



Improvement of ferrocene acylation. Conventional vs. microwave heating for scandium-catalyzed reaction in alkylmethylimidazolium-based ionic liquids

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ARTICLE INFO

Article history:

Received 22 May 2008

Received in revised form 13 June 2008

Accepted 13 June 2008

Available online 25 June 2008

Keywords:

Ferrocene

Acylation

Ionic liquids

Scandium

Metal catalysis

ABSTRACT

Acylation of ferrocene-catalyzed by scandium triflate was thoroughly investigated. Reaction time and temperature are important parameters, in that prolonged treatment causes substrate decomposition and/or catalyst deactivation. Hydrophobic alkylmethylimidazolium-based solvents gave best results, in particular 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide. Anhydrides behave as superior acylating reagents with respect to acyl chlorides. MW irradiation allowed to quantitatively acylate ferrocene within minutes.

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1. Introduction

Ferrocene derivatives find an ever growing application in many fields, from chiral catalysis [1] to medicinal chemistry [2], to material science [3]. A number of reasons may be enumerated to explain the success of ferrocenes, among which, its unusual stability for an organometallic species: ferrocenes can be handled in the air when solid and often in solution also. Ferrocenes are reactive aromatic compounds, but they are sensitive to oxidizing agents – as most electrophilic reagents are – as well as to acids. Thus, Friedel–Crafts acylation is useful in functionalizing ferrocenes, because oxidation can be easily avoided, reaction conditions are mild, and ferrocenyl ketones may be transformed into a variety of functional groups. However, Friedel–Crafts acylation needs more than stoichiometric amounts of $AlCl_3$, thus making it necessary to dispose large amounts of material. Alternative procedure for ferrocene acylation were devised to overcome the problem of Lewis acid disposal and, possibly, to reuse it. Among them, we can mention the in situ generated mixed trifluoroacetic anhydride [4], the heterogeneous system with alumina [5] or zeolites [6], and the electrochemical catalysis [7]. In recent years a growing number of organic reactions – especially catalytic ones – has been studied in different solvent systems, such as ionic liquids (ILs) [8]. The advantages of using ionic liquids are numerous: they are non-volatile solvents, dissolve a variety of compounds, can be tailor made, and in several cases they

can be reused [9]. In the first ferrocene acylation performed in an ionic liquid, 1-ethyl-3-methylimidazolium chloroaluminate was used [10]. This pioneering method, however, presents the drawback that haloaluminate ILs are difficult to handle and are very water sensitive. Moreover, $AlCl_3$ was still needed, carboxylic anhydrides were not much reactive, and diacylated products were also formed. Later, better results were achieved using *N*-butylpyridinium tetrafluoroborate as solvent [11]. Reactions were still carried out under dry nitrogen atmosphere, and high yields of monoacyl ferrocenes were reported with 10% molar ytterbium triflate, although not consistent with the “considerable abundance of oxidation” observed.

Metal triflates have been used as catalysts for acylation of other aromatic compounds, such as electron rich methoxybenzenes [12] and also methyl- and halobenzenes [13], in alkylmethylimidazolium ILs. Alkylation also has been performed in the same type of ILs [14]. As to metal triflates, the best performances were given by lanthanides and scandium. In fact, scandium triflate is a Lewis acid not decomposed by water [15] and was used as a Friedel–Crafts catalyst in molecular solvents also [16]. The use of lanthanides in ionic liquids has been recently reviewed [17]. In the last few years we were interested in exploring how metal-catalyzed reactions behave in ILs [18]. This and our long lasting interest in ferrocene chemistry [19] prompted us to investigate how Friedel–Crafts acylation can be performed in imidazolium-based ILs – more versatile than pyridium-based ones – with scandium triflate, less expensive than lanthanides, as catalyst. For comparison purposes, the reaction was performed also in molecular solvents. The screening

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was made exploring other reaction parameters also, such as reactants/catalyst ratio, catalyst nature, acylating reagent, temperature, added acid or base, workup procedure, recycle.

