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Synthetic approaches to trialkyl(ferrocenylmethyl)ammonium salts as cationic templates for the preparation of ferromagnets on the basis of bimetal oxalates

L. L. Troitskaya,[a]* **T. V. Demeshchik,**[a] **V. I. Sokolov,**[a] **I. A. Mamed'yarova,**[b] **B. Malezieux,**[c] **and M. Gruselle**[c]

[a]*A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,*
28 ul. Vavilova, 117813 Moscow, Russian Federation.
Fax: +7 (095) 135 5085. E-mail: sokol@ineos.ac.ru
[b]*Radiation Research, Department of Azerbaijan Academy of Sciences,*
31a H. Javid prosp., 370143 Baku, Azerbaijan.
Fax: +994 (12) 39 8318. E-mail: rad@dcacs.ab.az
[c]*National Center for Scientific Research,*
4 pl. Jussieu, Bat. 42, 75252 Paris, France.
Fax: +33 (1) 44 273841. E-mail: gruselle@ccr.jussieu.fr

Trialkyl(ferrocenylmethyl)ammonium salts and their 2-substituted analogs designed for the preparation of molecular ferromagnetics based on bimetallic oxalates were synthesized using classical alkylation of dialkylaminomethylferrocenes by alkyl halides and nucleophilic substitution reaction of 2-substituted dimethylaminomethylferrocene methiodides with trialkylamines. In the case of salts with electron-donating substituents in position 2, only the latter of the two proposed routes is applicable because *N*-alkylation with alkyl halides is accompanied by competing ferrocenylmethylation of the starting amine. On the contrary, the salts with electron-withdrawing 2-substituents should be prepared preferably by the reaction of amines with alkyl halides, while nucleophilic trialkylamination of methiodides is complicated by deprotonation induced by bases.

Key words: 2-substituted dialkylaminomethylferrocene, alkyl halides, methiodides of 2-derivatives of dimethylaminomethylferrocene, trialkylamines; 2-substituted trialkyl(ferrocenylmethyl)ammonium salts, preparation.

Unusual magnetic properties, especially ferromagnetism, displayed by organic and coordination compounds have attracted considerable attention in recent years. These compounds are exemplified by bimetallic oxalate salts $A^{n+}[M^1M^2(C_2O_4)_3]^{n-}$, where M^1 and M^2 are metal atoms and n = 1, 2, which are magnetics if the metals incorporated in them contain unpaired electrons capable of interaction, due to the formation of bimetallic oxalate polymer lattices upon chelation. The lattices consist of chiral octahedral "propeller" units, which are structurally equivalent but differ only in the central metal atom; the cations occur outside the lattices or in the cavities.[1,2] The configurations of the chiral lattice components with different metals can be either the same or opposite, and the polymer lattice composed of them is three-dimensional (3D) or two-dimensional (2D), respectively. The lattice dimensionality is determined by the nature of the cation.[3,4] Univalent onium cations, including quaternary ammonium cations, initiate the formation of planar 2D networks in which octahedra with different central atoms have opposite configurations.

Until now, achiral cations, most often Alk_4N^+X salts with identical organic groups, have always been used to construct 2D networks. The high symmetry of the cation promotes the formation of an ordered crystal structure. Later it has been shown that the ability of a salt to form a polymeric anionic 2D lattice is retained after replacement of one organic radical in the symmetrical cation.[5]

We propose for the first time constructing the systems of this type on the basis of chiral ammonium cation templates, including those in the optically active form, in order to find out how this would change the structure and the magnetic properties of the resulting anionic networks.

Ammonium salts of the ferrocenylmethyl series with planar chirality were chosen as the most convenient objects regarding their availability and stability, both chemical and configurational. We proceeded to the synthesis of derivatives of the general formula $[1\text{-}CH_2N^+R_3\text{-}2\text{-}R'\text{-}C_5H_3FeC_5H_5]I^-$ (**1a-d—6a-d**, where R′ = H (**1**), Me (**2**), COOMe (**3**), I (**4**), Cl (**5**), CH_2OMe (**6**); R = Et (**a**), Pr (**b**), Bu (**c**), C_5H_{11} (**d**)).

We covered a rather broad range of alkyl substituents with the purpose to have options, because the network formation depends on the steric parameters of the cation and the question of whether or not a network would be formed can be answered only experimentally.

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The achiral monosubstituted ammonium salts **1a—d** were synthesized as model compounds and to be used in experiments with the optically active chromium trioxalate anion. It was demonstrated in relation to salts **1a—d** that anionic networks with the 3D trialkyl(ferrocenylmethyl)ammonium cation as an auxiliary counter-ion can, in principle, arise. Salt **1c** was used to prepare optically active 2D networks (the results of studies of their structures and magnetic properties will be reported elsewhere).

