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Acylation of ferrocene: a new approach

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Abstract—Acylation of ferrocene by an acylating agent generated in situ from the corresponding carboxylic acid and phosphorus trichloride, in the presence of the catalyst generated electrochemically from a sacrificial aluminum anode, was investigated. The corresponding monoacylferrocenes were obtained in very high yields when the molar ratio of reactants was ferrocene/carboxylic acid/PCl_3=1:1.2:1, and by consumption 4.5 F/mol charge. The conditions for electrochemical diacylation of ferrocene were not found. However, acylation of ferrocene by the acylating agent generated in situ, but in the presence of commercial anhydrous aluminum trichloride as the catalyst, was successful in both monoacylation and diacylation processes.

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1. Introduction

Ferrocene and its derivatives play an important role in many fields of chemistry. For example, numerous ferrocene derivatives, or their complexes, are used as catalysts for asymmetric synthesis of a wide number of optically active organic compounds.[1,2] Of particular importance are ferrocene derivatives whose carbon atom connected to the ferrocene unit bears a functional group, because they mostly are optically active, or can easily be transformed into the optically active compounds. Acylferrocenes are sure of a place among them, because of the well-known high reactivity of the carbonyl group towards many reagents. Thus, they are prochiral starting materials for the synthesis of numerous ferrocene derivatives, like 1-ferrocenyl-1-alcohols (via simple reduction or the Grignard reaction), 1-ferrocenyl-1-amines (via reduction of the corresponding amino derivatives), etc.[1] Therefore, there is a permanent interest to facilitate the syntheses of these compounds. Since Woodward's discovery[3] and its further developments,[4,5] the Friedel–Crafts acylation of ferrocene with carboxylic acid chlorides and anhydrides, in the presence of anhydrous aluminum chloride as the catalyst, has become one of the most important methods to prepare substituted ferrocenes.

Although the Friedel–Crafts acylation of ferrocene works very well, there are three difficulties that chemists running this reaction meet, as well as in the case of the acylation of other aromatics: to prepare, to store and to handle anhydrous aluminum chloride.[6] A possible way to overcome these problems is to generate the catalyst in situ from a sacrificial aluminum anode, in an anhydrous media containing the acylating agent and the substrate to be acylated.[7] Recently, we reported that this methodology is not only a theoretical possibility as it was successfully applied in Friedel–Crafts aliphatic acylation.[8,9] Now, we applied this new methodology in order to obtain monoacylferrocenes, and we have already reported our preliminary results.[10] Moreover, during these investigations, we found that the acylating agent can be generated in situ from the corresponding carboxylic acids and phosphorus trichloride too, so that isolation of acyl halides, sensitive and inconvenient to handle, is not necessary. Our further investigations showed that acylation of ferrocene can also be performed by in situ generated acyl halide, but in the presence of commercially available aluminum chloride. As we also reported in the preliminary communication,[11] the corresponding mono- and diacylferrocenes were obtained by this methodology in excellent yields. Here we would like to report the complete results of these investigations.

2. Results and discussion

Our investigations were started using a constant current electrolysis (50 mA) of equimolar amounts of ferrocene and acetyl chloride in a dichloromethane solution of tetraethylammonium chloride using aluminum electrodes in an argon atmosphere. We intended to generate some aluminum

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Keywords: ferrocene; acylation; electrochemical acylation; acylferrocenes; diacylferrocenes.

