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α-Metallocenylalkylation

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Abstract. Experimental data on α-metallocenylalkylation reac**tions are generalised and systematised. These reactions are widely used for the synthesis of different metallocene derivatives, many of which may be of practical importance. Advantages and limitations of different variants of these reactions under homogeneous and heterogeneous conditions are discussed, new approaches to their efficient realisation are offered. The bibliography includes 160 references.**

I. Introduction

Dicyclopentadienyl complexes of subgroup VIIIA transition metals (metallocenes) as well as their derivatives played an important role in the progress of the chemistry of π-complexes of transition metals.[1–4] Reactions with the participation of α-metallocenylcarbocations (MCC) the enhanced stability of which is due to the presence of the electron-donating metallocene fragment in the α-position to the cationic centre are of considerable interest.[5] With the help of these reactions that we have named 'α-metallocenylalkylation', different α-metallocenylalkylated compounds, especially those that could not be synthesised by other methods, may be obtained.[6,7]

The early stage in the development of this field of chemistry of organometallic compounds (OMC) has been associated with the elaboration of methods of α-ferrocenylalkylation by trialkyl(ferrocenylmethyl)ammonium salts, chloromethylferrocene, and stable salts of α-ferrocenylcarbocations that allowed one to introduce the $FcCH_2$† group into the molecules of different organic and inorganic nucleophilic derivatives.[3] Each of these methods, however, has fundamental limitations in the choice of both the ferrocene-containing derivative and the nucleophilic substrate.

† Mc is $C_5H_5MC_5H_4$, Fc is $C_5H_5FeC_5H_4$, Rc is $C_5H_5RuC_5H_4$, and Oc is $C_5H_5OsC_5H_4$.

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More suitable and diverse ferrocene-containing reagents in these reactions are α-hydroxyalkylferrocenes which readily generate on treatment with mineral or strong carboxylic acids, the corresponding metallocene cations that react further with nucleophiles. Surprisingly, these ferrocene derivatives have not until recently found extensive application in α-ferrocenylalkylation reactions apart from a few special cases.[8–11]

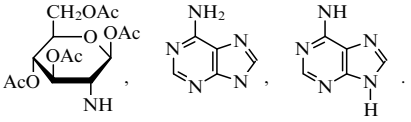
Annual reviews on ferrocene by Rockett and Marr that have been published over 20 years (the first review was published in 1972, and the last one was published in 1991) in the *Journal of Organometallic Chemistry* usually quoted 5 – 10 papers on ferrocenylalkyl compounds.[12] There are separate sections concerning the α-metallocenylalkylation reactions in a monograph[3] and Gmelin Handbook[13] containing extensive experimental data accumulated before 1979, however, there is no specialised review covering this subject. The interest in these studies at present does not decline which is associated with the development of the theoretical aspects of structure and reactivity of MCC[14] as well as with the search for convenient methods for the synthesis of valuable ferrocene-containing compounds.[15] The present report is devoted to the analysis and generalisation of the studies of α-metallocenylalkylation reactions performed during the last 15 years.

II. α-Ferrocenylalkylation with ferrocenylalkylammonium salts and other onium compounds

Among the reagents for the introduction of the ferrocenylmethyl group in nucleophilic substrates, most attention was paid to quaternary ammonium salts of *N*,*N*-dimethylaminomethylferrocene[3,13] which is due to their availability and high reactivity.[16,17] In particular, new reactions of N-, C-, S-, and P-ferrocenylmethylation of different compounds were performed with the help of *N*,*N*,*N*-trimethyl(ferrocenylmethyl)ammonium iodide (**1**).[18–23] In the presence of alkali or sodium carbonate in all the cases elimination of trimethylamine and the corresponding salt of the hydriodic acid occurs.[18–20] Thus, new ferrocenylalkyl derivatives of nitrogen bases were synthesised:

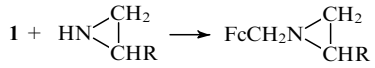
$$\underset{\mathbf{1}}{FcCH_2\overset{+}{N}Me_3\,I^-} + HNu \longrightarrow FcCH_2Nu + NMe_3 + HI$$

Nu = $NHNH_2$, NHNHPh, $NHC(O)NH_2$, $NHC(S)NH_2$, $NHNHC(O)NH_2$, $NHNHC(S)NH_2$, NHNHC(S)NHPh,



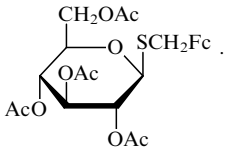
An 8–10-fold excess of hydrazine hydrate is necessary for the preparation of ferrocenylmethylhydrazine,[18] as the action of a 4-fold excess of the nucleophilic agent on the salt **1** gives the product of complete ferrocenylmethylation of hydrazine, tetrakis(ferrocenylmethyl)hydrazine, with a yield of higher than 80%. Condensation of the salt **1** with $AcNHCH(COOEt)_2$ in ethanol in the presence of EtONa gives the ethyl ester of *N*-acetyl-3-ferrocenyl-α-alanine, which was separated into enantiomers by column chromatography on solid chiral carriers such as *N*-*tert*-butylamides of L-amino acids.[21]

The condensation of 2-R-aziridines with the methiodide **1** in aqueous solution in the presence of potassium carbonate gives 2-R-1-(ferrocenylmethyl)aziridines in 70%–75% yields.[24]

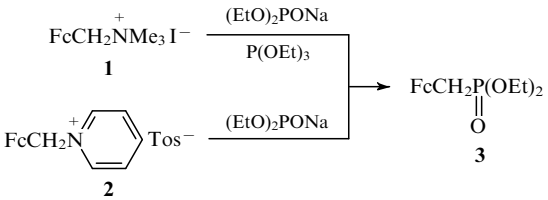


R = H, Me, Et.

In reactions of the methiodide **1** with sodium diethyldithiocarbamate in aqueous medium,[18] or with thiols (RSH) in the presence of EtONa in ethanol,[22] or with 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranose in acetonitrile in the presence of sodium carbonate,[19] the corresponding products of S-ferrocenylmethylation are formed in 50%–90% yield:

$FcCH_2SC(S)NEt_2$, $FcCH_2SR$, 

When a mixture of equimolar amounts of methiodide **1** and sodium diethyl phosphite was refluxed for 17 h in anhydrous xylene, the product of P-ferrocenylmethylation, *O*,*O*-diethyl ferrocenylmethylphosphonate (**3**), was formed in 45% yield.[18] The phosphonate **3** was prepared similarly from ferrocenylmethylpyridinium tosylate (**2**), however, the reaction conditions were milder (refluxing of the reagents for 2 h).[18] The product **3** was also synthesised by the reaction of the salt **1** with triethyl phosphite (the Arbuzov rearrangement) in aqueous medium.[18]



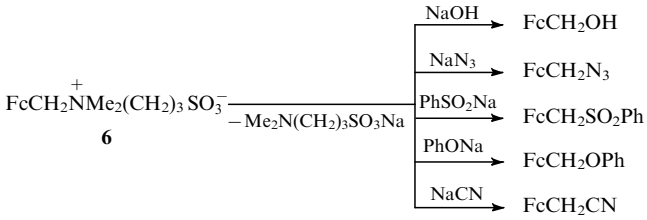
Other salts of *N*,*N*,-dimethylaminomethylferrocene can also enter into the ferrocenylmethylation reaction. Thus, upon reaction of different alcohols with the salt **4** in alkaline medium, O-ferrocenylmethylation occurs to give ethers **5** in 75%–92% yield.[25]

$$\underset{\mathbf{4}}{[FcCH_2\overset{+}{N}Me_2SO_2C_6H_4Me\text{-}4]\,Cl^-} + ROH \xrightarrow{NaOH} \underset{\mathbf{5}}{FcCH_2OR}$$

R = Et, Bu, C_8H_{17}, $CH_2CH=CH_2$, $CH_2CH_2OCH_2Fc$.

It has been found [26] that the ferrocenylmethylation of alcohols by the salts of *N*,*N*-dimethylaminomethylferrocene does not require the isolation of the ammonium salts in the pure state; it is quite sufficient to add the salt-forming reagent such as dichloroethane or *p*-toluenesulfonylchloride to the mixture of ferrocenylmethylamine, the corresponding alcohol, and alkali. This does not result in a decrease in the yields of the ethers **5**.

The betaine, dimethyl-3-sulfopropyl(ferrocenylmethyl)-ammonium (**6**), is yet another rather efficient ferrocenylalkylating reagent.[27] This compound reacts readily with different nucleophilic reagents in aqueous medium to form the products of O-, N-, S-, and C-ferrocenylmethylation in 92%–97% yield.[27]



As is evident from the scheme, the second reaction product is sodium *N*,*N*-dimethylaminopropyl-3-sulfonate, which can be readily separated from the ferrocenylmethyl derivatives due to its high solubility in water.

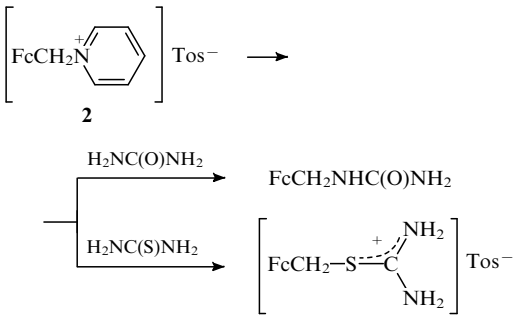
The activity of the betaine **6** is 10 times higher than that of the salt **1**, which allowed one to perform with its help direct ferrocenylmethylation of ammonia in aqueous solution.[27] This resulted in a mixture of products of N- and O-ferrocenylmethylation, which could be separated by chromatography on alumina.

$$\mathbf{6} + NH_4OH \xrightarrow[-\,Me_2N(CH_2)_3SO_3NH_4]{}$$

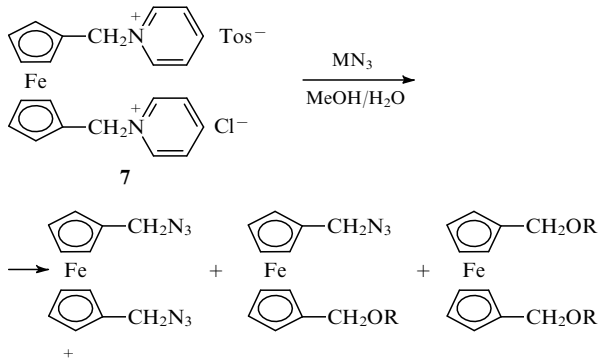
$$\longrightarrow \underset{(21\%)}{FcCH_2OH} + \underset{(32\%)}{FcCH_2NH_2} + \underset{(2\%)}{(FcCH_2)_2O} + \underset{(36\%)}{(FcCH_2)_2NH}$$

The salts **1** and **2** under analogous conditions practically do not react with aqueous ammonia.[27]

The pyridinium derivatives may be successfully used as the ferrocenylalkylation agents. In particular, the interaction of ferrocenylmethylpyridinium tosylate (**2**) with carbamide in methanol results in the formation of ferrocenylmethylcarbamide, while thiocarbamide under the same conditions formed only *S*-ferrocenylmethylthiouronium tosylate.[23]

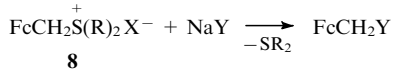


The reactions of the salt **7** with the salts of hydrazoic acid MN_3 in aqueous methanol gives a mixture of the products of N- and O-ferrocenylalkylation.[23]



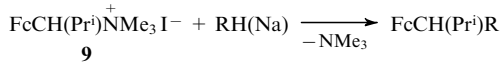
M = Na, NEt_4; R = H, Me.

Not only ammonium (compounds **1**, **2**, **4**, and **6**), but also sulfonium salts **8** proved to be rather efficient ferrocenylmethylating reagents.[28] In reactions with sodium cyanide and azide, they gave the corresponding ferrocenylmethylation products in 90% to 95% yield.[28]



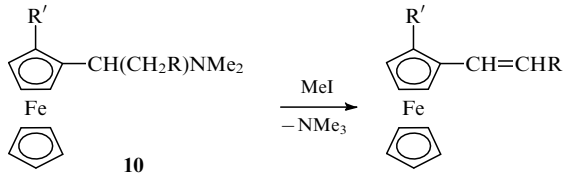
R = Me, Et, CH_2Ph; X = BF_4, ClO_4; Y = CN, N_3.

It is noteworthy that most of the salts, homologues of *N*,*N*-dimethylaminomethylferrocene of the $FcCH(R)N^+Me_3X^-$ (R = Alk) type, are thermally unstable and not easily accessible compounds.[29,30] Therefore, they did not find extensive application as ferrocenylalkylating reagents. Only the use of the methyl iodide **9** in reactions of α-ferrocenylalkylation of sodium azide and thioglycolic acid, has been reported.[31]



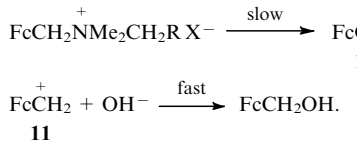
R = N_3, SCH_2COOH.

The salts of *N*,*N*,-dimethylaminoethylferrocene also turned out to be unstable and could not be isolated in the pure state. For instance, the interaction of amines **10** with MeI in acetone results in the formation of the corresponding substituted vinylferrocenes rather than ammonium salts.[32,33]



R = H, Ph; R′ = Alk, PPh_2, $SiMe_3$.