2. Results and discussion

2.1. Effect of solvent

The study began performing ferrocene (FcH) acetylation in molecular solvents, both with acetyl chloride (AcCl) and acetic anhydride (Ac₂O). 0.1 mmol Sc(OTf)₃ were used with 1 mmol FcH and 1 mmol acetylating reagent. In nitromethane, FcH conversion was quite low with AcCl, (10% at 25 °C, 37% at 50 °C) and isolated yields of acetylferrocene (FcAc) were even lower, most likely because FcH disappearance is partly due to decomposition. With Ac₂O, some better results were obtained (at 25 °C, only 10% conversion in dichloromethane, but 42% in MeNO₂ and 21% in MeCN). Increasing the temperature led to an improvement of conversion (38% in MeCN at 50 °C) and also of isolated FcAc, up to 30% on the basis of initial FcH.

These disappointing results notwithstanding, investigation was extended to Ionic Liquids as solvents, where improved reactivity is often observed [9,18]. Hydrophobic and hydrophilic imidazolium-based ILs were tested. The terms hydrophilic and hydrophobic are normally used with ionic liquids [9a], the former for ILs that form a single phase with water, the latter for ILs that dissolve very small quantities of water, thus forming two-phase systems. A list of ionic liquids used and relative abbreviations are in Scheme 1.

Hydrophilic 1-butyl-3-methylimidazolium triflate, bmimOTf, dissolves well Sc(OTf)₃, but almost no reaction occurred after days (1% acetylferrocene). Most likely, TfO⁻ exerts a common ion effect

and interferes with scandium triflate dissociation, thus inhibiting the catalyst.

In hydrophobic bmimPF₆, 1-butyl-3-methylimidazolium hexafluorophosphate, interesting conversions were obtained (around 80%, Table 1, entries 2–4). Isolated yields of acetylferrocene were up to 64% on the basis of reacted ferrocene (47% vs. initial FcH). Excess Ac₂O (Table 1, entry 3) did not give any disubstituted product, thus allowing to reduce reaction time and, consequently, the ferrocene decomposition due to prolonged exposure to acid [20]. Reduced decomposition was observed also raising the temperature from 25 °C to 50 °C, with resulting shorter reaction time (Table 1, entries 2 and 3).

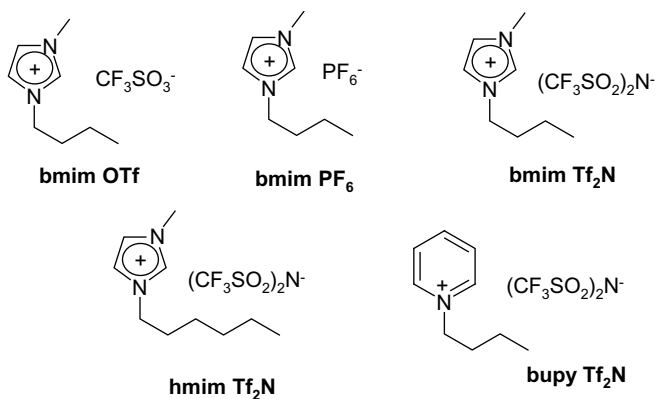
Even better results were obtained in bmimNTf₂, 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide, the other hydrophobic IL investigated (Table 1, entry 4), with 93% FcH conversion and 78% FcAc isolated yield (73% vs. initial FcH). However, ferrocene is not much soluble in bmimNTf₂ and therefore other bis(trifluoromethanesulfonyl) imides were tested, with cations that could ensure an improved solubility, such as *N*-butylpyridinium (bupyNTf₂, Table 2, entry 1) and 1-hexyl-3-methylimidazolium (hmimNTf₂, Table 2, entry 2). It is clear that bmimNTf₂ is the solvent where FcH conversion is higher and decomposition is lower. A reaction performed in Ac₂O as solvent under the same conditions – apart from the Ac₂O excess – gave 66% conversion and a FcH:FcAc ratio 48:52, with 20% decomposition. Therefore, for subsequent throughout investigation, the following reaction conditions were chosen: 1 mmol FcH in 1 mL bmimNTf₂ with excess Ac₂O was heated at 50 °C, added with catalyst, and let to react for 2.5 h, unless otherwise stated.

2.2. Effect of concentration

Increase of FcH concentration (Table 3, entry 2 vs. 1) accelerated conversion, but not yield. With reduced amounts of Ac₂O (Table 3, entries 3 and 4), conversion was very high, almost quantitative, but some decomposition of FcH occurred, because isolated FcAc reached 76% yield only.