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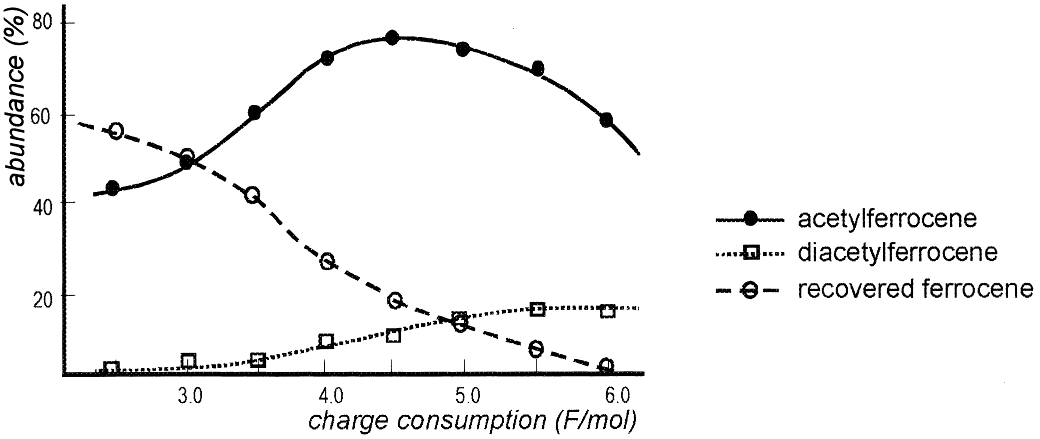
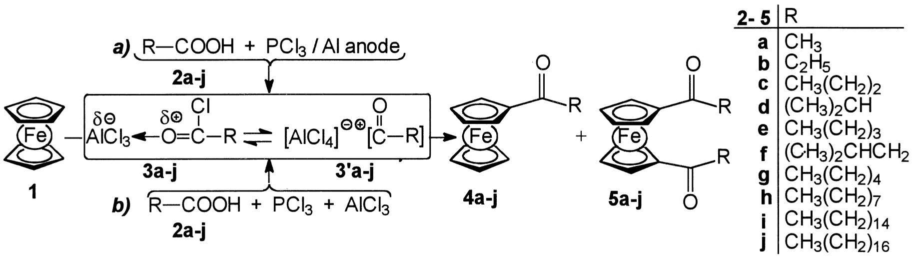


Figure 1. Product distribution by electrochemical acetylation of ferrocene ($C_5H_5FeC_5H_5/CH_3COCl$=1:1).



Scheme 1.

species from the anode, which we thought to be capable of promoting acetylation of ferrocene. The electrolysis was performed at ambient temperature in an undivided cell. Since the classical Friedel–Crafts acylation of aromatics needs at least an equimolar amount of the catalyst (the Lewis acid), we assumed that it is necessary to consume 3 F/mol charge by these experiments, in order to have the molar ratio ferrocene/acetyl chloride/$Al^{3\oplus}$=1:1:1. In parallel experiments, instead of acetyl chloride as the acylating agent we used acetic anhydride and simply a mixture of acetic acid and phosphorus trichloride. In all three experiments, the only reaction product that we isolated from the reaction mixtures by column chromatography (SiO_2/toluene or a toluene/ethyl acetate mixture) was acetylferrocene. However, in all three cases, under the described conditions, about 50% of starting ferrocene remains unchanged, although the consumed substrate was converted into acetylferrocene almost quantitatively. This fact prompted us to prolong the electrolysis time in order to generate more amounts of the catalyst up to 2 mol/mol, i.e. up to consumption 6 F/mol charge. As expected, the yield of monoacetylferrocene increased.

However, an extremely prolonged electrolysis time led to considerable abundance of unknown products[†] that we could not isolate and identify. In addition, the yield of diacetylferrocene increased, even in the presence of unchanged ferrocene. Fig. 1 illustrates these findings. As can be seen, the highest yield of monoacetylferrocene (73%) was achieved when the electricity consumption was 4.5 F/mol. The yield of the unknown products under these conditions was relatively low.