The preparation of salts **1a-d—6a-d** by classical alkylation of tertiary amines with alkyl halides was faced with difficulties discussed below; therefore, an alternative method of synthesis was developed.

The choice of the substituent R′ was dictated initially only by the reasons of availability of the starting compounds and was limited to salts **1—3**; subsequently, this set was supplemented by their analogs **4—6** in order to elucidate the role of the substituent R′ in the processes that accompany the formation of this type of salts.

By now, all the data available from the literature were concerned with quaternary ammonium derivatives, mainly methiodides, of $FcCH_2NMe_2$ [6] and $FcCH(Me)NMe_2$,[15] as well as methiodides of 2-substituted derivatives of these amines. They were prepared in nearly quantitative yields by treatment of a tertiary amine with MeI in MeCN. Methiodide homologs with higher alkyl groups at nitrogen have not been described.

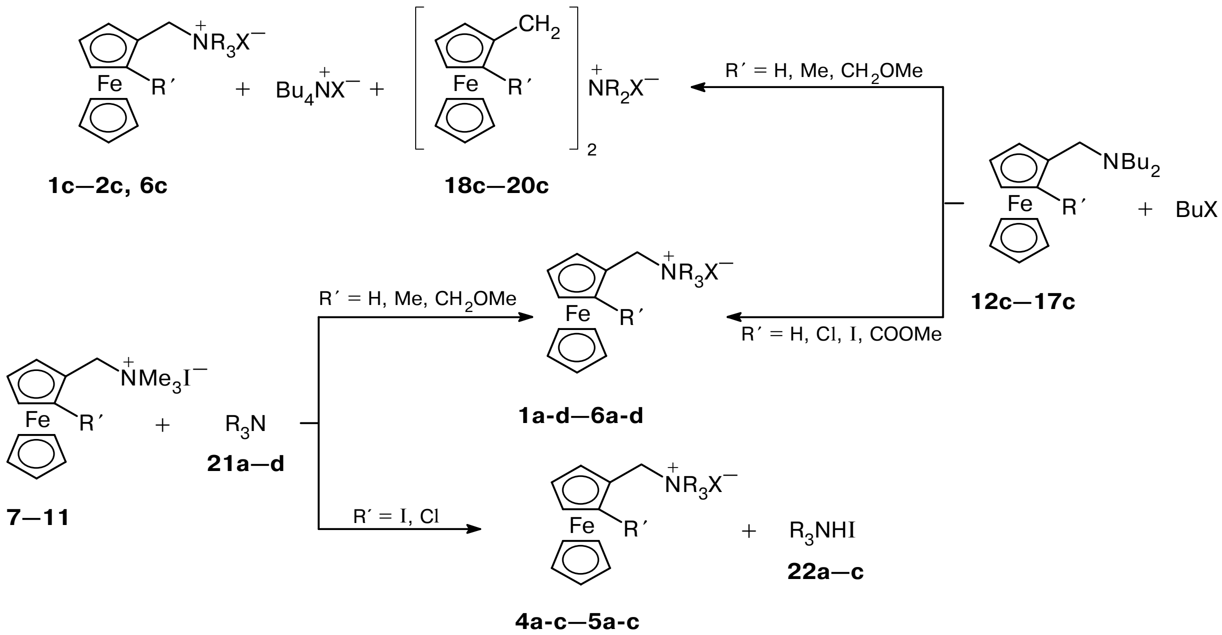
Due to the easy replacement of the trimethylammonium group by various nucleophiles, methiodides are often used to prepare various ferrocene derivatives. Using numerous examples,[7—9] it was demonstrated that reactions of methiodides with secondary amines permit the synthesis of virtually any tertiary amine of the ferrocenylmethyl series. Subsequently, these amines, synthesized, for example, from the methiodides $[1\text{-}CH_2N^+Me_3\text{-}2\text{-}R'\text{-}C_5H_3FeC_5H_5]I^-$, where R′ = H (**7**), Me (**8**), I (**9**), Cl (**10**), CH_2OMe (**11**), should be converted into the required quaternary ammonium salts on treatment with alkyl halides.