The study of the reactivity of different trialkyl(ferrocenylmethyl)ammonium salts in reactions with water in alkaline, neutral, and acidic media has revealed[17] that hydrolysis follows the S_N1 mechanism with the intermediate formation of ferrocenylmethyl cation **11** at the rate-determining stage.

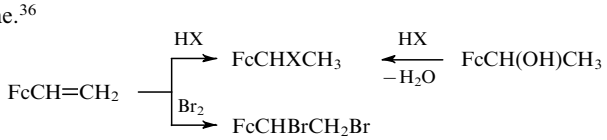


The kinetic isotope effect of the solvolysis of ferrocenyl-1,1-dideuteromethyltrimethylammonium iodide in aqueous medium is not more than 10% at 80 °C (K_H/K_D = 1.06±0.04), while the activation parameters of the reaction at 70–90 °C are close to those for the salt **1** ($\Delta H^{\neq}$ = 132.6±3.8 kJ mol^{-1}, $\Delta S^{\neq}$ = 54.0±2.1 kJ mol^{-1}). These data led to the conclusion[34] that in the transition state the α-carbon atom in the carbocation **11** is bound both with the carbon atom of the five-membered ring of the ferrocene system and with the iron atom; a transition state of the fulvene type is not realised.

Thus, the method of α-ferrocenylalkylation by ferrocenylammonium salts is widely used for the synthesis of numerous derivatives of the ferrocene series, however, it cannot be considered general, as only ferrocenylmethyl compounds may be thus obtained with high yields.

III. Reactions of α-haloalkyl derivatives of ferrocene with nucleophiles

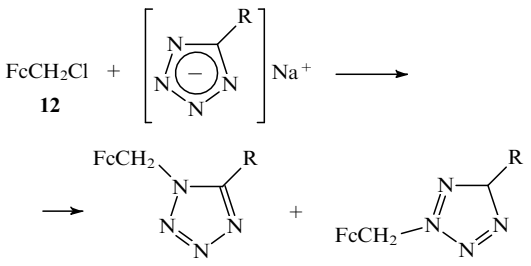
α-Halogen-containing derivatives of ferrocene are unstable at room temperature, they cannot be isolated in the pure state. Tidwell and Traylor[35] described the preparation of chloromethylferrocene (**12**) which involved bubbling of HCl through an ethereal solution of ferrocenylmethanol (**13**) in the presence of anhydrous calcium chloride, however neither the isolation procedure nor the constants of the isolated product were reported. When anhydrous hydrogen halides passed either through the solution of vinylferrocene in pentane or through the solution of α-hydroxyethylferrocene in diethyl ether in the presence of Al_2O_3 at −78 °C, α-chloro- and α-bromoethylferrocenes were obtained, and the reaction of bromine with vinylferrocene under the same conditions resulted in the formation of α,β-dibromoethylferrocene.[36]



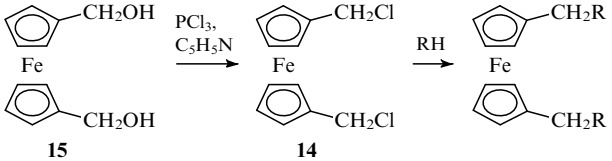
X = Cl, Br.

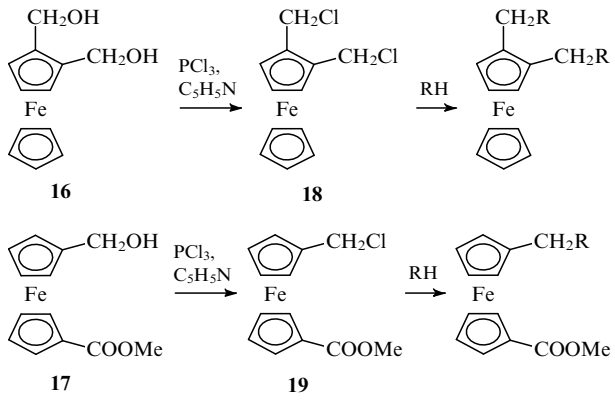
However, all the isolated compounds are extremely unstable and can be stored for several days at low temperature *in vacuo*; they readily undergo hydrolysis in the presence of moisture.[36]

Chloromethyl- and 1,1′-bis(chloromethyl)ferrocene (**14**) are also formed in the reaction of PCl_3 with the corresponding hydroxyl derivatives of ferrocene **13** and **15** in anhydrous acetone in the presence of pyridine at 0 °C.[37,38] However, due to their instability, they were used in the α-ferrocenylmethylation reactions of such nucleophilic compounds as sodium azide,[23] carbamide,[39] sodium salts of 1,2,4-triazoles[37,38] and tetrazoles without preliminary isolation. In the latter case, a mixture of 1- and 2-isomers was formed.[37,38]



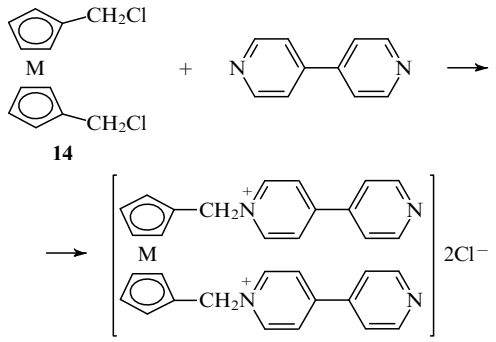
The reactions of ferrocene α-hydroxymethyl derivatives **15**–**17** with PCl_3 in the presence of pyridine in anhydrous THF are reported.[40,41] The chloromethyl derivatives thus formed **14**, **18**, **19** were used without isolation in the α-ferrocenylalkylation reactions of different nucleophilic substrates such as formamidomalonate, phenol, thiophenol, *N*-methylaniline, and acetylacetone.





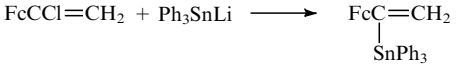
R = C(NHCHO)(COOEt)$_2$, OPh, SPh, N(Me)Ph, CH(COMe)$_2$.

In the reactions of dichlorides **14** with 4,4′-bipyridine in DMF, the corresponding pyridinium salts were synthesised with yields of 80% and 39%.[42]



M = Fe, Ru.

The reaction of relatively stable α-chlorovinylferrocene with lithium triphenylstannane in a mixture of anhydrous THF and diethyl ether results in the formation of 1-ferrocenyl-1-triphenylstannylethylene in 72% yield.[43]



α-Ferrocenylalkylation by haloalkyl derivatives of ferrocene did not find extensive application because of the low stability of α-haloalkylferrocenes.

IV. Application of α-hydroxyalkyl- and α-alkenylmetallocene derivatives in α-metallocenylalkylation reactions

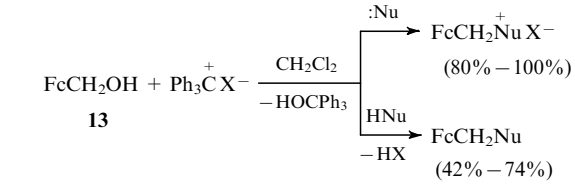
The synthetic potentialities of α-metallocenylalkylation of nucleophilic derivatives are primarily determined by the availability of the corresponding organometallic component. α-Hydroxyalkylmetallocenes of the VIIIA subgroup are the most convenient and promising alkylation reagents. They are synthetically accessible and demonstrate high stability at room temperature, while under certain conditions the hydroxy group can easily undergo nucleophilic substitution. α-Alkenyl derivatives of metallocenes have also found application as alkylating reagents. Metallocenylalkylation by α-hydroxyalkylmetallocenes can be subdivided into O-, S-, C-, N-, P- and other types of α-metallocenylkylation depending on the element that forms a new bond as a result of the substitution of the hydroxy group.

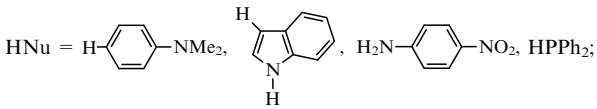
At present, a few methods for the preparation of α-hydroxyalkylmetallocenes are known.[1–3,7,44–71] Although their consideration is beyond the scope of the present review, the stereoselective reduction of metallocenylketones by lithium aluminium hydride in the presence of optically active compounds[48–50] is however worth mention. The enantiomeric metallocenyl-containing alcohols thus prepared on dissolution in acid, form optically active metallocenylcarbocations[49] that may be used for the synthesis of chiral derivatives of subgroup VIIIA metallocenes by α-metallocenylalkylation. A method of preparation of chiral ferrocenyl alcohols , which allows one to synthesise FcCH(OH)R with an optical purity of higher than 95% and the yields of 80%–89%, deserves special attention.[72]

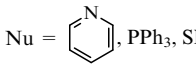
Two methodologies of α-metallocenylalkylation[3,6,7] by alcohols and alkenes, namely, reactions in homogeneous (HS) and two-phase (TS) systems, may be distinguished.

1. Reactions in homogeneous systems

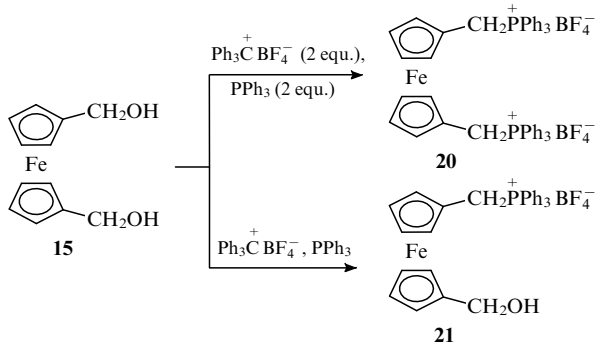
A general method for α-ferrocenylalkylation in a homogeneous system involves the action of triphenylcarbenium salts at room temperature on an equimolar mixture of α-hydroxyalkylferrocene derivative and a nucleophile in a polar solvent, (anhydrous dichloromethane).[6,73,74] This method proved especially useful for the synthesis of different onium salts, as they may be easily separated from triphenylmethanol, which is a nonpolar side product of the reaction.[73,74] In the case of non-ionic α-ferrocenylalkyl compounds chromatographic separation of the reaction products is necessary.[6]

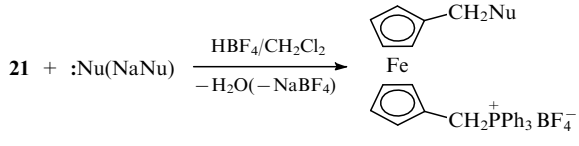






In the reaction of the diol **15** with triphenylphosphine under identical conditions different reaction products are formed depending on the reagent ratio.[6] The bistriphenylphosphonium salt **20** was obtained in quantitative yield when the ratio of **15**, triphenylphosphine, and triphenylcarbenium tetrafluoroborate was 1 : 2 : 2, while the monotriphenylphosphonium salt **21** was formed in 62% yield when the reagent ratio is 1:1:1.[6,73] Due to the presence of the hydroxymethyl group, the latter was successfully used in the synthesis of heteroannular disubstituted ferrocene derivatives in a two-phase liquid–liquid system (see Section VI).



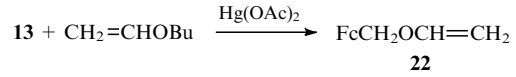


Nu = N_3, SCN, $SMe_2BF_4^-$, $-N^+$ BF_4^-, HN NO_2.

In contrast to ferrocenemethanols **13** and **15**, α-hydroxyalkyl derivatives of ruthenocene and osmocene do not react with nucleophilic reagents under the action of triphenylcarbenium salts under the same conditions.[6] In this case, only the known products of nucleophilic substitution of the triphenylmethyl series are formed.

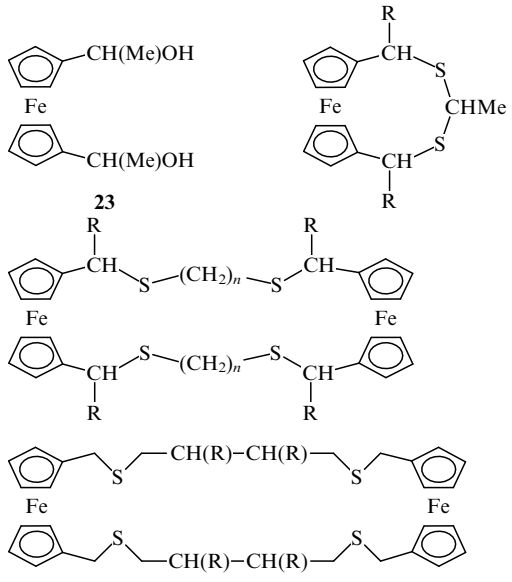
a. O-Alkylation

Numerous examples of α-ferrocenylalkylation of alcohols and phenols at the oxygen atom by α-hydroxyalkylferrocenes are known.[3] These reactions readily proceed in the presence of catalytic amounts of organic (acetic, trifluoroacetic) or Lewis acids in an organic solvent (alcohols, CH_2Cl_2). For instance, re-esterification of butyl vinyl ether by ferrocenemethanol **13** in the presence of mercuric acetate gives ferrocenylmethyl vinyl ether **22**, which readily polymerises under the action of cationic catalysts.[75]



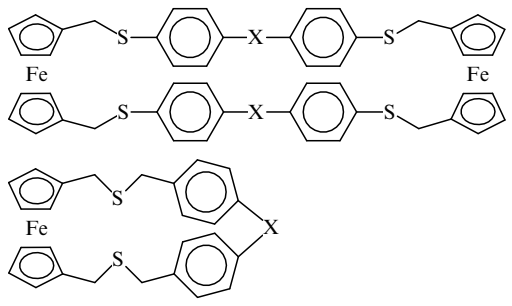
b. S-Alkylation

The reactions of α-hydroxyalkylferrocenes with sulfur-containing nucleophilic reagents have been studied rather thoroughly. For instance, the interaction of the diol **15** or 1,1′-bis(α-hydroxyethyl)ferrocene **23** with dithiols HSCH(R)CH(R)SH or $HS(CH_2)_nSH$ in CH_2Cl_2 in the presence of trifluoroacetic acid leads to the formation of ferrocenophanes with the bridging sulfur atoms,[76] which are of interest as complex forming ligands.