2.3. Effect of reaction conditions

Under all examined conditions, there is a loss of product, because isolated FcAc and recovered FcH did not sum up the initial amount of ferrocene, but no other product is formed. The reaction was performed also under inert atmosphere (nitrogen), with ILs degassed and dehydrated under vacuum at 60 °C 2–3 h. Results were the same, within experimental error, as those obtained in the presence of air. Therefore, decomposition is likely due to the acid formed as by-product from the acetylating agent. In fact, using acetyl chloride, that produces HCl, the reaction yielded mainly decomposition of FcH. To verify this hypothesis, experiments were performed, under different conditions. First, the reaction was per-



Scheme 1. Ionic liquids used as solvents in ferrocene acylation.

Table 1
Scandium-catalyzed acetylation of ferrocene in 1-butyl-3-methylimidazolium salts^a

Entry	Anion	Temp. (°C)	Time (h)	Molar ratio FcH:Ac ₂ O:Sc(OTf) ₃	Conversion ^b (%)	Relative ratio FcH:FcAc ^c	Yield ^d (%)
1	TfO	25	96	1:1:0.1	1	99:1	<1
2	PF ₆	25	4	1:1:0.1	79	75:25	21
3		50	3	1:1:0.1	67	20:80	57
4		50	2.5	1:5:0.1	73	32:68	64
5	Tf ₂ N	50	2.5	1:5:0.1	94	7:93	78

^a FcH 1 M.

^b Calculated from recovered FcH.

^c GC analysis with tetradecane as internal standard.

^d Isolated FcAc, yield relative to conversion.

Table 2
Scandium-catalyzed acetylation of ferrocene in bis(trifluoromethanesulfonyl)imides at 50 °C^a

Entry	Cation	Time (h)	Molar ratio FcH:Ac ₂ O:Sc(OTf) ₃	Conversion ^b (%)	Relative ratio FcH:FcAc ^c	Yield ^d (%)
1	bupy	2.5	1.0:1.3:0.10	89	15:85	75
2	hmim	2.5	1.0:1.3:0.10	17	93:3	2
3	bmim	2.5	1.0:5.0:0.10	94	7:93	78

^a FcH 1 M.^b Calculated from recovered FcH.^c Analysis with tetradecane as internal standard.^d Isolated FcAc, yield relative to conversion.**Table 3**
Scandium-catalyzed acetylation of ferrocene in bmimNTf₂, at 50 °C, with different Ac₂O excess

Entry	Time (h)	[FcH] (M)	Molar ratio FcH:Ac ₂ O:Sc(OTf) ₃	Conversion ^a (%)	Relative ratio FcH:FcAc ^b	Yield ^c (%)
1	2.5	1.0	1.0:5.0:0.10	94	7:93	78
2	2.0	2.0	1.0:5.0:0.10	ca. 100	1:99	76
3	3.5	1.0	1.0:2.5:0.10	100	0:100	66
4	3.5	2.0	1.0:2.5:0.10	79	22:78	76

^a Calculated from recovered FcH.^b Analysis with tetradecane as internal standard.^c Isolated FcAc, yield relative to conversion.**Table 4**
Scandium-catalyzed acetylation of ferrocene in bmimNTf₂, under different conditions^a

Entry	IL	Temp. (°C)	Time (h)	Molar ratio FcH:Ac ₂ O:Sc(OTf) ₃	Conversion ^b (%)	Relative ratio FcH:FcAc ^c	Yield ^d (%)
1 ^e	bmimNTf ₂	60 ^f	2.5	1:2.5:0.05	85	7:93	61
2 ^e	bmimNTf ₂ ^g	60	2.5	1:2.5:0.05	96	10:90	34
3	bmimNTf ₂ + Na ₂ CO ₃	50	2.5	1:3.0:0.10	17	94:6	57
4	bmimNTf ₂ + AcOH ^h	50	2.5	1:2.5:0.05	95	6:94	78
5	bmimNTf ₂ + TfOH ^h	50	2.5	1:2.5:0.05	100	0:100	10

^a FcH 1 M.^b Calculated from recovered FcH.^c GC analysis with tetradecane as internal standard.^d Isolated FcAc, yield relative to conversion.^e Workup: sublimation.^f Temperature was increased with the aim to completely transform ferrocene.^g Recycle of run 1.^h Equimolar with FcH.