Primary experiments were carried out with the amines $1\text{-}CH_2NBu_2\text{-}2\text{-}R'\text{-}C_5H_3FeC_5H_5$ (**12c—17c**, where R′ = H (**12**), Me (**13**), COOMe (**14**), I (**15**), Cl (**16**), CH_2OMe (**17**)) because butylammonium salts are used most often to prepare 2D bimetallic oxalate ferromagnetics. Amine **12c** was prepared by the reaction of **7** with Bu_2NH; compounds **14c** and **15c** were synthesized by the reaction of cyclopalladated amine **12c** with CO in MeOH and with I_2, respectively; compound **16c** was obtained from **15c** by replacement of I by Cl, and **13c** and **17c** were prepared from **14c** (see Experimental).

It was found that the reaction of BuBr with amine **12c** in acetone at room temperature proceeded slowly and, after keeping the mixture for 3 days, the yield of salt **1c** (X = Br) did not exceed 10%. When the reaction time was increased to two weeks, a new product was detected whose ^1H NMR spectrum and elemental analysis data corresponded to the structure $(FcCH_2)_2N^+Bu_2Br^-$ (**18**, R′ = H). The amount of salt **18** formed in the reaction changes appreciably even on minor (within 10 °C) temperature fluctuations. No analog of salt **18**, $(FcCH_2)_2N^+Bu_2I^-$, was detected in the reaction of amine **12c** with BuI; perhaps, this reaction occurs faster, while the reaction mixture was quenched only after three days. This gave the expected ammonium salt **1c** (X = I) in a yield of about 40%. When the same route was followed to prepare salt **2c** from amine **13c**, the individual salt **2c** could not be isolated. The reaction of **13c** with BuI or BuBr in an MeCN—acetone mixture or in acetone gave rise to a mixture of quaternary ammonium salts in which the expected salt **2c** and Bu_4NI were identified by ^1H NMR spectroscopy. The other salts might be diastereomers of the 2-methyl-substituted analog of salt **18** (**19c**, R′ = Me), as indicated by the presence of several signals for the unsubstituted Cp and Me groups and multiplets for the methylene protons. This suggestion is confirmed by the fact that the mixture of ferrocenyl ammonium salts formed is converted into the initial amine **13c** on treatment with Bu_2NH and by the presence of Bu_3N, identified by GLC, in the filtrate. The composition of the mixture of salts has barely changed in the temperature range from 20 °C to the solvent boiling point. The reaction follows the desired pattern, *i.e.* affords only **2c**, at 0 °C, but it proceeds very slowly; hence, the amount of the target product isolated was sufficient only to record a ^1H NMR spectrum. Alkyl halides such as EtI or PrI also react with amine **13c** to give a mixture of salts, whereas MeI smoothly alkylates this amine to give the salt with the expected structure. This conclusion was based on the ^1H NMR spectra of the products. It was also found that the reaction of **13c** with BuI either in a protic solvent (MeOH) or in an aprotic solvent (MeCN) in the presence of catalytic amounts of Lewis acids, added to activate the alkyl halide, gives hydroiodide of the initial amine as the only product, *i.e.*, the amine is protonated.

Meanwhile, amines **14c—16c**, containing the electron-withdrawing methoxycarbonyl group or the halogen atom in position 2 of the ferrocenyl nucleus react with BuI in MeCN at room temperature to give the expected quaternary salts **3c—5c**, although 2-halo-derivatives **4c** and **5c** are formed in very low yields. Performing the reaction at reflux did not increase the yields. The ^1H NMR spectra of the products exhibited several signals for unsubstituted Cp and three AB-systems for the CH_2 group adjacent to ferrocene; however, only salts with the expected structure, **4c, 5c**, were isolated by crystallization. The behavior of amine **17c** toward BuI was the same as observed for **13c**, namely, a product mixture was obtained at room temperature or at reflux, whereas pure salt **6c** without impurities (**20**, R′ = CH_2OMe) was formed in a low yield only when the reaction was carried out at 0 °C.

Scheme 1



R = Et (**a**); Pr (**b**); Bu (**c**); C_5H_{11} (**d**)
X = Br, I

Compound	R′	Compound	R′
1, 7, 12, 18	H	**4, 9, 15**	I
2, 8, 13, 19	Me	**5, 10, 16**	Cl
3, 14	COOMe	**6, 11, 17, 20**	CH_2OMe

Thus, the composition of products resulting from *N*-alkylation of tertiary amines of the ferrocenylmethyl series by alkyl halides, except MeI, is determined by the nature of the 2-substituent in the ferrocene nucleus: electron-donating substituents induce competing ferrocenylmethylation of the starting amine (Scheme 1).