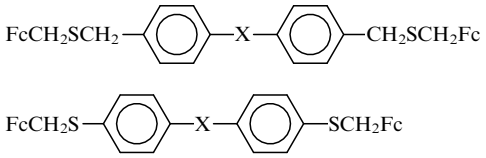
R = H, Me, Ph; n = 2, 3.

The analogous reactions of the diol **15** with mercapto derivatives $(4\text{-}RC_6H_4)_2X$, where R = SH, CH_2SH, and X = CH_2, O under similar conditions give the corresponding paracyclophanes.[77]

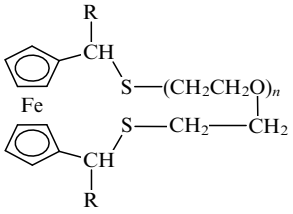


X = CH_2, O.

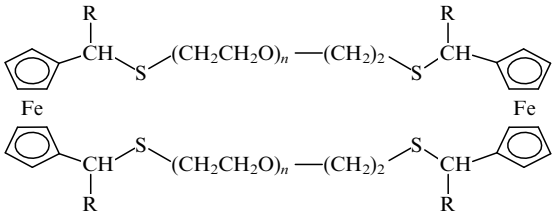
In reactions of the alcohol **13** with the same mercapto derivatives at a reagent ratio of 2:1, linear products of S-ferrocenylmethylation are formed.[77]



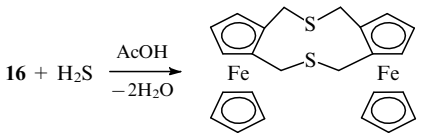
The interaction of the diols **15**, and **23** with bis-mercaptoethers $HS(CH_2CH_2O)_nCH_2CH_2SH$ (n = 2, 3) in a mixture of benzene and CH_2Cl_2 in the presence of CF_3COOH under high-dilution conditions, results in mononuclear ferrocenophanes in high yields.[78, 79]



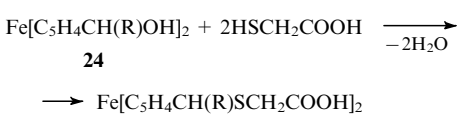
In solutions with higher concentrations the binuclear products may also be obtained; however, their yields are low (5% – 7%).[79]



A binuclear ferrocenophane was synthesised in 87% yield by reaction of the homoannular diol **16** with H_2S in acetic acid.[80]

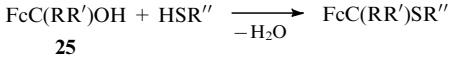


1,1′-Bis[(α-carboxymethylthio)alkyl]ferrocenes were synthesised in 75% – 90% yields in reactions of heteroannular ferrocenyldiols **24** with thioglycolic acid in CH_2Cl_2 in the presence of CF_3COOH. They are formed as a mixture of stereoisomers that could not be separated into enantiomers by TLC.[81]



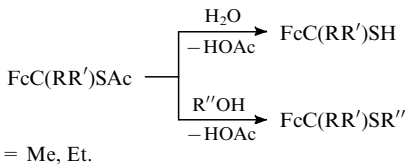
R = Me, Et, Pr^i.

The reaction of the α-hydroxyferrocenyl derivatives **25** with thiophenol,[82] $HSCH_2CH(OH)CH_2(OH)$ [83] and thioacetic acid [84] under the same conditions results in a high yield of the corresponding products of S-α-ferrocenylalkylation.



R = H, R′ = H, Me, Et, Pr^i, Ph; R = Me, R′ = Me, Ph;
R″ = SPh, $CH_2CH(OH)CH_2(OH)$, Ac.

The resulting thioacetates FcC(RR′)SAc readily undergo hydrolysis and alcoholysis, which allows one to obtain the corresponding thiols and thioethers in high yields.[84]



$R'' = Me, Et.$

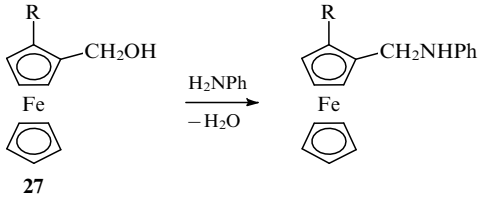
The study of the kinetics of S-α-ferrocenylalkylation of thioglycolic acid under the action of FcCH(Me)OH in CH_2Cl_2 in the presence of CF_3COOH demonstrated that the process has an activation energy of 83.04 kJ mol^{-1} (see Ref. 85); it is completed in 20 min at 20 °C and results in the formation of the acid $FcCH(Me)SCH_2COOH$. The authors discovered the intermediate formation of vinylferrocene $FcCH=CH_2$. Its quantity is minimised in the temperature range of 20–30 °C.

c. N-Alkylation

The synthesis of ferrocenylalkylazide in the reaction of hydrazoic acid with the alcohol **26** (R = Ph) in benzene in the presence of trichloroacetic acid is one of the first examples of N-α-ferrocenylalkylation.[86]

$$\underset{\mathbf{26}}{FcCH(R)OH} + HN_3 \xrightarrow[-H_2O]{Cl_3CCOOH} FcCH(R)N_3\,.$$

Later, this reaction was extended to a wide range of nitrogen-containing nucleophiles.[87] Thus the interaction of aniline with alcohols **27** in aqueous medium gives products of N-ferrocenylalkylation in poor yields.[87,88] Benzylamine and piperidine[88] under these conditions proved to be non-reactive, which is evidently due to their high basicity in comparison with aniline.



$R = H, I, CH_2NHPh.$

Heating of equimolar amounts of ferrocenemethanolylcarbinol **13** with aniline in AcOH at 130 °C leads to the products of C-ferrocenylmethylation at the aromatic nucleus, which is explained by the possibility of migration of the ferrocenylmethyl group from the nitrogen atom towards the aromatic nucleus at high temperature.[89]

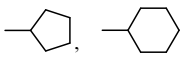
$$\mathbf{13} + H_2NPh \longrightarrow 2\text{-}H_2NC_6H_4CH_2Fc + 4\text{-}H_2NC_6H_4CH_2Fc.$$

Indeed, heating of *N*-ferrocenylmethylaniline up to 130 °C results in rearrangement with the formation of the above-mentioned products of C-alkylation with the ratio of *ortho*- and *para*-isomers 1.6 : 1. However, if the ratio of the starting reagents, the alcohol **13** and aniline, is 2 : 1, only the products of di- and mono-N-ferrocenylmethylation, $PhN(CH_2Fc)_2$ and $PhNHCH_2Fc$, are formed under the same conditions.[89]

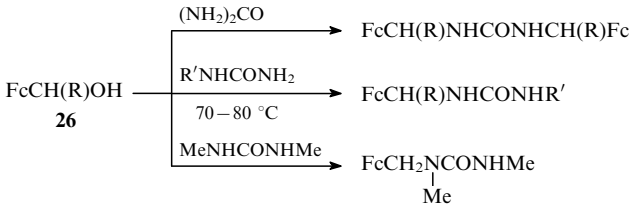
The study of the effect of the acidity of the medium on the reaction of the alcohol **13** with different amines has demonstrated that in the case of aliphatic amines the highest yields (up to 97%) are achieved in acetic acid at pH = 5.2–4.9, while in the case of aromatic amines yields of 70%–95% are achieved in aqueous methanol at pH = 7.9–9.7.[10,90]

$$\mathbf{13} + H_2NR \longrightarrow FcCH_2NHR$$

$R = Bu^t, CH_2Ph, Ph, 4\text{-}NO_2C_6H_4, 2,4\text{-}(NO_2)_2C_6H_3, C(O)NH_2,$



N-α-Ferrocenylalkylation of urea and its derivatives is also performed in high yields (70%–90%) by alcohols **26** in acetic acid. Usually, alkylation proceeds at the unsubstituted aminogroup, however in the case of *N*,*N*′-dimethylurea the product of substitution at the *N*-methylaminogroup has also been isolated. An excess of alcohols **26** results in the formation of the products of the double *N*,*N*′-di-α-ferrocenylalkylation in low yields.[91]



$R = H, Me, Ph; R' = Me, Ph.$

A method for the conversion of α-hydroxyalkylferrocenes into amines[92–94] by substitution of the hydroxyl group under the action of dimethylamine or tetramethyldiaminomethane in the presence of acetic acid or $Me_2NH \cdot AlCl_3$ in CH_2Cl_2 has been developed.

$$FcCH(R)OH + Me_2NH \xrightarrow[CH_2Cl_2]{AlCl_3} FcCH(R)NMe_2$$

$R = H, Me, Et.$

However, the amines formed (R = Me, Et) undergo the Hoffmann degradation on heating in AcOH with the formation of α-substituted vinylferrocenes, which readily polymerise under the reaction conditions.[92]

Another method for the preparation of α-ferrocenylalkylamines[95,96] is based on the generation of the corresponding α-ferrocenylcarbocations from α-ferrocenylalkanols in strong acids and their further reaction with amines. It is sometimes possible to isolate the carbenium salts. Thus, the alcohols **26** (R = Me, Ph) under the action of HBF_4 in a mixture of diethyl ether and acetic anhydride are converted into carbenium salts **28**, which have been isolated in the pure state.[95] They readily react with amines in CH_2Cl_2 to form α-ferrocenylalkylamines.[95,96]

$$FcCH(R)OH \xrightarrow[-H_2O]{HBF_4} \underset{\mathbf{28}}{[FcCH(R)]^+\,BF_4^-} \xrightarrow[-HBF_4]{R'_2NH} FcCH(R)NR'_2$$

$R = Me, Ph; R' = Me, Et.$

Hermann and Ugi[66,70] synthesised a large series of α-ferrocenylalkylamines by a 'three component' reaction of ferrocene with a carbonyl compound and an amine in a mixture of CCl_3COOH and AcOH in the presence of fluorosulfonic acid.

$$FcH + O{=}CRR' + HNR''R''' \xrightarrow{HSO_3F} FcC(RR')NR''R'''$$

$R, R' = H, Alk, Ph; R'', R''' = H, Alk.$

Taking into account the availability of the initial reagents, this reaction may be considered as a simple preparative method for the synthesis of α-ferrocenylalkylamines despite the low yields. Ugi *et al.*[97] extended this method for the preparation of chiral α-ferrocenylalkylamines which were used for the stereospecific synthesis of peptides.

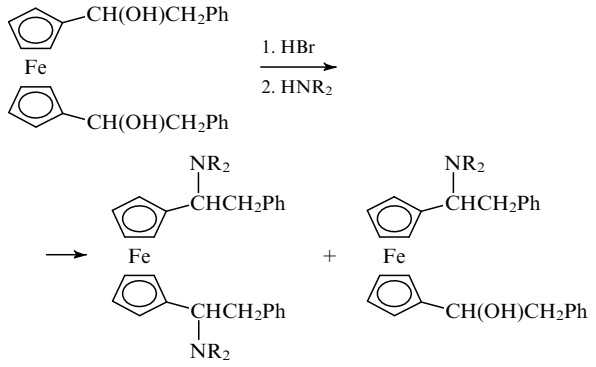
Successive interaction of α-hydroxyethylferrocene with gaseous HBr in benzene and then with amines results in the corresponding α-aminoethylferrocenes which were synthesised in 60%–85% yields.[98]

$$FcCH(Me)OH + HNR_2 \xrightarrow[2.\ HNR_2]{1.\ HBr} FcCHMeNR_2$$

$R = Me, Pr^i,$ .

Reactions with ammonia lead to a mixture of mono-, bis-, and tris-α-ferrocenylethylamines.[98]

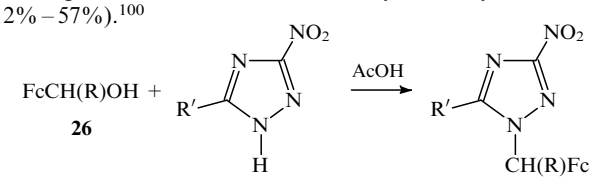
The reaction of 1,1′-bis(α-hydroxy-β-phenylethyl)ferrocene with the excess of R_2NH under analogous conditions results in a mixture of products, *viz.*, 1,1′-bis(α-amino-β-phenylethyl)ferrocenes (yield 50% – 70%) and 1-(α-hydroxy-β-phenylethyl)-1′-(α-amino-β-phenylethyl)ferrocenes (yield 15% – 30%).[99]



R = Me, Et.