For the further investigations, i.e. acylation of ferrocene with other carboxylic acid chlorides, we continued using only the mixture of the corresponding acids and phosphorus trichloride as the acylating agents (Scheme 1, pathway a). The results obtained are listed in Table 1 (experiments carried out by method A), and can be summarized as follows. The mixture of the corresponding carboxylic acid and phosphorus trichloride, i.e. in situ generated acyl chloride can be successfully used as the acylating agent, without isolation of it. The liberated phosphorus species, whatever they are (phosphorus acid or, more probable, phosphorus trioxide), does not hinder the catalyst action. Moreover, we believe that these moieties, together with a slight excess of phosphorus trichloride, protect the reaction mixture from air moisture and moisture originated from commercial tetraethylammonium chloride and the solvent (dichloromethane). This conclusion we base on the fact that high yields of the corresponding monoacylferrocenes were achieved even by acylations carried out in the open cell and with the electrolyte and the solvent that have not been purified and dried before use.

Since the yields of the corresponding monoacylferrocenes in these reactions generally are very high, it may be stated that the electrochemically generated catalyst from the aluminum anode is, at least, as efficient as commercial anhydrous aluminum trichloride. Given the problems associated with the preparation and handling of anhydrous

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[†] These compounds were of high polarity and probably were the products of some kind of polymerization.

Table 1. Acylation of ferrocene by in situ generated acyl chlorides

Run	Carboxylic acid **2a–q**	Yields of products (%)[a]								
		Method A[b]			Method B[b]			Method C[b]		
		Ferrocene recovered (%)	**4a–q** (%)	**5a–q** (%)	Ferrocene recovered (%)	**4a–q** (%)	**5a–q** (%)	Ferrocene recovered (%)	**4a–q** (%)	**5a–q** (%)
1	**a**	16	73	6	7	88	T[c]	T[c]	18	75
2	**b**	21	68	9	T[c]	95	T[c]	T[c]	T[c]	90
3	**c**	22	65	7	6	86	T[c]	T[c]	2	89
4	**d**	3	91	T[c]	6	86	T[c]	T[c]	9	83
5	**e**	20	75	T[c]	4	85	T[c]	T[c]	9	87
6	**f**	–	93	T[c]	5	85	T[c]	T[c]	14	78
7	**g**	–	92	T[c]	5	88	T[c]	T[c]	T[c]	97
8	**h**	–	96	T[c]	T[c]	95	T[c]	T[c]	18	73
9	**I**	–	98	T[c]	T[c]	96	T[c]	T[c]	5	90
10	**j**	–	96	T[c]	5	83	T[c]	T[c]	T[c]	92
11	**k**	No acylation occurs under all described reaction conditions								
12	**l**	No acylation occurs under all described reaction conditions								
13	**m**	56	15		63	20	–			
14	**n**	57	28	–	60	30	–			
15	**o**	No acylation occurs under all described reaction conditions								
16	**p**	No acylation occurs under all described reaction conditions								
17	**q**	15	62	8	12	66	T[c]	10	75	
18	**r**	70	11	–	75	15	–			
19	**s**	Ketone **4a** was obtained under all reaction conditions in 45–50%, followed with trace amounts of ketone **4r**								

[a] Isolated yields based on the starting substrate.

[b] Reaction conditions: A—acylation by electrochemical generation of the catalyst; B—monoacylation catalyzed by commercially available anhydrous $AlCl_3$ (ferrocene/RCOOH/PCl_3/$AlCl_3$=1:1.2:1:1.5); C—diacylation catalyzed by commercially available anhydrous $AlCl_3$ (ferrocene/RCOOH/PCl_3/$AlCl_3$=1:2.4:1:3.75); For more experimental details see Section 4.