The formation of anomalous products in the alkylation of tertiary amines with alkyl halides was first described for the reaction of 3-dimethylaminomethylindole with methyl iodide.[10] An unusual pattern of alkylation of dimethylaminomethylferrocene on refluxing with isopropyl bromide in acetonitrile was noted by Perevalova *et al.*,[6] who isolated the ammonium salt $(FcCH_2)_2N^+Me_2Br^-$ in a high yield. Subsequently, it has been suggested that the initial "normal" quaternary salt disproportionates as a result of unfavorable steric interactions and the initial amine is alkylated by the intermediate α-ferrocenylcarbenium ion.[11] In our opinion, the side reaction is facilitated by the ease of formation of this intermediate carbocation, whose stability increases as the electron-releasing properties of substituents both in the ferrocene nucleus and at the nitrogen atom are enhanced. Destabilization of this cation by, for example, electron-withdrawing groups makes the side process unfavorable and can even totally prevent it, as in the alkylation of amines **14c—16c** with butyl iodide.

Thus, the reaction of amine **13c** with BuI in aprotic polar solvents can probably occur as follows:

$$YNBu_2 + BuI \longrightarrow YNBu_3^+, \qquad (1)$$

$$YNBu_3^+ \rightleftharpoons Y^+ + NBu_3, \qquad (2)$$

$$YNBu_2 + Y^+ \rightleftharpoons Y_2NBu_2^+, \qquad (3)$$

$$NBu_3 + BuI \longrightarrow NBu_4I, \qquad (4)$$

$Y = C_5H_5FeC_5H_3\text{-}1\text{-}CH_2\text{-}2\text{-}Me$.

Reactions (1) and (4) are irreversible, while reactions (2) and (3) are expected to be reversible in view of the relative instability of the quaternary ammonium salts of the given series. Thus, when methiodides of dimethylaminomethylferrocene or its 2-derivatives are treated with excess tertiary amine R_3N (**21a—d**) with heating, the reaction can be directed exclusively along the required pathway. The advantages of this route with efficient removal of trimethylamine from the reaction mixture are obvious: only one step and high yield. This approach resembles the known method[12] used to prepare the triphenylphosphonium salt $FcCH_2PPh_3^+I^-$ by the reaction of $FcCH_2NMe_3^+I^-$ with PPh_3.

The yields, elemental analysis data, and the ^1H NMR spectra of the trialkyl(ferrocenylmethyl)ammonium salts

Table 1. Methods of synthesis, chemical yields, and the data of elemental analysis for trialkyl(ferrocenylmethyl)ammonium salts

Salt	R	R′	Preparation method	Yield[a] (%)	Found/Calculated (%)			Molecular formula
					C	H	N	
1a	Et	H	*A*	59	47.90 47.80	6.24 6.14	3.24 3.28	$C_{17}H_{26}FeIN$
1b	Pr	H	*A*	66.7	51.32 51.19	6.93 6.87	3.03 2.99	$C_{20}H_{31}FeIN$
1c	Bu	H	*B*[b]	13	58.28 58.36	8.23 8.31	2.71 2.96	$C_{23}H_{38}BrFeN \cdot 0.5H_2O$
1c	Bu	H	*A*	60	—	—	—	
1e	C_5H_{11}	H	*A*	57	56.45 56.43	8.05 8.01	2.59 2.53	$C_{26}H_{44}FeIN$
2a	Et	CH_3	*A*	60.6	48.96 49.00	6.42 6.40	3.11 3.17	$C_{18}H_{28}FeIN$
2b	Pr	CH_3	*A*	93.6	51.97 52.19	7.08 7.09	2.83 2.90	$C_{21}H_{43}FeIN$
2c	Bu	CH_3	*A*	54.4	54.73 54.87	7.76 7.67	2.84 2.67	$C_{24}H_{40}FeIN$
3c	Bu	COOMe	*B*	57.4	51.87 51.91	7.01 7.14	2.43 2.42	$C_{25}H_{40}FeINO_2 \cdot 0.5H_2O$
4a	Et	I	*A*	(66.8)	—	—	—	
4b	Pr	I	*A*	(68.4)	40.18 40.36	5.00 5.25	2.17 2.55	$C_{20}H_{31}FeI_2N$
4c	Bu	I	*B*[c]	10	44.19 44.17	6.00 6.05	2.02 2.10	$C_{23}H_{37}FeI_2N \cdot 0.5CH_3COCH_3$
4c	Bu	I	*A*	55.4	—	—	—	
4c	Bu	I	*B*[d]	30	—	—	—	
5a	Et	Cl	*A*	(58)	—	—	—	
5b	Pr	Cl	*A*	(63)	47.51 47.49	6.36 6.20	2.81 2.78	$C_{20}H_{31}ClFeIN$
5c	Bu	Cl	*B*[c]	10	50.78 50.63	7.09 6.84	2.51 2.57	$C_{23}H_{37}ClFeIN$
5c	Bu	Cl	*A*	(39)	—	—	—	
5c	Bu	Cl	*B*[d]	20	—	—	—	
6c	Bu	CH_2OMe	*A*	20	53.81 54.07	7.73 7.62	2.39 2.52	$C_{25}H_{42}FeINO$
18	Bu	H	*B*	3.5	57.54 57.52	6.79 6.78	2.17 2.24	$C_{30}H_{40}BrFeN \cdot H_2O$