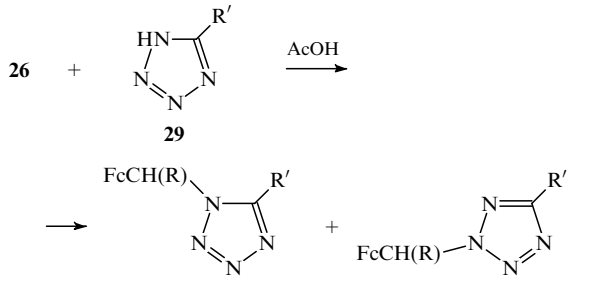
It is interesting to note that the reaction of 1,1′-bis(α-hydroxyethyl)ferrocene **23** with HBr and then with dimethylamine leads to a more complicated mixture of products, which contains 1,1′-bis(α-dimethylaminoethyl)ferrocene, 1-(α-dimethylaminoethyl)-1′-vinylferrocene, and 1,1′-divinylferrocene in the yields of 35%, 45%, and 15% respectively.[99] Butler *et al.*[98,99] suggest that under the specified conditions the alcohols are first converted into α-bromo-, or α,α′-dibromoalkylferrocenes, and then nucleophilic substitution of bromine by the amino group occurs.

Besides amines, the nitrogen-containing heterocyclic compounds, such as 1,2,4-triazole [100] and tetrazole [100–102] derivatives also readily enter into the reaction of N-α-ferrocenylalkylation. The interaction of the alcohols **26** with 3-nitro- and 3,5-dinitro-1,2,4-triazoles in AcOH results in the formation of the corresponding 1-substituted triazoles whose yields vary considerably (12% – 57%).[100]



R = H, Me, Ph; R′ = H, NO_2.

The products of the reactions of the alcohols **26** with the substituted tetrazoles **29** are mixtures of isomeric 1- and 2-α-ferrocenylalkyltetrazoles,[100] the ratio thereof depending on the nature of both the substituent R′ in the heterocycle and on the substituent R in the alcohols. In particular, increase in the size of the substituent R results in a decrease in the yield of the 1-isomer.

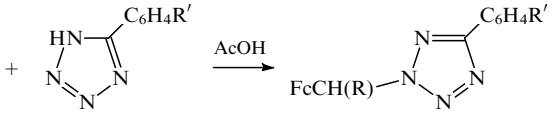


R′ = H, Me, NO_2.

The following results were obtained in the alkylation of the derivatives of tetrazole **29** and 1,2,4-triazole by the diols **15**, and **23** in AcOH.[100] A mixture of all three possible isomers (1,1′-, 2,2′-, 1,2′-) is formed from tetrazole; 5-methyltetrazole gives two isomers (2,2′- and 1,2′-), while only the 2,2′-substituted isomer is obtained from 5-nitrotetrazole. In the reaction of 3-nitro- and 3,5-dinitro-1,2,4-triazoles only 1,1′-disubstituted products of α-ferrocenylalkylation have been isolated.

The detailed study of the alkylation of tetrazole by α-hydroxyethylferrocene in carboxylic acids [101] has demonstrated that in CF_3COOH, 1-and 2-isomers are formed in the ratio of 2.4:1, while in AcOH the ratio between these isomers is close to 1:1. These differences in the isomeric composition are due to the formation of the protonated tetrazole in CF_3COOH, and as a consequence ferrocenylalkylation proceeds *via* a different mechanism.[101]

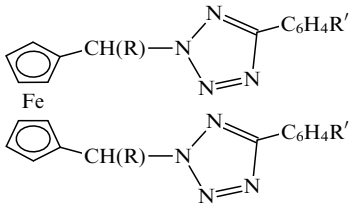
The α-ferrocenylalkylation of 5-aryltetrazoles in AcOH, independent of the structure of alcohols **26** and the electronic properties of the substituents in the heterocyclic nucleus, results only in 2-(α-ferrocenylalkyl)-5-aryltetrazoles in 80% – 85% yield.[102]



R = H, Me, Ph; R′ = H, 3-Me, 4-Me, 4-Br, 4-OMe, 3-NO_2.

According to Shirobokov *et al.*,[102] tetrazolate-anions and α-ferrocenylcarbocations are the reactive species in this reaction, and the selectivity of the process is determined by steric factors in the substrate and alkylation agent.

In the alkylation of 5-aryltetrazoles by the diols **15**, and **23** under the same conditions, ferrocene compounds containing two tetrazole rings with the C – N bond in position 2 are formed.[102]



R = H, Me.

d. C-Alkylation

There are only few examples of the reactions of α-hydroxyalkylferrocenes with CH-acids performed in homogeneous systems.[103] The CH-acids with activated methylene and methine groups have been most studied. Thus heating of alcohol **13** with the C-substituted diethyl malonates in DMF gave the corresponding ferrocenylmethyl derivatives in 40% – 50% yield.[103]

13 + $HCR(COOEt)_2$ ⟶ $FcCH_2CR(COOEt)_2$

R = H, Me, Ph.

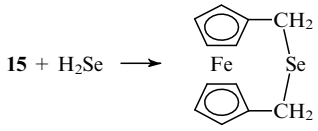
α-Hydroxyalkylferrocenes react with organomagnesium compounds [104] to form a multicomponent mixture. It should be noted that under these conditions neither diphenyl- nor triphenylmethanols react with MeMgI.[104]

$FcC(RR')OH + R''MgX \longrightarrow FcC(RR')R''$

R = R′ = Me, Ph; R = H, R′ = CH=CHPh; R = H, R′ = Ph; R″ = Me, Et, X = Br, I.

e. Se-Alkylation

The interaction of the diol **15** with hydrogen selenide in AcOH in the presence of CF_3COOH, resulting in the formation of 2-seleno-[3]-1,1′-ferrocenophane in 51% yield, has been reported.[105]



2. Reactions in two-component systems

Reactions of α-hydroxyalkylmetallocenes with different nucleophilic compounds proceed most efficiently in two-component systems, such as liquid-liquid (system *A*)[106] and liquid-solid (system *B*).[73, 107] In the former case, the reaction of equimolar amounts of α-hydroxyalkylmetallocenes and nucleophilic substrates is carried out at room temperature with vigorous stirring in a two-phase system consisting of an organic solvent (CH_2Cl_2, $C_2H_4Cl_2$, $CHCl_3$, CCl_4, or benzene) and aqueous solution (45% – 70%) of an acid HX (X = BF_4, ClO_4, or I).[106, 108] Under these conditions reactions proceed predominantly at the organic-inorganic interface: the organic phase contains the hydrophobic metallocene-containing compound (initial and/or reaction product), and the aqueous phase contains acid HX and/or water-soluble reaction products (NaX, KX, BrMgX, *etc*.). The polar hydroxy group of the organometallic substrate is probably exposed to the aqueous phase and is thus available for protonation, while the metallocene nucleus, on the contrary remains in the organic phase and is not subjected to protonation and oxidation. The procedure of α-ferrocenylalkylation in the system *A*, allows one on the one hand, to attain high acidity at the interface (H_0 = −7 to −9),[109] which facilitates the formation under mild conditions of thermodynamically stable MCC,[5] and, on the other hand, to reduce the possibility of oxidation of the metallocene-containing substrates, which readily occurs in acidic media.[110] This is obviously due to the small probability for the contact (except for the interface) of the metallocene-containing component in the organic phase with the acid HX in the aqueous phase. The carbenium reaction centre and the non-polar part of the MCC formed are in different phases. Therefore, the efficient interaction of the carbenium centre with the corresponding nucleophilic reagent may occur, other side reactions (rearrangement, dimerisation, polymerisation, formation of ethers, *etc*.) which are characteristic of the MCC are practically excluded.[1–4]

When system *B* is used,[73, 107, 111] the interaction of the equimolar amounts of α-hydroxyalkylmetallocenes with the nucleophilic reagents occurs under vigorous stirring of an organic solvent (CH_2Cl_2, $C_2H_4Cl_2$, $CHCl_3$, benzene, or xylene) and solid (cation-exchange resins or zeolites in the H-form). In this case, the formation of the corresponding MCC occurs only in the adsorption layer on the surface of the solid phase, they react further with the nucleophilic substrate. As in the case of system *A*, side transformations of MCC are minimal.

The above-mentioned advantages and peculiarities of the α-metallocenylalkylation in the two-phase systems *A* and *B* allow one to extend considerably the range of both metallocenyl and nucleophilic reagents and to increase the yields and purity of the products isolated. Moreover, reactions of organometallic compounds can be thus performed in aqueous-organic media in air rather than in anhydrous solvents and in an inert atmosphere.

For the sake of completeness and for better systematisation of the synthetic data, and convenience of their use, the information of this section is presented largely in the form of tables containing the detailed information concerning the initial compounds and reagents, reaction conditions, yields, and the structure of the products of α-metallocenylalkylation.

a. C-α-Metallocenylalkylation

Weak CH-acids, activated aromatic, organomagnesium and organomercury derivatives, and alkyl derivatives of ferrocene may be used as nucleophilic reagents when reactions are performed in the two-phase systems *A* and *B*. Various α-hydroxymetallocenyl derivatives of the subgroup VIIIA elements were used in these reactions (Table 1), however, their structural peculiarities in most cases only slightly affected the character of the products formed. The choice of the nucleophilic reagents was mostly determined by both their reactivity and the stability of the functional groups of the molecule under the reaction conditions.

In the system *A*, α-hydroxymetallocenyl derivatives (Table 1) react[108] only with CH-acids with pK_a's in the range of 9 – 13.[117] Compounds with lower mobility of the hydrogen atoms (pK_a = 16 – 21),[117] such as phenylbenzoylmethane, acetophenone, acetone, and fluorene, do not react under these conditions.[108] It is interesting that phenol and α-naphthol react neither in the system *A*, nor *B*.[108, 112]

The interaction of α-hydroxyalkylmetallocenes with highly nucleophilic aromatic compounds (Table 1) in the systems *A* and *B* occurs[112] chemoselectively in accordance with the general features[118] of electrophilic substitution. In this case, it is possible to introduce sequentially several similar or different metallocenylalkyl groups into the molecules of nucleophilic compounds.

Under the conditions described, organomercury or organomagnesium compounds may enter into the metallocenylalkylation reaction. The direction of the reaction in this case sometimes greatly depends on the peculiarities of the nucleophile structure. Thus, the reaction of 1-bromomagnesiumindole with the alcohols **13** or $CpRuC_5H_4CH(R)OH$ in the system *A* gives only products of N-α-metallocenylalkylation (Table 2) rather than C-alkylation.[112] In the system *A*, the organomagnesium derivatives RMgBr with alkyl radicals (R = Me, Et, CH_2Ph, $CH_2CH=CH_2$) decompose with the elimination of the corresponding hydrocarbons RH, the decomposition is too fast to allow reactions with alcohols.[112] Reactions of these alcohols with organomagnesium compounds, containing aryl radicals or with Iotsich reagents gives the products of decomposition of initial reagents (benzene, naphthalene, phenylacetylene) in 10% – 25% yields together with the products of α-metallocenylalkylation (Table 1).[112] Also, the reaction of Grignard reagents with the alcohol **13** gives 2% – 3% of 1,2-diferrocenylethane, while in the reaction with $CpRuC_5H_4CH(Me)OH$, 3% – 5% of polymeric substances are formed.[112]

The interaction of α-hydroxyalkylmetallocenes with the organomercury compounds R′HgBr in the system *A* containing different types of protic acids HX, in most cases results in the products of α-metallocenylalkyldemercuration with considerably variable yields (see Table 1).[116] In this case, side products are also formed: R′H, polymeric compounds, and mercury-containing metallocenes. Obviously, the formation of R′H occurs as a result of the competitive protodemercuration of the initial mercury-containing derivatives, which in many cases is the main direction of the reaction. It has been found,[116] that the activity of the mercury-containing substrates in α-metallocenylalkyldemercuration reactions decreases with the decrease in the electron accepting character of the R′ radicals in the series: CH_2CHO > $CH_2C(O)Ph$ > $CH_2C(O)Me$ > CH_2COOMe > Ph > Alk.

The maximum yields of the products of α-metallocenylalkyldemercuration were achieved when 56% HI was used, while the minimum yields were observed with HCl, $HClO_4$, and HBF_4.[116] This can probably be explained by the specific role of the iodide ion: because of its high nucleophilicity iodide is readily coordinated by the mercury atom, thus polarising the C – Hg bond of the initial complex.[120] As a result, the reactivity of R′HgBr is enhanced at the final stage of α-metallocenylalkyldemercuration.

Comparison of the yields in bromomercurioacetaldehyde reactions with different α-hydroxyalkylmetallocenes in the two-phase system CH_2Cl_2 – HI testifies[116] that their activity changes in the series: $FcCH_2OH$ > [FcCH(Me)OH; RcCH(Me)OH] > FcCH(Ph)OH > OcCH(Ph)OH. This regularity is presumably determined by the increase in the steric hindrance of the hydroxy group. The nature of the metal atom in this case practically does not affect the yields of the products of α-ferrocenylalkyldemercuration.[116]

In contrast to α-hydroxyalkylferrocenes,[115] the analogous ruthenocene and osmocene compounds do not give the corresponding derivatives of 1,2-dimetallocenylethane in reactions with powdered copper in system *A*.[6]

In system *A*, it is possible to perform the alkylation of ferrocene and its homologues, sym-octamethyl- and 1,1′-diethylferrocene; the corresponding binuclear diferrocenylalkanes were

Table 1. Reagents, conditions and yields of product of C-α-metallocenylalkylation.