formed at higher temperature (with half catalyst) and repeated on the same batch of IL/catalyst, removing by sublimation FcH and FcAc (Table 4, entry 1) and recharging with ferrocene and Ac₂O (Table 4, entry 2). After the same reaction time, FcH conversion was higher in the second run, but FcAc was obtained in much lower yield, thus indicating a higher extent of decomposition, no other product being present. Then, the reaction was performed in the presence of a base, such as sodium carbonate, not completely dissolved, in order to neutralized the acid formed. However, in this conditions deactivation of the catalyst occurs, since a very low conversion was achieved (Table 4, entry 3). Finally, the reaction was carried on with added AcOH (Table 4, entry 5), with no effect on either conversion or FcAc yield. These experiments suggest that the prolonged contact with acids (that in ILs should have an increased acidity) decomposes ferrocene and, likely, the catalyst. To verify the hypothesis, the reaction was made in the presence of an equimolar amount of triflic acid, as suggested by one referee. However, extensive decomposition resulted, with very low amount of acetylferrocene recovered (Table 4, entry 5). This results seems to indicate that catalysis by free acid, that is at work in metal triflate-catalyzed benzoylation of anisole in ILs [21], is not effective with ferrocene with which it is advisable to perform the reaction

under conditions that ensure a fast transformation, keeping decomposition at the minimum.

2.4. Effect of catalyst triflate

Different catalysts were also tested, under the best reaction conditions (FcH 1 M, 50 °C, 2.5 h, 10% molar catalyst, fivefold excess Ac₂O). After the same reaction time, scandium triflate resulted more efficient than yttrium and ytterbium salts (Table 5, entries 5, 1 and 3), producing the highest isolated yield of FcAc, whereas FcH conversion was slightly lower. However, longer reaction times, with yttrium catalyst caused quantitative disappearance of FcH, without any increase of FcAc yield (Table 5, entry 2).

As to the ytterbium catalyst, FcH conversion is the same as that with scandium, but yields are definitely lower (Table 5, entry 4). Thus, the less expensive Sc(OTf)₃ was a better Friedel–Crafts catalyst for ferrocene acetylation than lanthanides.

2.5. Effect of catalyst amount

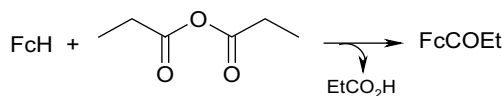
Although 10% molar for the Lewis acid is an improvement with respect of the stoichiometric AlCl₃, it is still a considerable amount

Table 5
Acetylation of ferrocene in bmimNTf₂, at 50 °C, with different metal triflates^a

Entry	Catalyst	Time (h)	Molar ratio FcH:Ac ₂ O:Sc(OTf) ₃	Conversion ^b (%)	Relative ratio FcH:FcAc ^c	Yield ^d (%)
1	Y(OTf) ₃	2.5	1:5:0.10	94	12:88	66
2		8.0	1:5:0.10	100	0:100	67
3	Yb(OTf) ₃	2.5	1:5:0.10	95	17:83	59
4		5.5	1:5:0.10	95	5:95	64
5	Sc(OTf) ₃	2.5	1:5:0.10	94	7:93	78

^a FcH 1 M.^b Calculated from recovered FcH.^c Analysis with tetradecane as internal standard.^d Isolated FcAc, yield relative to conversion.**Table 6**
Acetylation of ferrocene in bmimNTf₂, at 50 °C, with different amounts of Sc(OTf)₃

Entry	Catalyst (mol%)	[FcH] (M)	Time (h)	Molar ratio FcH:Ac ₂ O:Sc(OTf) ₃	Conversion ^a (%)	Relative ratio FcH:FcAc ^b	Yield ^c (%)
1	10	1.0	2.5	1:5:0.1	94	7:93	76
2	5	1.0	2.5	1:5:0.05	89	32:69	43
3	5	1.0	9.0	1:5:0.05	94	14:86	55
4	5	1.0	2.5 (60 °C)	1:5:0.05	100	0:100	60
5	1	1.0	2.5	1:5:0.01	32	90:10	20
6	1	1.0	29.5	1:2.5:0.01	95	83:17	37

^a Calculated from recovered FcH.^b GC analysis with tetradecane as internal standard.^c Isolated FcAc, yield relative to conversion.**Table 7**
Sc(OTf)₃-catalyzed acylation of ferrocene with propanoic anhydride under different conditions