[a] The yield of the recrystallized product (acetone—ether); the yield determined by ^1H NMR spectroscopy is given in parentheses.
[b] 14 days.
[c] With refluxing.
[d] At room temperature.

prepared by classical alkylation of **12c** with alkyl halides or by the reaction of **7—11** with tertiary amines proposed here are listed in Tables 1 and 2.

It can be seen from the foregoing that the new approach proves valuable as applied to the synthesis of monosubstituted derivatives **1a—d** and their analogs **2a—c** and **6c** with electron-donating substituents in position 2. If bromide is required as the counterion, ferrocenylmethyl(triethyl)ammonium bromide or its 2-derivatives are employed in place of methiodides. However, the reaction of salts **9—10** with tertiary amines proceeds slowly and requires prolonged refluxing. For example, the reaction of **9—10** with Et_3N could never be brought to the complete consumption of the initial methiodides. The reaction mixture was substantially resinified and side products containing no ferrocene were accumulated. By comparison with authentic compounds using ^1H NMR spectroscopy, these products were identified as $R_3N^+HI^-$ (**22a—c**), hydroiodides of the initial tertiary amines. Thus, the amines act not only as nucleophiles but also as bases eliminating hydrogen iodide from, most likely, the resulting salts **4a—c, 5a—c**, whose alkyl groups contain active methylene protons in the α-position relative to nitrogen. The purification of salts **4a,b**, **5a—c** by crystallization is either impossible or accompanied by a heavy loss; therefore, the yield of the salts was determined from the ^1H NMR data for the crude product. Only salt **4c** was isolated in a reasonable yield. It follows from the above results that the synthesis of ammonium salts from 2-halo-substituted dialkylaminomethylferrocenes should preferably be performed by the conventional route based on *N*-alky-

Table 2. ^{1}H NMR spectra of trialkyl(ferrocenylmethyl)ammonium salts (δ, J/Hz)