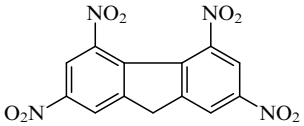
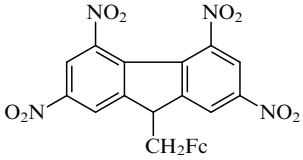
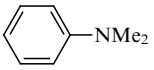
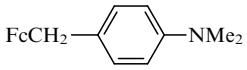
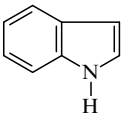
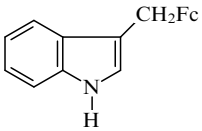
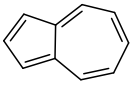
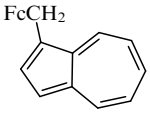
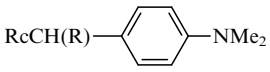
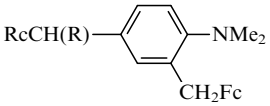
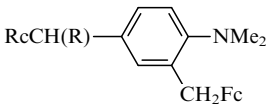
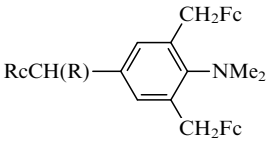
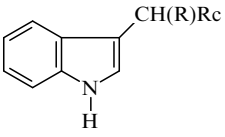
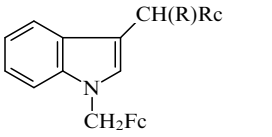
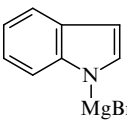
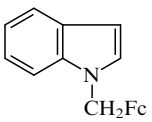
α-Hydroxy-alkylmetal-locene	Nucleophile	Reaction conditions	Reac-tion time /min	Product	Yield (%)	Ref.
$FcCH_2OH$	$H_2C(COR)_2$	*A* (CH_2Cl_2/ HX, X = BF_4, ClO_4)	30 30 120 120 120	$FcCH_2CH(COR)_2$	100 (R = Me) 100 (R = Ph) 98 (R = C_6H_4OMe-4) 78 (R = $C_6H_3(OMe)_2$-2,4) 100 (R = $C_6H_2(OMe)_3$-3,4,5)	108
		*A* (CH_2Cl_2/ HBF_4)	240		100	108
	$H_2C(COMe)_2$ [a]	*A* (CH_2Cl_2/ HBF_4)	120	$(FcCH_2)_2C(COMe)_2$	94	108
		*A* (CH_2Cl_2/ HBF_4)	160		73	108
		*A* (CH_2Cl_2/ HBF_4)	40		95	108
		*A* (CH_2Cl_2/ HBF_4)	65		77	73
		*A* (CH_2Cl_2/ $HClO_4$)	60		58 (R = Me) 53 (R = Ph)	112
		*A* (CH_2Cl_2/ $HClO_4$)	120		62 (R = Me) 56 (R = Ph)	112
		*A* (CH_2Cl_2/ $HClO_4$)	120		43 (R = Me) 45 (R = Ph)	112
		*A* (CH_2Cl_2/ $HClO_4$)	10		83	112
	ArMgBr	*A* (CH_2Cl_2/ $HClO_4$)	5	$ArCH_2Fc$	43 (Ar = Ph) 54 (Ar = 1-Naphthyl)	112
	$PhC{\equiv}CMgBr$	*A* (CH_2Cl_2/ $HClO_4$)	15	$PhC{\equiv}CCH_2Fc$	62	112
	$BrMgC{\equiv}CMgBr$	*A* (CH_2Cl_2/ $HClO_4$)	10	$FcCH_2C{\equiv}CCH_2Fc$	62	112

Table 1 (continued).

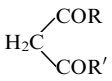
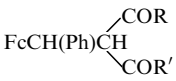
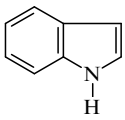
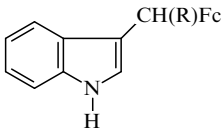
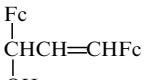
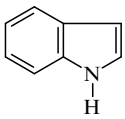
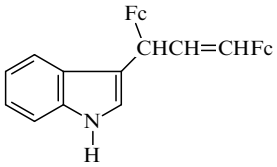
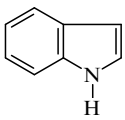
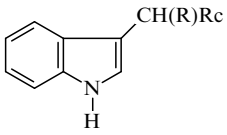
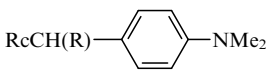
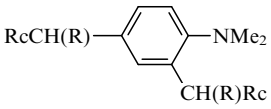
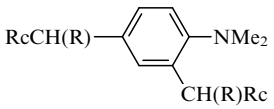
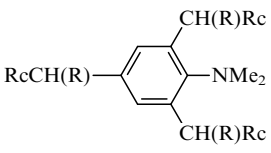
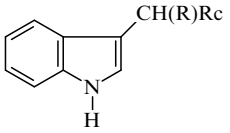
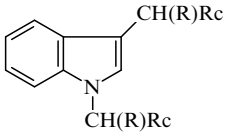
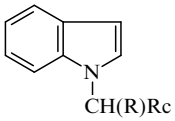
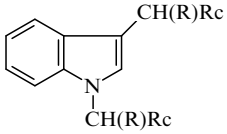
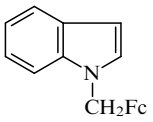
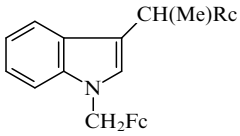
α-Hydroxy-alkylmetal-locene	Nucleophile	Reaction conditions	Reac-tion time /min	Product	Yield (%)	Ref.
$FcCH_2OH$	$HCR(COR')_2$	*B* (C_6H_6 – Ca^{2+} – montmo-rillonite)	120 – 150	$FcCH_2CR(COR')_2$	70 – 80 (R = H, NHCHO; R′ = Me, OEt)	111
FcCH(R)OH	$H_2C(COR')_2$	*A* (CH_2Cl_2/ HBF_4)	30 45	FcCH(R)CH(COR′)$_2$	81 (R = Me, R′ = OEt) 85 (R = Ph, R′ = Me)	108
FcCH(Ph)OH		*B* [MeC_6H_5 or C_6H_6 – zeolites NaA (5Å) CaA (3Å)]	3600		56 (R = R′ = Me) 65 (R = Me, R′ = OEt) 60 (R = R′ = OEt)	107 113 113
FcCH(R)OH		*B* (CH_2Cl_2/ cationite KU-2)	200 180		66 (R = Me) 77 (R = Ph)	73
FcCH(Me)OH	FcH	*A* (CH_2Cl_2/ HBF_4)	3	FcCH(Me)Fc	60	114
	$(C_5H_4Et)_2Fe$	*A* (CH_2Cl_2/ HBF_4)	5	[C_5H_3(FcCHMe)Et]Fe(C_5H_4Et) [C_5H_3(FcCHMe)Et]$_2$Fe	54	114
	$(C_5HMe_4)_2Fe$	*A* (CH_2Cl_2/ HBF_4)	5	[C_5Me_4(FcCHMe)]Fe(C_5HMe_4)	50	114
		*B* (CH_2Cl_2/ cationite KU-2)	92		66	73
RcCH(R)OH	$C_6H_5NMe_2$	*A* (CH_2Cl_2/ HBF_4)	60 90	RcCH(R)$C_6H_4NMe_2$-4	72 (R = Me) 68 (R = Ph)	112
		*A* (CH_2Cl_2/ HBF_4)	120 150		78 (R = Me) 72 (R = Ph)	112
		*A* (CH_2Cl_2/ HBF_4)	120		57 (R = Me) 43 (R = Ph)	112
		*A* (CH_2Cl_2/ HBF_4)	150		45 (R = Me) 38 (R = Ph)	112
		*A* (CH_2Cl_2/ HBF_4)	150 180		64 (R = Me) 56 (R = Ph)	112

Table 1 (continued).

α-Hydroxy-alkylmetal-locene	Nucleophile	Reaction conditions	Reac-tion time /min	Product	Yield (%)	Ref.
RcCH(R)OH		*A* (CH_2Cl_2/HBF_4)	150 180		78 (R = Me) 71 (R = Ph)	112
RcCH(Me)OH		*A* (CH_2Cl_2/HBF_4)	120		43	112
	ArMgBr	*A* (CH_2Cl_2/$HClO_4$)	15	ArCH(Me)Rc	45 (Ar = Ph) 37 (Ar = 1-Naphthyl)	112
RcCH(R)OH	PhC≡CMgBr	*A* (CH_2Cl_2/$HClO_4$)	20	PhC≡CCH(R)Rc	61 (R = Me) 46 (R = Ph)	112
RcCH(Me)OH	BrMgC≡CMgBr	*A* (CH_2Cl_2/$HClO_4$)	20	RcCH(Me)C≡CCH(Me)Rc	59	112
FcCH(R)OH		*A* Cu (CH_2Cl_2/HX, X = BF_4, ClO_4)	120 240	FcCH(R)−CH(R)Fc	72 (R = H) 70 (R = Ph)	115
$FcCH_2OH$		*B* Cu (CH_2Cl_2/cationite KU-2)	300	$FcCH_2CH_2Fc$	62	73
FcCH(R)OH	R′HgBr	*A* (CH_2Cl_2/HI)	120	FcCH(R)R′	6 (R = H, R′ = Me) 8 (R = H, R′ = Et) 21 (R = Me, R′ = Ph) 33 (R = H, R′ = CH_2Ph) 36 (R = Me, R′ = CH_2COMe) 62 (R = H, R′ = CH_2COPh)	116
Fc | CHCH=CHPh | OH	RHgBr	*A* (CH_2Cl_2/HI)	120	FcCH(R)CH=CHPh	46 (R = CH_2CHO) 38 (R = CH_2COPh)	116
Fc | CHC≡CPh | OH	RHgBr	*A* (CH_2Cl_2/HI)	120	FcCH(R)C≡CPh	28 (R = CH_2CHO) 26 (R = CH_2COPh)	116
RcCH(R)OH	R′HgBr	*A* (CH_2Cl_2/HI)	120	RcCH(R)R′	45 (R = Me, R′ = CH_2CHO) 38 (R = Ph, R′ = CH_2CHO) 38 (R = Me, R′ = CH_2COMe) 42 (R = Ph, R′ = CH_2COPh)	116
OcCH(R)OH	R′HgBr	*A* (CH_2Cl_2/HI)	120	OcCH(R)R′	34 (R = Me, R′ = CH_2CHO) 33 (R = Ph, R′ = CH_2COMe)	116

[a] Reagent ratio is 2 : 1.

thus formed in high yields.[114] In this system, the 1,1'-diethylferrocenium salt can also be alkylated:[7]

$$FcCH(Me)OH + (EtC_5H_4)_2Fe^+ PF_6^- \xrightarrow[-H_2O]{HBF_4/CH_2Cl_2}$$

$$\longrightarrow EtC_5H_3FeC_5H_4Et + [FcCH(Me)C_5H_3Et]_2Fe\,.$$

$$\quad\quad\quad

Table 2. Reagents, conditions and yields of product (non-ionic compounds) of N-α-metallocenylalkylation in two-phase systems.

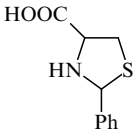
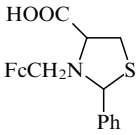
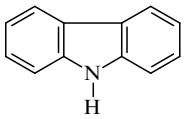
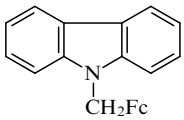
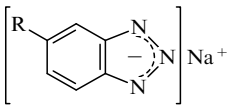
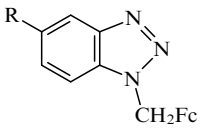
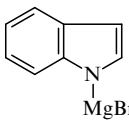
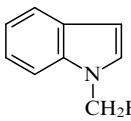
α-Hydroxy-alkylmetal-locene	Nucleophile	Reaction conditions	Reaction time /min	Product	Yield (%)	Ref.
$FcCH_2OH$	NaN_3	*A* (CH_2Cl_2/HX, X = BF_4, ClO_4)	30	$FcCH_2N_3$	83	108
	$H_2NC_6H_4R$-4	*A* (CH_2Cl_2/HBF_4)	30 30 30 60	$FcCH_2NHC_6H_4R$-4	29 (R = H) 18 (R = Me) 87 (R = Br) 96 (R = NO_2)	108
	$H_2NC(O)NH_2$	*A* (CH_2Cl_2/HBF_4)	30	$FcCH_2NHC(O)NH_2$	81	108
	$H_2NC(O)Me$	*A* (CH_2Cl_2/HBF_4)	60	$FcCH_2NHC(O)Me$	37	108
	$H_2NC(O)Me$	*B* (CH_2Cl_2/cationite KU-2)	240	$FcCH_2NHC(O)Me$	84	73
	H_2NSO_2Ph	*A* (CH_2Cl_2/HBF_4)	90	$FcCH_2NHSO_2Ph$	70	108
		*A* (CH_2Cl_2/$HClO_4$)	60		49	108
		*A* (CH_2Cl_2/HBF_4)	15		96	108
		*A* (CH_2Cl_2/HX, X = BF_4, ClO_4)	15		96 (R = H) 85 (R = Me) 85 (R = Br) 85 (R = NO_2)	7, 119
	$H_2N-Y-NH_2$	*A* (CH_2Cl_2/HBF_4)	75 100 90	$[FcCH_2\overset{+}{N}H_2-Y-\overset{+}{N}H_2CH_2Fc]2X^-$	71 (Y = 1,2-Phenylene) 90 (Y = 1,4-Phenylene) 93 (Y = 4,4′-Biphenylene)	108
	$FcCH_2NHC(O)NH_2$	*A* (CH_2Cl_2/HBF_4)	60	$FcCH_2NHC(O)NHCH_2Fc$	78	6
		*A* (CH_2Cl_2/$HClO_4$)	10		83	112
	$4\text{-}H_2NC_6H_4N=NPh$	*B* (CH_2Cl_2/cationite KU-2)	240	$4\text{-}FcCH_2NHC_6H_4N=NPh$	96	73

Table 2 (continued).