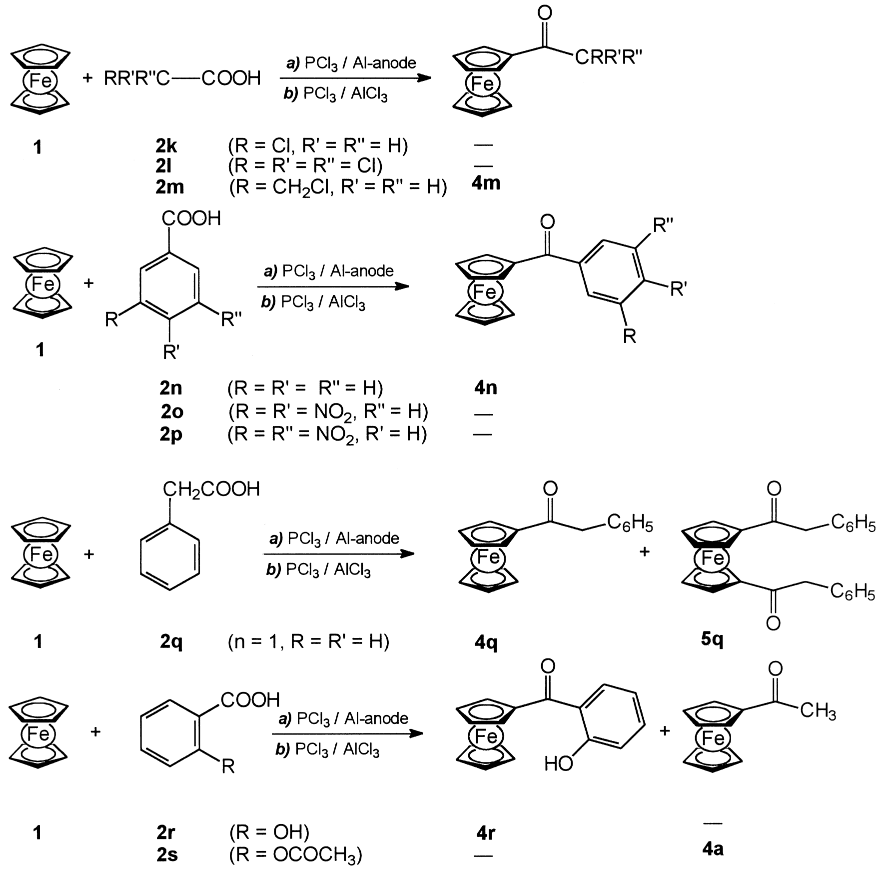
[c] Trace amounts.

aluminum chloride,[6] we think that the present method represents, if not superior then an equal alternative for classical chemical monoacylation of ferrocene.

The results listed in Table 1 show that acids containing up to five carbon atoms and an unbranched skeleton (acids **2a–c**, **e**) give always some amounts of the corresponding diacylferrocenes (up to 9%), and the corresponding monoacylderivatives in lower yields than their higher homologues (**2g–j**) and acids with a branched chain (**2d**, **f**). We think that it is a consequence of the given reaction mechanism. Namely, aluminum metal oxidizes electrochemically to $Al^{3\oplus}$ ion in a chloride medium, so that aluminum trichloride can be assumed as the catalyst. In that case, the reactive electrophilic moiety is either the complex **3** or the ion pair **3′** (Scheme 1). Both of these species are better stabilized with more branched alkyl groups. These statements are also supported by the fact that the present reaction allows very poor yields, or completely fails if there is an electron-withdrawing group connected to the α-position of the carboxylic acid. Thus, chloroacetic (**2k**), and trichloroacetic acid (**2l**) under the described conditions failed to give the corresponding ketones (Scheme 2). The chlorine atom, even in the β-position, causes a drastic decrease in yield (acid **2m**, Scheme 2, Table 1). In addition, aromatic acids in general are not suitable for this reaction (Scheme 2). For example, benzoic acid (**2n**) gave benzoylferrocene (**4n**) in less than 30% yield, whereas 3,4- and 3,5-dinitrobenzoic acids (**2o** and **2p**), like acids **2k** and **2l**, failed to give the corresponding acylferrocenes under these conditions. Phenylacetic acid (**2q**), however, reacted in a similar manner to the aliphatic ones. Acylation of ferrocene with salicylic acid (**2r**) gave the corresponding ketone—(*o*-hydroxybenzoyl)ferrocene (**4r**) in very poor yield (less than 15%), as can be expected from a substrate possessing a free phenolic hydroxyl group. On the other hand, acylation of ferrocene with acetylsalicylic acid (aspirin, **2s**) unexpectedly gave acetylferrocene (**4a**) through a transacetylation process (up to 50%). However, an alkylthio group at the α- or β-position does not hinder the reaction.[12]