Salt	Alk			C_5H_5	C_5H_3 or C_5H_4	$NC\underline{H}_2C_5H_3$	Other
	CH_3	CH_2	CH_2N				
1a	1.33 (t, 9 H, J = 6.6)	—	3.22 (q, 6 H)	4.27 (s, 5 H)	4.25 (m, 2 H); 4.34 (m, 2 H)	4.51 (s, 2 H)	—
1b	1.02 (t, 9 H, J = 7.2)	1.74—1.90 (m, 6 H)	3.11—3.19 (m, 6 H)	4.36 (s)	4.35—4.36 (m, 9 H)[a]	4.69 (s, 2 H)	—
1c	0.97 (t, 9 H, J = 7.2)	1.35—1.42 (m, 6 H); 1.65—1.75 (m, 6 H)	3.11—3.17 (m, 6 H)	4.35 (s)	4.27—4.33 (m, 9 H)[a]	4.64 (s, 2 H)	—
1d	0.91 (t, 9 H, J = 6.9)	1.25—1.45 (m, 12 H); 1.65—1.80 (m, 6 H)	3.12—3.18 (m, 6 H)	4.35 (s)	4.33—4.35 (m, 9 H)[a]	4.69 (s, 2 H)	—
2a	1.43 (t, 9 H, J = 7.2)	—	3.33 (m, 6 H)	4.24 (s, 7 H)[b]	4.34 (m, 1 H)	4.67 (br.s, 2 H)	2.11 (s, 3 H, CH_3)
2b	1.00 (t, 9 H, J = 7.2)	1.73—1.85 (m, 6 H)	3.12—3.22 (m, 6 H)	4.24 (s)	4.24—4.27 (m, 8 H)[a]	4.69, 4.86 (AB-system, 2 H, J = 13.4)	2.10 (s, 3 H, CH_3)
2c	0.98 (t, 9 H, J = 7.2)	1.34—1.45 (m, 6 H); 1.60—1.79 (m, 6 H)	3.17—3.25 (m, 6 H)	4.25 (s)	4.24—4.28 (m, 8 H)[a]	4.69, 4.85 (AB-system, 2 H, J = 14.1)	2.11 (s, 3 H, CH_3)
3c	0.92 (t, 9 H, J = 7.0)	1.07—1.46 (m, 6 H); 1.46—1.86 (m, 6 H)	3.24—3.35 (m, 6 H)	4.37 (s, 5 H)	4.56 (m, 1 H); 4.88 (m, 1 H); 5.00 (m, 1 H)	5.10, 5.36 (AB-system, 2 H, J = 13.9)	3.72 (s, 3 H, COOMe)
4a	1.42 (t, 9 H, J = 7.3)	—	3.44 (q, 6 H)	4.34 (s, 5 H)	4.44 (m, 1 H); 4.58 (m, 1 H); 4.69 (m, 1 H)	5.10, 5.36 (AB-system, 2 H, J = 13.2)	—
4b	1.00 (t, 9 H, J = 7.1)	1.74—1.93 (m, 6 H)	3.18—3.33 (m, 6 H)	4.35 (s, 5 H)	4.46 (m, 1 H); 4.60 (m, 2 H)	4.28, 5.43 (AB-system, 2 H, J = 14.3)	—
4c	0.97 (t, 9 H, J = 7.2)	1.23—1.48 (m, 6 H); 1.48—1.79 (m, 6 H)	3.13—3.46 (m, 6 H)	4.37 (s, 5 H)	4.47 (m, 1 H); 4.59 (m, 1 H); 4.70 (m, 1 H)	4.25, 5.53 (AB-system, 2 H, J = 14.2)	—
5a	1.42 (t, 9 H, J = 6.8)	—	3.38 (q, 6 H)	4.39 (s, 5 H)	4.28 (m, 1 H); 4.48 (m, 2 H)	4.44, 5.20 (AB-system, 2 H, J = 14.2)	—
5b	0.99 (t, 9 H, J = 7.1)	1.65—1.97 (m, 6 H)	3.16—3.25 (m, 6 H)	4.40 (s, 5 H)	4.28 (m, 1 H); 4.51 (m, 1 H); 4.59 (m, 1 H)	4.46, 5.43 (AB-system, 2 H, J = 14)	—
5c	0.96 (t, 9 H, J = 7.1)	1.27—1.53 (m, 6 H); 1.53—1.85 (m, 6 H)	3.09—3.51 (m, 6 H)	4.41 (s, 5 H)	4.28 (m, 1 H) 4.58	4.45, 5.47 (AB-system, 2 H, J = 14.6)	—
6c	0.99 (t, 9 H, J = 7.2)	1.33—1.45 (m, 6 H) 1.63—1.76 (m, 6 H)	3.25—3.32 (m, 6 H)	4.37 (s, 5 H)	4.38 (m, 1 H); 4.44 (m, 1 H); 4.50 (m, 1 H)	4.67, 4.99 (AB-system, 2 H, J = 14.1)	4.18, 4.54 (2 H, AB-system, $C\underline{H}_2O$, J = 11.5); 3.25 (s, 3 H, $OC\underline{H}_3$)
18c	0.92 (t, 6 H, J = 7.2)	1.20—1.41 (m, 4 H); 1.63—1.94 (m, 4 H and H_2O)	2.75—2.91 (m, 4 H)	4.31 (c)	4.30 (m, 12 H)[b]; 4.39 (m, 4 H)	4.72 (s, 4 H)	—

[a] The integral intensity includes the Cp system.

[b] The integral intensity includes the signals of two protons of substituted Cp.

lation with an alkyl halide, despite the low reaction yields.

Experimental

All experiments were carried out in an argon atmosphere. Organic solvents were purified by standard procedures.[13] ^{1}H NMR spectra were recorded in $CDCl_3$ using a Bruker WP-200-SY spectrometer (200.13 MHz). *N,N*-Dimethylaminomethyl-2-methyl- and *N,N*-dimethylaminomethyl-2-iodoferrocenes were synthesized by a previously described scheme.[14] Methiodides were prepared by a standard procedure.[15]

2-Iodo-1-trimethylammoniomethylferrocene iodide (9). ^{1}H NMR, δ: 3.37 (s, 9 H, 3 CH_3); 4.31 (s, 5 H, C_5H_5); 4.47 (m, 1 H, C_5H_3); 4.60 and 4.93 (both m, 2 H, C_5H_3); 4.21 and 5.70 (2 H, AB-system, CH_2N, α-ferrocenyl, J = 13.6 Hz). Found (%): C, 32.91; H, 3.68; N, 2.69. $C_{14}H_{19}FeI_2N$. Calculated: C, 32.91; H, 3.75; N, 2.74.