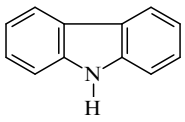
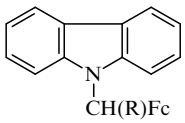
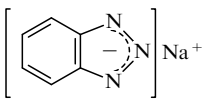
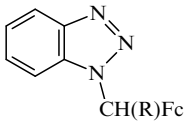
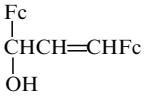
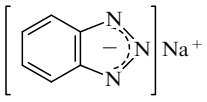
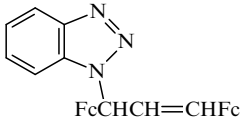
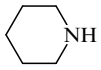
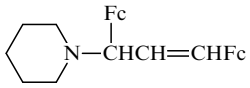
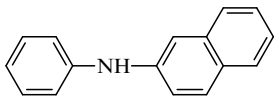
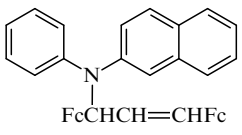
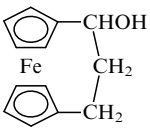
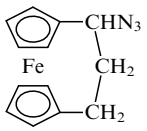
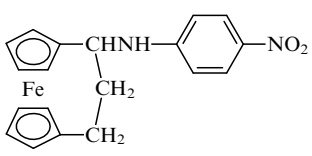
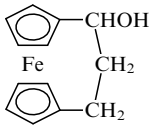
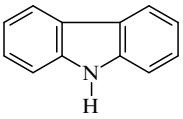
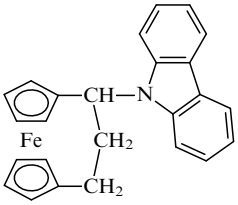
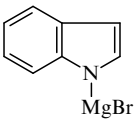
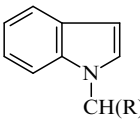
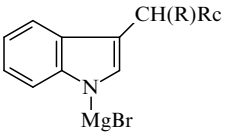
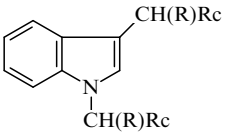
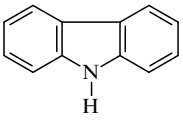
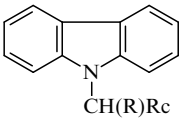
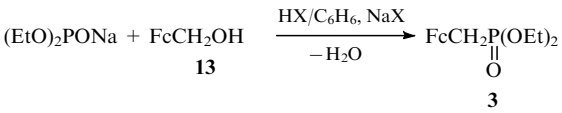
α-Hydroxy-alkylmetal-locene	Nucleophile	Reaction conditions	Reaction time /min	Product	Yield (%)	Ref.
FcCH(R)OH	$HNPh_2$	*A* (CH_2Cl_2/ HBF_4)	60	$FcCH(R)NPh_2$	92 (R = Me) 90 (R = Ph)	108
		*A* (CH_2Cl_2/ $HClO_4$)	30		75 (R = Me) 64 (R = Ph)	108
		*A* (CH_2Cl_2/ HBF_4)	5		96 (R = Me) 80 (R = Ph)	7, 119
	$FcCH_2NHC(O)NH_2$	*A* (CH_2Cl_2/ HBF_4)	60	$FcCH_2NHC(O)NHCH(R)Fc$	64 (R = Me) 61 (R = Ph)	6
	KSCN	*A* (CH_2Cl_2/ HX, X = BF_4, ClO_4)	60	FcCH(NCS)CH = CHFc	64	46
		*A* (CH_2Cl_2/ HBF_4)	1200		79	119
	$HNEt_2$	*B* (CH_2Cl_2/ cationite KU-2)	120	$FcCH(NEt_2)CH=CHFc$	71	73
		*A* (CH_2Cl_2/ HBF_4)	140		70	73
	$H_2NC_6H_4Br$-4	*A* (CH_2Cl_2/ HBF_4)	240	$FcCH(NHC_6H_4Br\text{-}4)CH=CHFc$	70	73
	NaN_3	*A* (CH_2Cl_2/ HBF_4)	150	$FcCH(N_3)CH=CHFc$	64	73
		*A* (CH_2Cl_2/ HBF_4)	180		69	73
	NaN_3	*A* (CH_2Cl_2/ $HClO_4$)	30		84	6
	$H_2NC_6H_4NO_2$-4	*A* (CH_2Cl_2/ HBF_4)	60		92	6

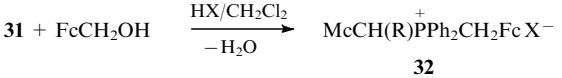
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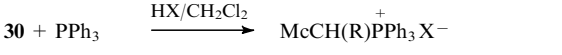
α-Hydroxy-alkylmetal-locene	Nucleophile	Reaction conditions	Reaction time /min	Product	Yield (%)	Ref.
		*A* (CH_2Cl_2/ HBF_4)	60		90	6
RcCH(R)OH		*A* (CH_2Cl_2/ HX, X = BF_4, ClO_4)	15		82 (R = Me) 76 (R = Ph)	112
		*A* (CH_2Cl_2/ HBF_4)	150 180		64 (R = Me) 56 (R = Ph)	112
	NaN_3	*A* (CH_2Cl_2/ HBF_4)	30 20	$RcCH(R)N_3$	91 (R = Me) 89 (R = Ph)	112
	H_2NPh	*A* (CH_2Cl_2/ HBF_4)	45 60	RcCH(R)NHPh	54 (R = Me) 55 (R = Ph)	112
	$H_2NC_6H_4Br$-4	*A* (CH_2Cl_2/ HBF_4)	45 60	$RcCH(R)NHC_6H_4Br$-4	64 (R = Me) 51 (R = Ph)	112
		*A* (CH_2Cl_2/ HBF_4)	60 120		71 (R = Me) 56 (R = Ph)	112

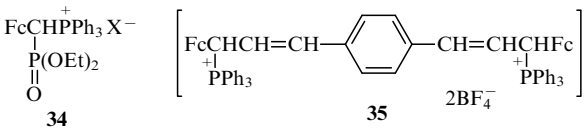


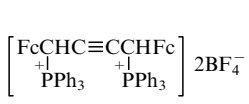
X = BF_4, ClO_4.

The reaction of the tertiary phosphines **31** and triphenylphosphine (pK_a = 2.67)[127] with different α-hydroxyalkylmetallocenes under the analogous conditions gives the corresponding α-metallocenyl-containing phosphonium salts **32**–**38** in 60%–100% yields.[6, 28, 46, 51, 124, 126]

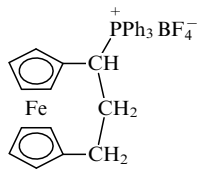




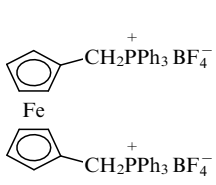




36



38



37

X = BF_4, ClO_4.

The α-metallocenylalkylation of triphenylphosphine with the formation of the corresponding triphenylphosphonium salts **39** readily proceeds also in system *B* in the presence of the salts of alkali metals NaX or KX.[73]

Table 3. Reagents, conditions and yields of product (onium compounds) of N-α-metallocenylalkylation in two-phase system *A*.

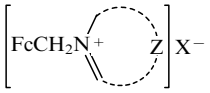
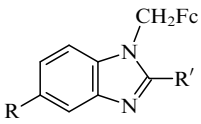
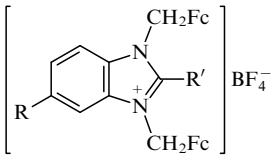
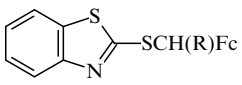
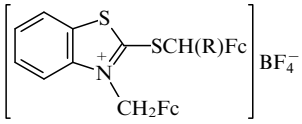
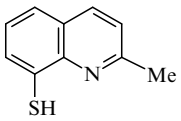
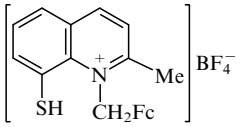
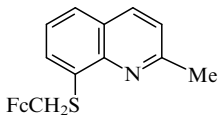
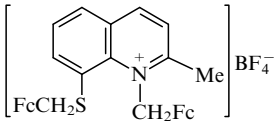
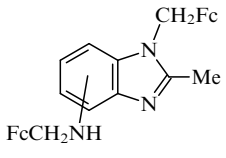
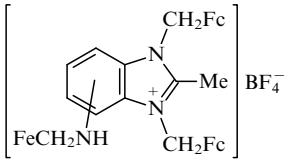
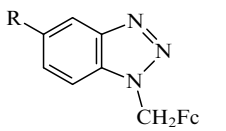
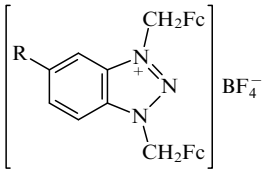
α-Hydroxy-alkylmetal-locene	Nucleophile	Reaction conditions	Reaction time /min	Product	Yield (%)	Ref.
$FcCH_2OH$		CH_2Cl_2/ HX, X = BF_4, ClO_4				
	Pyridine		60	X = BF_4	100	28
			15	ClO_4	100	28
	2-Methylpyridine		60	BF_4	66	121
			30	ClO_4	77	121
	3-Methylpyridine		60	BF_4	82	
	4-Methylpyridine		60	BF_4	37	6
	2-Chloropyridine		60	BF_4	96	6
	3-Chloropyridine		60	BF_4	100	6
	4-Chloropyridine		60	BF_4	100	6
	2,3-Dichloropyridine		60	BF_4	89	6
	2,5-Dichloropyridine		60	BF_4	67	6
	Quinoline		30	ClO_4	100	28
	Isoquinoline		15	BF_4	72	28
	Lepidine		30	BF_4	93	121
	2-Methylbenzoxazole		60	BF_4	100	121
			30	ClO_4	100	121
	2-Methylbenzothiazole		15	BF_4	100	121
			15	ClO_4	100	121
	Hexamethylenetetramine		40	BF_4	85	28
	Ferrocenylideneaniline		30	ClO_4	97	28
		CH_2Cl_2/ HBF_4	15 40 40		68 (R = R′ = H) 65 (R = NO_2, R′ = H) 62 (R = NO_2, R′ = Me)	122
		CH_2Cl_2/ HBF_4	60		82 (R = H) 74 (R = Me) 72 (R = Ph)	122
		CH_2Cl_2/ HBF_4	20		45	122
		CH_2Cl_2/ HBF_4	30		63	122
		CH_2Cl_2/ HBF_4	45		99	122
		CH_2Cl_2/ HBF_4	5		94 (R = H, Me, Br, NO_2)	123

Table 3 (continued).

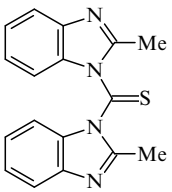
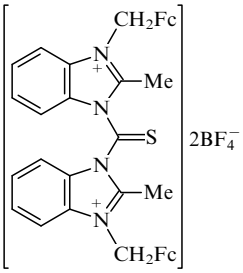
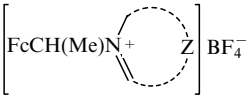
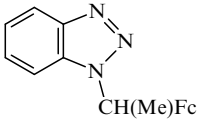
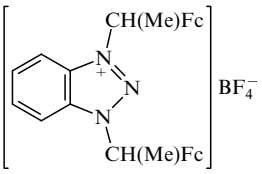
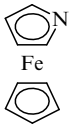
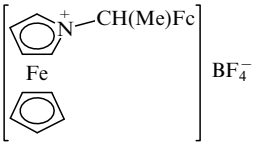
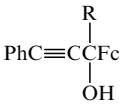
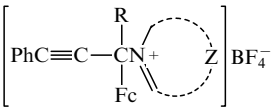
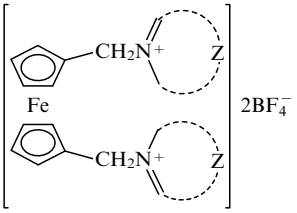
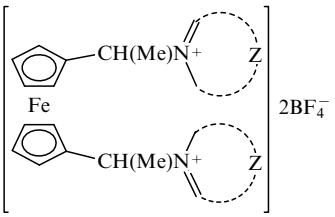
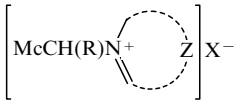
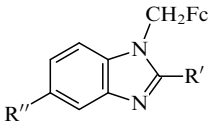
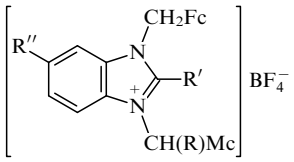
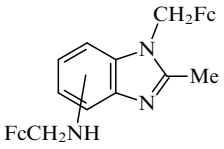
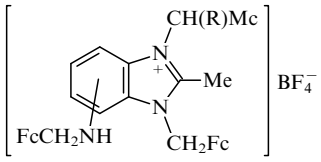
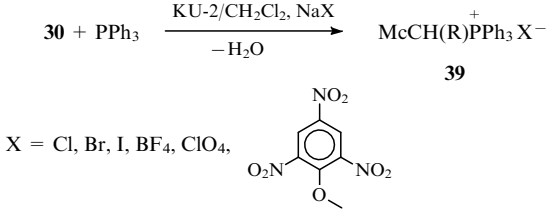
α-Hydroxy-alkylmetal-locene	Nucleophile	Reaction condi-tions	Reaction time /min	Product	Yield (%)	Ref.
$FcCH_2OH$		CH_2Cl_2/ HBF_4	60		99	122
FcCH(Me)OH		CH_2Cl_2/ HBF_4				6, 28
	Pyridine,		45		92	
	2-Methylbenzothiazole		35		71	
	Hexamethylenetetramine		60		59	
		CH_2Cl_2/ HBF_4	5		94	123
		CH_2Cl_2/ HBF_4	5		93	123
		CH_2Cl_2/ HBF_4				51
	Pyridine		60		22	
	Hexamethylenetetramine				56	
$Fe(C_5H_4CH_2OH)_2$		CH_2Cl_2/ HBF_4				
	Pyridine,		90		79	73
	2-Methyl-5-trifluoro-methylsulfonyl-1--ethylbenzimidazole		60		56	
$Fe[C_5H_4CH(Me)OH]_2$		CH_2Cl_2/ HBF_4				
	1-Ferrocenylmethyl-benzotriazole		5		92	123
	Hexamethylenetetramine		5		94	

Table 3 (continued).