Although some amount of the corresponding diacylferrocenes were obtained by monoacylation of ferrocene with acids **3a–c**, our attempts to find optimal reaction conditions for the successful electrochemical diacylation of this metallocene failed. The simple increase of the ferrocene/carboxylic acid/PCl_3 ratio from ~1:1:1 up to ~1:2:2, and the corresponding increase of the electricity consumption, did not give satisfactory results: the reaction mixtures always consisted of mono- and diacylderivatives in which the first ones predominated. Moreover, abundance of the unknown products in this case increased.

This new procedure for monoacylation of ferrocene is simple and does not require complex and expensive equipment; it can be easily carried out in all organic laboratories. The only required apparatus is a cheap and easily available source of the constant direct current. Nevertheless, it is known that most organic chemists are not familiar with electrochemical technique, and would prefer to get their catalysts from the shelf. That prompted us to optimize the reaction conditions for the acylation of ferrocene with the acylating agent generated in situ (like in the above described electrochemical experiments) but by using commercially available anhydrous aluminum trichloride as the catalyst (Scheme 1, pathway b). As expected,



Scheme 2.

the reaction worked very well. Thus, stirring a mixture of ferrocene, the corresponding carboxylic acid, phosphorus trichloride and aluminum trichloride in the molar ratio 1:1.2:1:1.5 we obtained the corresponding monoacylferrocenes in excellent yields (up to 96%; see Table 1, experiments carried out by method B).

As it can be seen from Table 1, monoacylation of ferrocene by in situ generated carboxylic acid chlorides, catalyzed by anhydrous aluminum trichloride, gave almost the same results as the electrochemical method. Here also were observed higher yields and 'cleaner' reactions when acids containing branched alkyl groups were used. Chlorocarboxylic acids **2k**, **2l** and **2m**, aromatic acids **2n**–**p**, **2r**, and **2s**, and phenylacetic acid (**2q**) behaved in the same way as in the electrochemical experiments.

Contrary to the electrochemical method, we found reaction conditions for diacylation of ferrocene with in situ generated acylating agent, in the presence of anhydrous aluminum trichloride. All the aliphatic carboxylic acids that were used in monoacylation reactions were successfully applied in diacylation of this metallocene also. The diacylation procedure differs from that for monoacylation only in the ratio of reactants. Stirring the mixtures of ferrocene, the corresponding carboxylic acids, phosphorus trichloride and aluminum trichloride in the molar ratio 1:2.4:2:3,75, the corresponding 1,1′-diketones were obtained in yields from 73% up to almost quantitative conversion of the starting substrates (see Table 1, experiments carried out by method C). Products of 1,2-and 1,3-substitions were not detected.

3. Conclusions

In conclusion, we can maintain that these two methodologies for the acylation of ferrocene have a significant advantage over existing methods. They avoid the synthesis of acyl chlorides in the separate experiments and, in the case of electrochemical monoacylation, avoid handling aluminum trichloride, a corrosive and sensitive reagent. These statements are also supported by the fact that ferrocene, monoacylferrocene and diacylferrocene can be easily separated by column chromatography, and that only impurities accompanying the reaction products are phosphorus and aluminum species, as well as the corresponding carboxylic acids, which can be readily removed by the work up.