2-Chloro-1-trimethylammoniomethylferrocene iodide (10). The reaction of 2-iodo-*N,N*-dimethylaminomethylferrocene (0.5 g, 1.4 mmol) with Cu_2Cl_2 according to a known procedure[15] gave its chloro analog, which was converted into methiodide **10**, yield 67.3%. ^{1}H NMR, δ: 3.33 (s, 9 H, 3 CH_3); 4.35 (s, 5 H, C_5H_5); 4.30 (m, 1 H, C_5H_3); 4.59 and 4.83 (both m, 2 H, C_5H_3); 4.40 and 5.69 (2 H, AB-system, CH_2N, α-ferrocenyl, J = 13.4 Hz). Found (%): C, 39.96; H, 4.61; N, 3.21. $C_{14}H_{19}ClFeIN$. Calculated: C, 40.08; H, 4.56; N, 3.34.

***N,N*-Dibutylaminomethylferrocene (12c).** Methiodide **7** (7.8 g, 0.02 mol) in 10 mL of acetonitrile was refluxed with excess dibutylamine until the solid methiodide dissolved (6 h). The solvent was evaporated, the residue was treated with hexane, the hexane solution was washed with water and dried, the solvent was evaporated, and the residue was kept *in vacuo* over P_2O_5 for several days to remove the remaining dibutylamine. This gave 6.2 g of amine **12c,** yield 95%. ^{1}H NMR, δ: 0.85 (t, 6 H, 2 CH_3, Bu, J = 7.4 Hz); 1.18—1.40 (m, 8 H, 2 $C\underline{H}_2C\underline{H}_2$, Bu); 2.28 (t, 4 H, 2 NCH_2, Bu, J = 7.4 Hz); 3.45 (s, 2 H, CH_2N); 4.06 (s, 5 H, C_5H_5); 4.09—4.03 (m, 4 H, C_5H_4).

1-(*N,N*-Dibutylaminomethyl)-2-methylferrocene (13c). Consecutive cyclopalladation and carbonylation[14] of amine **12c** (3 g, 9 mmol) gave 1-(*N,N*-dimethylaminomethyl)-2-methoxycarbonylferrocene (**14c**) in 62.5% overall yield. ^{1}H NMR, δ: 0.85 (t, 6 H, 2 CH_3, Bu, J = 6.9 Hz); 1.09—1.46 (m, 8 H, 2 $C\underline{H}_2C\underline{H}_2$, Bu); 2.17—2.48 (m, 4 H, 2 $NC\underline{H}_2$, Bu); 3.58 and 4.01 (2 H, AB-system, CH_2N, α-ferrocenyl, J = 13.8 Hz); 3.74 (s, 3 H, $COOCH_3$); 4.07 (s, 5 H, C_5H_5); 4.26 (m, 1 H, C_5H_3); 4.45 (m, 1 H, C_5H_3); 4.67 (m, 1 H, C_5H_3). Amine **14c** (1.62 g, 4.2 mmol) was reduced by $LiAlH_4$ in anhydrous ether. The usual workup gave 1.36 g of **2-dibutylaminomethylferrocenylcarbinol**, yield 91%. ^{1}H NMR, δ: 0.78 (t, 6 H, 2 CH_3, Bu, J = 7.3 Hz); 1.00—1.53 (m, 8 H, 2 $C\underline{H}_2C\underline{H}_2$, Bu); 1.99—2.34 (m, 2 H, NCH_2, Bu); 2.34—2.59 (m, 2 H, NCH_2, Bu); 2.86 (1 H, part of an AB-system, CH_2N, α-ferrocenyl, J = 13.8 Hz); 3.9 (s, 5 H, C_5H_5); 3.85—4.08 (group of signals, 10 H, C_5H_5, C_5H_3, part of an AB-system CH_2N, part of an AB-system CH_2O); 4.70 (1 H, part of an AB-system, CH_2O, α-ferrocenyl, J = 12.1 Hz). Triethylsilane (5 mL) was added to the obtained carbinol in 5 mL of CF_3COOH; after 2 h the mixture was poured into an ice-containing solution of Na_2CO_3, Na_2SO_3 was added to reduce the ferricinium compound formed to some extent, and the product was extracted with petroleum ether. The usual workup gave 1.06 g of amine **13c,** yield 81.5%. ^{1}H NMR, δ: 0.85 (t, 6 H, 2 CH_3, Bu, J = 7.3 Hz); 1.13—1.50 (m, 8 H, 2 $C\underline{H}_2C\underline{H}_2$, Bu); 1.94 (s, 3 H, CH_3); 2.21—2.43 (m, 4 H, NCH_2, Bu); 3.31 and 3.52 (2 H, AB-system, CH_2N, α-ferrocenyl, J = 13.4 Hz); 3.98 (s, 5 H, C_5H_5); 3.84, 4.00 and 4.05 (all m, 3 H, C_5H_3).