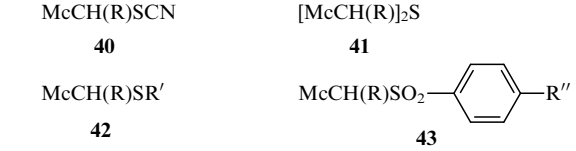
α-Hydroxyalkylmetallocene	Nucleophile	Reaction conditions	Reaction time /min	Product	Yield (%)	Ref.
McCH(R)OH		CH_2Cl_2/HX (X = BF_4, ClO_4)				
	Pyridine		60	X = BF_4	72 (Mc = Rc, R = Me)	124
	2-Methylpyridine		90	BF_4	75 (Mc = Rc, R = Me)	
	4-Methylpyridine		90	ClO_4	52 (Mc = Oc, R = Ph)	
	Lepidine		120	BF_4	66 (Mc = Oc, R = Me)	
	2-Methylbenzoxazole		45	ClO_4	75 (Mc = Rc, R = Me)	
	2-Methylbenzothiazole		45	BF_4	72 (Mc = Oc, R = Me)	
	Benzylideneaniline		180	ClO_4	48 (Mc = Rc, R = Me)	
	Ferrocenylideneaniline		120	ClO_4	67 (Mc = Rc, R = Me)	
		CH_2Cl_2/HBF_4	30		100 (Mc = Rc, R = R′ = Me, R″ = H)	6
			30		81 (Mc = Rc, R = Ph, R′ = Me, R″ = H)	
			30		96 (Mc = Oc, R = R′ = Me, R″ = H)	
			60		76 (Mc = Rc, R = R′ = Me, R″ = NO_2)	
			80		70 (Mc = Rc, R = Ph, R′ = H, R″ = NO_2)	
			60		74 (Mc = Oc, R = R′ = Me, R″ = NO_2)	
		CH_2Cl_2/HBF_4	90 120		71 (Mc = Rc, R = Me) 63 (Mc = Os, R = Ph)	6



It should be noted that the triphenylphosphonium salts **33**–**38** and phosphonate **3** may be used as reagents in the Wittig and Horner [127] reactions for the synthesis of unsaturated compounds of the subgroup VIIIA metallocenes.[46, 124, 126]

d. S-α-Metallocenylalkylation

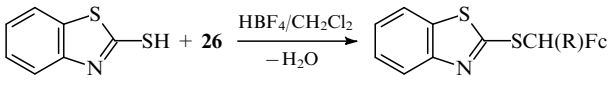
In contrast to CH-acids and nitrogen-containing compounds with an N–H bond, compounds containing SH groups do not react with α-hydroxyalkylmetallocenes in the two-phase systems *A* and *B*.[6] However the interaction of alcohols **30** with sodium thiocyanate, sulfide, methanethiolate, *N*,*N*-diethyldithiocarbamate, thiophenoxide, and arenesulfonate in the systems *A* and *B* gives S-α-metallocenyl compounds (**40**–**43**) in 60%–90% yields.[73, 108, 112]



R = H, Me, Ph, CH=CHFc; R′ = Me, Ph, C(S)NEt_2; R″ = H, Me.

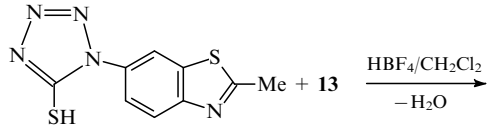
It was estimated by IR-spectroscopy that in the course of reactions with sodium thiocyanate rearrangement products, the corresponding isothiocyanates **40**, are not formed.[6]

The reactions of α-ferrocenylalkylation of the bifunctional nucleophiles **44**–**46** containing both nitrogen and sulfur atoms as two reaction centres with the alcohols **26** in systems *A* and *B* yield the products of both N- and S- alkylation.[122] Ferrocenylalkylation of 2-mercaptobenzothiazole (**44**) and 2-mercaptobenzimidazole under the action of equimolar amounts of alcohols **26** and HBF_4 occurs at the sulfur atoms in 80%–90% yields.[7, 122]

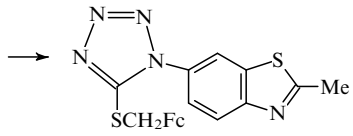


R = H, Me, Ph.

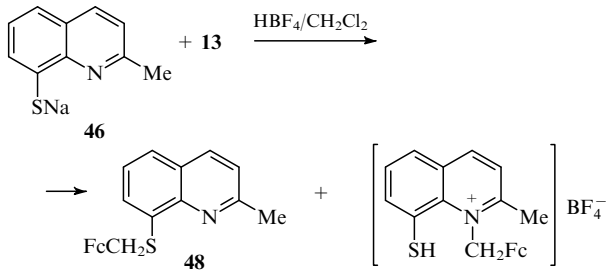
The analogous reaction of S-α-ferrocenylalkylation occurs also under the action of ferrocenemethanol **13** on 2-methyl-6-(5-mercapto-1-tetrazolyl)-benzothiazole, **45** but under more rigorous conditions.[122]



45



In reactions of equimolar amounts of sodium 2-methylquinoline-8-thiolate **46**, the alcohol **13**, and HBF_4, a mixture of products of ferrocenylmethylation at both sulfur **48** and nitrogen **49** atoms is formed.[122]



48 **49**

The interaction of sulfides with the alcohols **30** in system *A* leads to *S*-α-metallocenylalkylsulfonium salts **50** in 50% – 100% yields:[28, 51, 124]

$$\mathbf{30} + SR'_2 \xrightarrow[-H_2O]{HX/CH_2Cl_2} McCH(R)\overset{+}{S}R'_2\ X^- \quad \mathbf{50}$$

R′ = Me, Et, CH_2Ph; X = BF_4, ClO_4.

It has already been mentioned above that, like trialkylferrocenylmethylammonium salts, the salts **50** also proved to be efficient α-metallocenylalkylating reagents.[28, 124]

e. Sb-α-metallocenylalkylation

The α-metallocenylalkylation by alcohols **30** of triphenylantimony in the two-phase system *A* has been described.[6] The triphenylstibonium salts **51** are formed in this reaction.

$$\mathbf{30} + SbPh_3 \xrightarrow[-H_2O]{HX/CH_2Cl_2} McCH(R)\overset{+}{S}bPh_3X^- \quad \mathbf{51}$$

Mc = Fc, Rc, Oc; R = H, Me.

It turned out that the yields of the salts **51**, in contrast to the triphenylphosphonium salts, depend to a considerable extent on both the size of the substituents R at the α-carbon atom and on the size of the metal atom in the metallocene core. Increase in the steric hindrance lowers the yields from 74% to 17%;[6] in the case of hydroxy derivatives of ruthenocene and osmocene and R = Ph the triphenylstibonium salts are not formed at all.[6]

f. α-Metallocenylalkylation by vinylmetallocenes

Similarly to the α-hydroxyalkylmetallocenes, vinyl derivatives of ferrocene, ruthenocene, and osmocene **52** may be also successfully used in α-metallocenylalkylation reactions[6, 115, 124] for the synthesis of the same products. For instance, in systems *A* and *B*[6, 115] 2,3-diferrocenylbutane was obtained in the presence of powdered copper in 70% – 72% yields (see Table 1), while the interaction of alkenes **52** with triphenylphosphine in the system *A* leads to the corresponding triphenylphosphonium salts **53** with 80% – 95% yields:[6, 124]

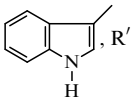
$$McCH{=}CH_2 + PPh_3 \xrightarrow{HX/CH_2Cl_2} McCH(Me)\overset{+}{P}Ph_3\,X^- \quad \mathbf{52} \rightarrow \mathbf{53}$$

X = BF_4, ClO_4.

V. α-Hydrogen-containing metallocenes in α-metallocenylalkylation reactions

New methods of α-metallocenylalkylation of nucleophilic substrates with the use of α-hydrogen-containing metallocene derivatives as alkylation agents have been proposed.[6, 74, 128] For instance, the action of triphenylcarbenium salts on an equimolar mixture of α-hydrogen-containing derivatives of ferrocene and nucleophile in anhydrous dichloromethane gives the corresponding products of α-ferrocenylalkylation and triphenylmethane in high yields.[6, 128]

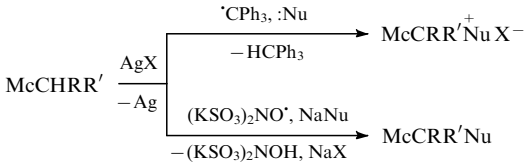
$$FcCHRR' + :Nu + \overset{+}{C}Ph_3X^- \xrightarrow{CH_2Cl_2} FcCRR'\overset{+}{N}uX^- + HCPh_3 \quad (50\% - 70\%)$$

R = R′ = H; R = , R′ = H;

R = , R′ = P(O)(OEt)$_2$; Nu = PPh_3, ; X = BF_4, ClO_4.

However, the α-hydrogen-containing ruthenocene and osmocene derivatives turned out to be unreactive.[6]

A more general method of α-metallocenylalkylation of nucleophilic compounds by α-hydrogen-containing metallocene derivatives of subgroup VIIIA was proposed by Boev.[74] The essence of this method is as follows: at first, α-hydrogen-containing derivatives of metallocenes are treated with oxidizing agents ($AgClO_4$, $AgBF_4$, $FeCl_3$) in dichloromethane, then an equimolar mixture of a free radical (triphenylmethyl or Fremy's salt[129]) and a nucleophilic substrate is added to the oxidation products. As a result, the products of substitution of the α-hydrogen atom by a nucleophile are formed with high yields. In the case of the use of Fremy's salt $(KSO_3)_2N-O^{\bullet}$ and anionic nucleophiles (NaNu), the second step of the process is performed in a two-phase system $CH_2Cl_2 - H_2O$ with intense stirring at room temperature.[6, 74]



Mc = Fc, Rc, Oc; R = R′ = H; R = H, R′ = Me; R = H, R′ = Ph;

Nu = PPh_3, , ;

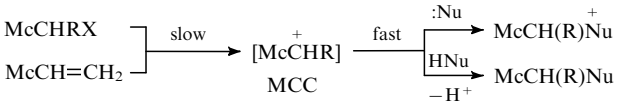
Nu^- = CN^-, N_3^-, PhS^-, PhO_2S^-; X = BF_4, ClO_4.

Along with the target products, triphenylmethane (in 86% to 94%yield) or potassium hydroxylamine disulphonate (in 80% to 90% yield) were isolated.

VI. On the mechanism of α-metallocenylalkylation reactions

The analysis of literature data[3–11] reveals that all reactions of α-metallocenylalkylation proceed *via* the formation of thermally stable[3, 5] α-metallocenylcarbocations (MCC), the mechanism of their formation depending on both the nature of the initial

substrates and on the reaction conditions. The MCC then react quite rapidly with the nucleophilic reagents to yield the products of α-metallocenylalkylation. Some researchers [3, 8, 10, 17] believe that the mechanism of these reactions may be classified as S_N1.



X = $\overset{+}{N}Me_3$, $\overset{+}{S}Me_2$, Hal, OH; Mc = Fc, Rc, Os.

Unfortunately, no special kinetic studies that would confirm the formation of MCC as a kinetically independent species corresponding to a definite point on the reaction coordinate have been performed so far, but a series of indirect experimental data support an S_N1 mechanism.

In particular, it has been shown by numerous experiments,[6, 7] that α-metallocenylalkylation in the two-phase systems *A* and *B* may proceed only at the interface of phases with high acidity ($H_0 \approx -7$ to -9).[109] It is under these conditions that the generation [3, 5] of metallocenylcarbocations from α-hydroxyalkyl- and α-alkenylmetallocenes readily occurs. In this case, the proton is thought to attack the oxygen atom of the hydroxyl group or the double bond as centres with the highest nucleophilicity in the substrates.

Attack of the proton at the metallocene fragment is also possible, as it is known [1–3] that ferrocene, ruthenocene, and osmocene, under certain conditions, can be protonated. It has however been established by Boev,[6] that these metallocenes practically do not undergo any changes under the action of aqueous acids HX (X = BF_4, ClO_4) or a cation-exchange resin KU-2 in systems *A* and *B* (according to UV and NMR data), while in the presence of nucleophilic reagents only the salts of the latter are formed. Besides, as has been mentioned above, the metallocene nucleus in the two-phase systems is in the organic phase and therefore it is inaccessible to protons. Therefore, initial attack of the proton at the metal atom, as the potential basic centre in organometallic substrates in the two-phase systems *A* and *B*, may be excluded.