4. Experimental

All chemicals used were commercially available and were used as received. Dichloromethane was dried over P_2O_5 and distilled just before use; the other solvents are purified only by distillation. Aceticsalicylic acid (aspirin) was synthesized by literature procedure.[13] IR measurements were carried out with a Perkin–Elmer 457 grating FT instrument. NMR spectra were recorded on a Varian Gemini 200 (200 MHz) or a Bruker AC (300 MHz) spectrometer, using $CDCl_3$ as the solvent. Chemical shifts are expressed in ppm using TMS as an internal standard. Mass spectra were measured with a MAT 95 (FAB) spectrometer. Melting points were determined by a Kofler hot-plate apparatus. As a direct current source, a Uniwatt, Beha Labor-Netzgerät (NG 394) was used. A cylindrical glass vessel supplied with a magnetic stirrer and two concentric Al-springs served as the electrodes (Ø=2.5 cm for the anode and 1 cm for the cathode).

4.1. General procedure for electrochemical acylation of ferrocene (method A)

A solution of 1 mmol (186 mg) of ferrocene (**1**), 1.2 mmol of the corresponding carboxylic acid (**2a–s**), ~1 mmol (0.1 mL) of phosphorus trichloride, and 320 mg of tetraethylammonium chloride in 20 mL of dichloromethane was stirred under an argon atmosphere at ambient temperature for 1 h, then electrolyzed at a constant current (50 mA). After 30–40 min the reaction mixture becomes dark violet. When 4.5 F/mol of charge was passed (145 min) electrolysis was stopped, and the reaction mixture stirred for additional 2 h. The resulting mixture was then diluted with 20 mL of ether and poured into a cold solution of KOH (40 mL, 1 mol/L) in order to remove aluminum and phosphorus species, the electrolyte and unreacted carboxylic acid. The organic layer was separated and the aqueous one was extracted with additional 20 mL of ether. The organic layers were collected and washed with water, a saturated solution of NaCl, and water, and dried over anhydrous Na_2SO_4. After evaporation of the solvents, the obtained row reaction mixture was purified by column chromatography (SiO_2/toluene then toluene/ethyl acetate 9:1). The first fraction is unchanged ferrocene, the second monoacyl derivative and the third one—diacylferrocene.[‡]

4.2. General procedure for monoacylation of ferrocene in the presence of $AlCl_3$ (method B)

The solution of 1.2 mmol the corresponding carboxylic acid (**2a–q**), 1 mmol (186 mg) of ferrocene (**1**), ~1 mmol (0.1 mL) of phosphorus trichloride in 20 mL of dichloromethane was stirred for 1 h at room temperature in a two necked round bottom bottle, supplied with a magnetic stirrer and a reflux condenser under an argon atmosphere (or simply protected from air moisture with a $CaCl_2$ tube). After that, 200 mg (~1.5 mmol) of aluminum trichloride was added to this mixture, which immediately becomes dark violet. Resulted mixture was stirred for an additional hour, then worked up as in the method A.

4.3. General procedure for diacylation of ferrocene in the presence of $AlCl_3$ (method C)

The same procedure as for monoacylation of ferrocene (method B) was employed except that 1 mmol (186 mg) of ferrocene (**1**), 2.4 mmol of the corresponding carboxylic acid (**2a–q**), ~2 mmol (0.2 mL) of phosphorus trichloride and ~3.75 mmol (500 mg) of aluminum trichloride in 40 mL of dichloromethane were used, and that reaction mixture was stirred for two hours after addition of the catalyst. In addition, 40 mL of ether was added to dilute reaction mixture.

4.4. Spectral data of obtained compounds

Most of products of the present reaction are known compounds, and were already described in the literature: Thus, spectral data of compounds **4a**,[14,15] **4b**,[16,17] **4c**,[16,17] **4d**,[14] **4e**,[14,16] **4f**,[17] **4g**,[16] **4i**,[18,19] **4j**,[17] **4m**,[20,21] **4n**,[14,15] **4q**,[17] **5a**,[15,22] **5b**,[16] **5c**,[16,22] **5d**,[14,22] **5e**,[14] **5g**,[22] **5i**,[17] **5j**[17] and **5q**[23] were consistent with those from the literature.