1-(*N,N*-Dibutylaminomethyl)-2-iodoferrocene (15c). Consecutive cyclopalladation and iodination of amine **12c** (2.12 g, 6.5 mmol) by known procedures[14] gave amine **15c**, yield 44.3%. ^{1}H NMR, (C_6D_6), δ: 0.84 (t, 6 H, 2 CH_3, Bu, J = 7.0 Hz); 1.12—1.51 (m, 8 H, 2 $C\underline{H}_2C\underline{H}_2$, Bu); 2.25—2.47 (m, 4 H, 2 NCH_2, Bu); 3.41 and 3.51 (2 H, AB-system, CH_2N, α-ferrocenyl, J = 12.6 Hz); 4.06 (s, 5 H, C_5H_5); 4.16, 4.25 and 4.38 (all m, 3 H, C_5H_3). **Amine 15c methiodide.** Found (%): C, 40.45; H, 5.36; N, 2.33. $C_{20}H_{31}FeI_2N$. Calculated (%): C, 40.34; H, 5.25; N, 2.35.

1-(*N,N*-Dibutylaminomethyl)-2-chloroferrocene (16c). The reaction of amine **15c** (0.45 g, 1 mmol) with $CuCl_2$ carried out by a known procedure[16] gave amine **16c,** yield 58%. ^{1}H NMR, δ: 0.84 (t, 6 H, 2 CH_3, Bu, J = 7.1 Hz); 1.12—1.51 (m, 8 H, 2 $C\underline{H}_2C\underline{H}_2$, Bu); 2.25—2.47 (m, 4 H, 2 NCH_2, Bu); 3.41 and 3.51 (2 H, AB-system, CH_2N, α-ferrocenyl, J = 13.8 Hz); 4.06 (s, 5 H, C_5H_5); 4.16, 4.25 and 4.38 (all m, 3 H, C_5H_3). **Amine 16c methiodide.** Found (%): C, 47.69; H, 6.16; N, 2.71. $C_{20}H_{31}ClFeIN$. Calculated: C, 47.71; H, 6.21; N, 2.78.

The reaction of methiodides 7—11 with tertiary amines (general procedure). Method A. Salt **7—11** (1.5 mmol) was refluxed with 3 equiv. of a tertiary amine in 25 mL of acetonitrile for 17—80 h. After cooling, the solvent was evaporated, the residue was dissolved in acetone, the acetone solution was diluted with a large amount of ether and left in a refrigerator at −2—4 °C for crystallization of ammonium salts. The yields, the physicochemical characteristics, and elemental analysis data for these compounds are listed in Tables 1 and 2.

The reaction of amines 12c—17c with butyl halides (general procedure). Method B. Butyl iodide or bromide (3 equiv.) was added to a solution of amine in acetone or in an acetone—MeCN mixture. After 3—14 days, the solvent was evaporated, the residue was treated with ether, the ether was decanted, the product was dissolved in the minimum amount of acetone, and ether was added. Keeping in a refrigerator at −8—10 °C for several days gave ammonium salts as dark-yellow crystals.

Tributyl(ferrocenylmethyl)ammonium bromide (1c) and dibutylbis(ferrocenylmethyl)ammonium bromide (18). A mixture of **12c** with BuBr (3 equiv.) was worked-up after 14 days, and the product was recrysallized from an acetone—ether mixture (1 : 3). The first portion of crystals was collected to give salt **18**, yield 3.5%. Gradual addition of ether to the filtrate gave initially a mixture of salts **1c** and **18**, and then pure salt **1c**. Yield 0.6 g (13%).

The product of reaction of amine 13c with BuI. Yield 60.5%. ^{1}H NMR, δ: 0.81—0.99 (m, 8 H, 2—3 CH_3, Bu); 1.32—1.46 (both m, 11 H, 4—6 $C\underline{H}_2C\underline{H}_2$, Bu); 1.96, 2.05, 2.07, 2.13 (all s, 3 H, $C_5H_3CH_3$); 3.14—3.36 (both m, 4.7 H, 2—3 CH_2, NCH_2, Bu); 3.99 (s), 4.17 (s), 4.18 (s), 4.22 (s), 3.99—4.50 (m) (8 H, C_5H_5 and C_5H_3); 4.52—4.85 (m, 2 H, CH_2N, α-ferrocenyl).

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