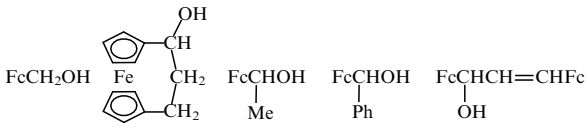
On the other hand, the action of aqueous acids HX on α-hydroxyalkylmetallocene derivatives [6, 108] and vinylferrocene [6] in dichloromethane in the absence of the nucleophilic substrates results in the quantitative formation of MCC (according to UV-spectral data), identified by comparison with the authentic [95, 124] species. Therefore, high acidity of the medium, that arises at the interface in the system *A* guarantees the efficient formation of the corresponding MCC from vinylferrocene and ferrocenylalkanols. The study of the reactions of the authentic MCC with different nucleophiles has shown that they lead to formation of the corresponding derivatives of FcCHRNu type with quantitative yields.[6]

All these data indicate that MCC correspond to a definite point on the reaction coordinate of metallocenylalkylation.

In the two-phase system *B* (liquid – solid phase), the formation of MCC may occur only at the surface of KU-2 in the H-form. This is indirectly confirmed by the fact that the rate and the yield of the reaction of α-metallocenylalkylation in the system *B* are directly affected by the intensity of mixing of the reaction system, that is by the efficiency of the contact of the reacting substrates with the surface of the cation-exchange resin KU-2, where the MCC is generated.[6, 73]

The observation [73] (both visual and microscopic) of the resin surface during the reaction leads also to the conclusion of possible generation of MCC at its surface. At first, the resin grains change their colour from light-brown to dark-red or dark-blue, which is characteristic of MCC,[3] and then as the MCC formed react with nucleophiles, the initial light-brown colour is restored.

The comparison of the rate of reactions of the ferrocene-containing alcohols of different structural types with aqueous solutions of HX and triphenylphosphine (system *A*) by the method of competing reactions [124] demonstrates that the activity of alcohols in alkylation reactions decreases with the increase in the steric hindrance at the α-carbon atom independently of the thermodynamic stability (pK_{R^+}) values of the corresponding carbocations.[3]

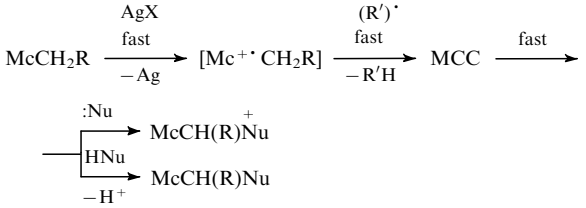


pK_{R^+}	−1.75	−3.20	−0.92	−0.15	+4.18

The activity of the structurally similar alcohols of ferrocene, ruthenocene, and osmocene decreases with decrease in the pK_{R^+} of the corresponding carboxylic acids in the following series:[124] OcCH(Me)OH (+1.75) > RcCH(Me)OH (+1.20) > FcCH(Me)OH (−0.92).

The generation of MCC from α-hydrogen-containing metallocene derivatives in reactions of α-metallocenylalkylation of nucleophiles presumably proceeds in a different way. In this case, MCC are formed as a result of the oxidative dehydration of α-hydrogen-containing metallocene derivatives subjected to the action of the triphenylcarbocation salts.[130]

An analogous mechanism is presumably realised in the reaction of the α-hydrogen-containing metallocene derivatives first with an oxidant and then with a mixture of the stable radical with a nucleophile.[74]



$(R')^{\bullet}$ = $Ph_3C^{\bullet}$, $(KSO_3)_2NO^{\bullet}$.

Thus, the reactions of α-metallocenylalkylation of nucleophilic reagents may proceed according to two alternative mechanisms depending on the nature of the initial reagents and the reaction conditions.

One of them, the S_N1 mechanism, is realised in reactions of ammonium,[3] and sulfonium [124] salts, or of α-halogen derivatives [3] of metallocenes with the nucleophilic reagents, or in reactions of α-hydroxy or α-alkenyl derivatives of metallocenes with acids HX or a cation-exchange resin in the two-phase systems *A* and *B*.[6, 7]

Another mechanism, $S_{RN}2$,[4, 6] is involved in the consecutive interaction of α-hydrogen-containing metallocene derivatives with one- [74] or two-electron [128] oxidizing agents, and then with nucleophiles as the reducing agents.

While discussing the mechanism of reactions of α-ferrocenylalkylation, one should not neglect the possible contribution of free-radical and redox processes, if only because of easy oxidizability of the ferrocene nucleus in acidic media in the presence of oxygen. These processes can in general be initiated in at least two ways, either through protonation and further oxidation of the central atom or by migration of an electron from the central metal atom to the carbenium centre.

As has been mentioned earlier in connection with the reactions proceeding in system *A*, the first way seems improbable, because the reaction centre (in this case the iron atom), located in the organic phase, is shielded from proton attack by the interface. Such shielding occurs in systems of *B* type, the difference, however, is that the carbenium centre is located in the adsorption layer of the cation-exchange resin. However, in those cases the reaction proceeds in a single-phase system, especially in the presence of strong acids, the contribution of protonation at the main metal centre may become significant.

As to the second reaction pathway, the general possibility of the migration of an electron from iron to the carbenium α-carbon with the formation of a paramagnetic compound has been unambiguously demonstrated in the example of the diamagnetic nonamethylferrocenylcarbenium salt.[131] It has also been demonstrated that the biradicals thus formed may recombine, to give the corresponding binuclear dications.[131] It has also been found that phenylferrocenylcarbenium tetrafluoroborate undergoes the analogous transformations. In this case as well, the dication is formed, which may be reduced to 1,2-diphenyl-1,2-diferrocenylethane.‡ The doublet states E_{2g} and A_{1g} are close in energy, thus ensuring the possibility of the thermal occupation of the d_{z^2} iron orbital and facilitating electron transfer from iron to the carbon atom without disturbance of the orbital symmetry.[132] Taking these facts into account, formation of ferrocenium salts and diferrocenylalkanes in reactions of α-ferrocenylalkylation may be regarded as indirect evidence for realisation of the pathway initiated by electron transfer from iron to carbon atoms.

In the two-phase systems, where reactions usually proceed with quantitative yields, the contribution of the reaction following this pathway is rather small. Nevertheless, it becomes noticeable when reactions are performed under more drastic conditions, which is in agreement with the increase of the yield of the side products of dimerisation and polymerisation.

Some ferrocenium salts may oxidise some nucleophiles, especially anions (*e.g.*, azole anions).[133] It cannot be excluded that the final products of ferrocenylalkylation in certain situations may be formed according to the free-radical scheme with initiation by single-electron transfer:

$$C_5H_5Fe^{+\bullet}C_5H_4CH_2^{\bullet} + Nu^- \longrightarrow C_5H_5FeC_5H_4CH_2^{\bullet} + Nu^{\bullet},$$

$$C_5H_5FeC_5H_4CH_2^{\bullet} + Nu^{\bullet} \longrightarrow C_5H_5FeC_5H_4CH_2Nu.$$

In this case, realisation of the redox mechanism results not only in dimerisation and polymerisation products, but also leads to the target products.

On the other hand, in Ru and Os compounds, the formation of direct metal-α-carbon contact and the corresponding onium derivatives, which has been demonstrated recently,[134] should most likely result in blocking of the reaction centre and decrease in the reactivity in α-metallocenylalkylation. In these systems the contribution of redox processes seems highly improbable.

‡ L V Snegur, unpublished data.

VII. Conclusion

The data of the present review demonstrate, that during recent years many studies aimed at both the extention of known and the search for the new methods of α-metallocenylalkylation of different nucleophilic reagents have been carried out. At present a vast variety of different ferrocenylalkylating reagents is used, *viz.*, ferrocenylalkylammonium salts and the like (especially, the corresponding pyridinium salts), ferrocenylsulfonium salts, α-haloalkyl ferrocene derivatives, α-hydroxyalkyl-, as well as α-alkenyl derivatives of metallocenes. It allows one to perform reaction at quite different reactivity centres (N-, C-, O-, S-, P-). The use of various additives (oxidative, acid-base, radical) offers further possibilities.

The synthetic potential is considerably extended by metallocenylalkylation in liquid–liquid or liquid–solid two-phase systems. In these systems most reactions proceed under mild conditions with high yields of the final products, which often do not require special purification. This allows one to overcome the limitations associated with the acid–base characteristic of the nucleophilic reagents. Besides, the use in these systems of the ferrocene-containing alcohols allows one not only to work with stable initial reagents, but also to vary considerably the substituents at the α-carbenium centre. The advantages of the two-phase systems are illustrated in Table 4, in which the possibilities and conditions of α-ferrocenylalkylation reactions are compared.

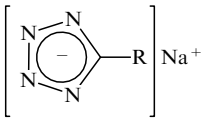
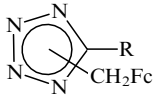
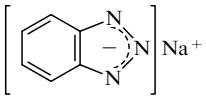
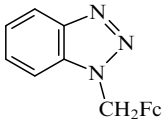
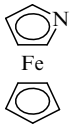
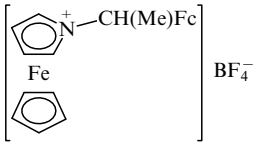
The variety of methods of ferrocenylalkylation allows one to perform the synthesis of different functionally substituted derivatives of ferrocene and other α-metallocenyl compounds of subgroup VIIIA metals.

The practical use of these compounds is rather extensive.[3] Many of the newly synthesised α-ferrocenylalkyl compounds may be of interest as medicinals with antimicrobial,[136–142] antiinflammatory,[143,144] antitumor,[6,7,145–149] activity as well as chemical means of plant protection.[150] Photosensitive materials with α-ferrocenylalkyl compounds as electron-donating components[151–155] or organic photoconductors[156] have been developed. A series of ferrocene derivatives of this class found application as stabilisers of rubbers,[157] latent image centres in high-resolution photographic materials,[158] regulators of burning

Table 4. α-Ferrocenylalkylation of nucleophile compounds.

Ferrocenylalkylating reagent	Nucleophile	T /°C	Time /h	Solvent	Additional conditions	Type of product	Yield (%)	Ref.
$[FcCH_2NMe_3]^+I^-$	NH_2NHPh	100	1	H_2O	NaOH	$FcCH_2NHNHPh$	80	18
	Na_2S	100	1	H_2O		$FcCH_2SCH_2Fc$	54	135
	$(EtO)_2PONa$	138	17	*p*-Xylene		$FcCH_2P(O)(OEt)_2$	45	18
	$C_6H_5NH_2$	100	1.5	H_2O		$FcCH_2NHC_6H_5$	75	135
$FcCH_2NMe_2$	$(CH_3CO)_2O$	100	20	–	Sealed tube	$FcCH_2OCOCH_3$	89	135
$[FcCH_2NMe(CH_2)_3]^+SO_3^-$	NaN_3	100	0.03	H_2O		$FcCH_2N_3$	98	27
	NH_4OH	20	15	C_6H_6		$FcCH_2NH_2$	30	27
	NH_4OH	60	2	C_6H_6		$FcCH_2NH_2$	30	27
$[FcCH_2SMe_2]^+BF_4^-$	NaN_3	100	1	H_2O		$FcCH_2N_3$	90	28

Table 4 (continued).

Ferrocenyl-alkylating reagent	Nucleophile	T /°C	Time /h	Solvent	Additional conditions	Type of product	Yield (%)	Ref.
$FcCH_2Cl$ (without isolation)		56	4–6	Acetone	N_2		Not indicated	37, 38
	$H_2NC(O)NH_2$	70	7	Acetone	N_2	$FcCH_2NHC(O)NH_2$	29	39
$[FcCHPh]^+BF_4^-$ (freshly prepared)	NaCN	20	0.08	CH_2Cl_2		FcCH(Ph)CN	90	95
$FcCH_2OH$	PPh_3	20	1	CH_2Cl_2	$[Ph_3C]^+BF_4^-$	$[FcCH_2PPh_3]^+BF_4^-$	95	73
		20	1	CH_2Cl_2	HBF_4/H_2O	$[FcCH_2PPh_3]^+BF_4^-$	100	28
	C_5H_5N	20	1	CH_2Cl_2	HBF_4/H_2O	$[FcCH_2NC_5H_5]^+BF_4^-$	100	28
		20	0.08	CH_2Cl_2	HBF_4/H_2O		95	7, 119
	Na_2S	20	0.5	CH_2Cl_2	HBF_4/H_2O	$FcCH_2SCH_2Fc$	93	108
$FcCH(Me)OH$	FcH	20	0.05	CH_2Cl_2	HBF_4/H_2O	FcCH(Me)Fc	60	114
		20	0.08	CH_2Cl_2	HBF_4/H_2O		93	123

processes,[159] macroenergetic compounds,[160] and indicators of radioactivity.[6]

Taking into account the dynamics of the development of the synthetic and applied studies in this field of organometallic chemistry, one may anticipate the elaboration of technological aspects of ferrocenylalkylation reactions, new investigations leading to α-metallocenylalkyl compounds of various structures that may find extensive applications in different fields of science, technology, medicine, and agriculture.

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