 132.35 (1+1) 159.20, 159.86 (1+1)	–	–	28.86 (1) 34.61 (1)	–	–	52.02 (1) 52.08 (1)	170.56 (1) 171.01 (1)
5b	Me	67.79–70.46 (8)	90.02 (1) 95.34 (1)	117.99, 119.66 (1+1) 128.29, 128.70 (1+1) 134.75, 135.84 (1+1)	112.57, 113.15 (1+1) 137.18, 139.56 (1+1) 159.29, 160.73 (1+1)	32.19 (1) 39.45 (1)	–	–	–	20.98 (1) 22.87 (1)	52.84 (1) 52.98 (1)	171.37 (1) 171.96 (1)
5c [a]	Ph	68.03–69.89 (8)	91.22 (1) 91.52 (1)	117.09, 118.25 (1+1) 127.78, 128.00 (1+1) 128.35, 129.37 (1+1)	111.58, 111.79 (1+1) 133.94, 135.67 (1+1) 158.57, 159.91 (1+1)	43.17 (1) 50.42 (1)	–	–	–	–	52.03 (1) 52.08 (1)	170.55 (1) 170.92 (1)
6c [a]	–	68.37–69.41 (8)	91.51 (2)	117.16 (2) 128.03 (2) 129.38 (2)	111.59 (2) 135.72 (2) 159.92 (2)	50.42 (2)	–	–	–	–	52.03 (2)	170.46 (2)
7	–	68.03–70.22 (8)	84.67 (1) 95.07 (1)	119.66 (1) 128.29 (1) 134.75 (1)	112.56 (1) 137.21 (1) 159.34 (1)	31.87 (1)	130.76 (1)	–	111.35 (1)	20.78 (1)	52.91 (1)	171.96 (1)
8	–	67.98–70.24 (8)	84.71 (1) 95.61 (1)	118.06 (1) 128.70 (1) 135.86 (1)	112.62 (1) 139.75 (1) 160.75 (1)	38.96 (1)	135.51 (1)	–	111.37 (1)	22.69 (1)	52.88 (1)	171.39 (1)

[a] ^{13}C NMR signals (δ/ppm) of phenyl group in **4c**:125.94 (2C), 128.73 (4C), 135.45 (4C), 143.70 (2C);
5c: 126.00 (2C), 128.77 (4C), 135.35 (2C), 136.07 (2C), 143.66 (1), 144.61 (1);
6c: 126.11 (2C), 128.40 (4C), 135.99 (4C), 144.53 (2C).

*1,1'-Ferrocenylenebis(salicylic acids) **9** and **10***

A solution of bisester **4a** or **5a** (0.150 mmol) in ethanol (30 ml) containing sodium hydroxide (250 mg, 6.25 mmol) and one drop of water was refluxed for 2–3 h. Ethanol was evaporated, the residuum was diluted with water and washed with diethyl ether, leaving an alkaline solution of sodium salicylate. It was acidified with a 16 % aqueous solution of hydrochloric acid to pH ~ 1 and extracted with diethyl ether to yield bright yellow crystalline bisacids **9a** and **10a** on evaporation of the solvent.

9a: 60 %, m.p. 199.5–200.5 °C;

IR (KBr) ν_{max}/cm^{-1}: 3075 b (OH) COOH, 1657 s (C=O) COOH, 1299 s (C–O) COOH.

Anal. Calcd. for $C_{26}H_{22}FeO_6$ (M_r = 486.3): C 64.22, H 4.56 %; found C 64.08, H 4.38 %.

10a: 68 %, m.p. 198.5–200.1 °C;

IR (KBr) ν_{max}/cm^{-1}: 3075 b (OH) COOH, 1659 s (C=O) COOH, 1299 s (C–O) COOH.

Anal. Calcd. for $C_{26}H_{22}FeO_6$ (M_r = 486.3): C 64.22, H 4.56 %; found C 64.10, H 4.41 %.

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SAŽETAK

Reakcije 1,1'-ferocenilenbis(karbinil-acetatâ) i izvedenih kvaternih amonijevih jodidâ s metil-salicilatom

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Prema postupcima opisanima u literaturi iz odgovarajućih karbinola pripravljeni su acetati **1**. Kvaternizacijom odgovarajućih amina **2** metil-jodidom u acetonu dobiveni su jodidi **3**. Dvosatnim refluksiranjem otopina reagensâ **1a** (**3a**) u suvišku metil-salicilata u prisutnosti 6 molova natrija nastaju smjese **4a** [8 (14) %] i **5a** [10 (15) %]. U sličnim okolnostima **1b** (**3b**) daju **4b** [10 (3) %] i **5b** [4 (9) %], popraćenih eliminacijskim produktima **7** i **8**. Slično, iz acetata **1c** dobiveni su **4c** (8 %), **5c** (15 %) i **6c** (6 %). Struktura heteroanularno supstituiranih nesimetričnih ferocenskih derivata **4**–**8** nedvoumno je potvrđena na temelju elementarne i spektroskopske analize te su predloženi reakcijski mehanizmi njihova nastajanja. Karakter vodikovih veza i stabilnost disupstituiranih

ferocenskih spojeva **4–6** razmatrana je na temelju *ab initio* MO računa.