4.4.1. Pelargonylferrocene (4h). Orange red oil; IR (KBr): ν_{max}=3097, 2926, 2854, 1670, 1455, 1411, 1379, 1256, 1107, 1075, 1026, 1002, 885, 822, 724, 533, 482 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ=0.89 (t, J=6.9 Hz, 3H), 1.28 (m, 10H), 1.70 (m, 2H), 2.69 (t, J=7.5 Hz, 2H), 4.19 (s, 5H), 4.48 (t, J=1.9 Hz, 2H), 4.78 (t, J=1.9 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ=13.9, 22.4, 24.4, 29.0, 29.2, 29.3, 31.6, 39.5, 69.1, 69.5, 71.8, 79.0, 204.3; HR-MS (FAB): m/z 326.1330, $C_{19}H_{26}OFe$ requires 326.1328.

4.4.2. (*o*-Hydroxybenzoyl)ferrocene (4r). Purple red crystals, mp 87.0–87.5°C; IR (KBr): ν_{max}=3932, 3435, 3089, 2977, 2929, 2858, 1723, 1622, 1586, 1515, 1485, 1445, 1380 1351, 1331, 1304, 1266, 1250, 1230, 1150, 1108, 1053, 1033, 1003, 955, 865, 825, 808, 758, 741, 711, 670, 574, 505, 477 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ=4.24 (s, 5H), 4.64 (t, J=1.9 Hz, 2H), 4.98 (t, J=1.9 Hz, 2H), 6.95 (m, 2H), 7.44 (m, 1H), 8.16 (m, 1H), 12.10 (s, 1H); ^{13}C NMR ($CDCl_3$) δ=70.5, 71.8, 72.5, 78.7, 118.3, 118.4, 120.6, 130.8, 135.0, 161.7, 202.3; HR-MS (FAB): m/z 306.0244, $C_{17}H_{14}O_2Fe$ requires 306.0338.

4.4.3. 1,1′-Bis(β-methylbutanoyl)ferrocene (5f). Orange red crystals, mp 59.8–60.7°C; IR (KBr): ν_{max}=3454, 3112, 3092, 2952, 2924, 2866, 1666, 1453, 1377, 1294, 1238, 1171, 133, 1093, 1066, 1029, 1001, 951, 892, 829, 751, 651, 596, 540, 464, 430, 408 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.98 (d, J=6.8 Hz, 12H), 2.24 (nonet, J=6.8 Hz, 2H), 2.54 (m, 4H), 4.46 (t, J=1.9 Hz, 4H), 4.74 (t, J=1.9 Hz, 4H); ^{13}C NMR ($CDCl_3$) δ=22.7, 24.9, 48.8, 70.5, 73.3, 80.6, 203.1; HR-MS (FAB): m/z 354.1302, $C_{20}H_{26}O_2Fe$ requires 354.1277.

4.4.4. 1,1′-Dipelargonylferrocene (5h). Deep red crystals, mp 64.1–65.2°C; IR (KBr): ν_{max}=3054, 2956, 2927, 2855, 2305, 1671, 1455, 1411, 1398, 1378, 1346, 1265, 1122, 1077, 1029, 978, 895, 827, 740, 705, 669, 595, 536, 483 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.86 (t, J=6.6 Hz, 6H), 1.27 (m, 20H), 1.66 (m, 4H), 2.62 (t, J=7.3 Hz, 4H), 4.45 (t, J=1.9 Hz, 4H), 4.74 (t, J=1.9 Hz, 4H); ^{13}C NMR ($CDCl_3$) δ=14.0, 22.6, 24.3, 29.1, 29.4, 31.8, 39.9, 70.5, 73.3, 80.4, 203.6; HR-MS (FAB): m/z 466.2533, $C_{28}H_{42}O_2Fe$ requires 466.2529.

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[‡] In the case of acetylation of ferrocene, separation of the unchanged substrate **1**, monoacetylferrocene (**4a**) and diacetylferrocene (**5a**) can be achieved by selective extraction of the crude reaction mixture (supported on SiO_2) with hexane, toluene and toluene/ethyl acetate mixture (9:1), respectively.

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