Run	IL	Fc:(EtCO) ₂ O:cat	Time (h)	Temp. (°C)	Workup	Conversion ^a (%)	FcCOEt ^b (%)
1	bmimNTf ₂	1:3:0.1	2.5	50	Extraction	78	63
2	bmimNTf ₂	1:3:0.1	2	60	Extraction	71	71
3	bmimNTf ₂	1:1:0.1	48	50	Extraction	57	52
4	bmimNTf ₂	1:1:0.1	48	50	Distillation	57	52
5	bmimNTf ₂ ^c	1:1:0.1	96	50	Distillation	38	6
6	bmimNTf ₂	1:2:0.1	17	60	Extraction	98	72
7	bmimNTf ₂ ^d	1:2:0.1	17	60	Distillation	97	2.4
8	bupyNTf ₂	1:2:0.1	56	50	Extraction	78	31
9 ^e	bupyNTf ₂	1:2:0.1	56	50	Distillation	83	36

^a Calculated from recovered FcH.^b Isolated FcCOEt, yield relative to conversion.^c Recycle of run 4.^d Recycle of run 6.^e Recycle of run 8.

of a precious catalyst. Therefore, experiments were performed reducing the catalyst. Five percent molar Sc(OTf)₃ is still efficient, but it is advisable to increase the temperature up to 60 °C, to avoid prolonged reaction times (Table 6, entries 2–4). With 1% molar Sc(OTf)₃, efficiency decreased too much and increasing reaction time did not affect significantly FcH conversion, nor isolated quantity of ketone (Table 6, entries 5 and 6).

To summarize results of acetylation, acetylferrocene can be obtained in good yields using scandium triflate as Lewis acid and bmimNTf₂ as solvent. Excess Ac₂O is advisable, because it helps in solubilizing FcH and speeding up the reaction; moreover, no

diacetylferrocene was ever found. No oxidation of ferrocene occurred in bmimNTf₂, at odd from what reported for the reaction in bupyBF₄ [11].

2.6. Effect of different acylating reagents

In order to establish the scope of the reaction, different acylating reagents were used. Experiments with acyl chlorides were abandoned after some attempts that gave disappointing results, likely because of the formation of HCl, that in IL at 50 °C causes extensive decomposition of ferrocene. Propanoic anhydride (Table

Table 8
Acylation of ferrocene in bmimTf₂N-catalyzed by Sc(OTf)₃ with MW irradiation^a

Entry	A ^b	FcH:A:cat molar ratio	T _{bulk} (°C)	Time (min)	Conversion ^c (%)	GC yield ^c (%)
1	Ac ₂ O	1:5:0.05	80	3.5	80	77
2 ^d	Ac ₂ O	1:10:0.05	105–110	3.5	94	93
3 ^{d,e}	Ac ₂ O	1:5:0.05	105–110	7.0	88	79
4 ^f	Ac ₂ O	1:5:0.05	95	4.5	100	100
5	Ac ₂ O	1:5:0.05	115	1.5	100	100
6 ^g	Ac ₂ O	1:5:0.05	72–74	2.0		30
7 ^g	Ac ₂ O	1:5:0.05	65	5.0		38
8	(EtCO) ₂ O	1:5:0.05	116–120	4.5 ^h	92	84 ⁱ
9	(EtCO) ₂ O	1:5:0.05	92–96	2.0 ^j	>99	86 ^k
10	(PhCO) ₂ O	1:5:0.05	127–155	4.5	98	42

^a 1 mmol FcH in 1 mL IL, previously dried; MW irradiation at W = 5 W (10 W in entry 1, 40 W in entry 7), under stirring and simultaneous cooling with compressed air at 30–40 (or 40–50) psi.

^b Acylating reagent.

^c Conversion determined by GC analysis with dodecane as internal standard.

^d 0.5 mmol FcH.

^e Catalyst added in two portions.

^f 0.25 mmol FcH.

^g In MeCN.

^h Three irradiation cycles, 1.5 min each.

ⁱ After column chromatography, 72% propanoylferrocene was isolated, together with 18% disubstituted ketones.

^j Single irradiation cycle.

^k After column chromatography, 84% propanoylferrocene was recovered, together with 13% disubstituted ketones.

7) gave good yields of propanoylferrocene, that was isolated either by extraction with diethyl ether, or by direct distillation under vacuum from the reaction mixture. After the latter workup, a recycle was attempted, re-loading with FcH and propanoic anhydride. Unfortunately, even after prolonged reaction times, only a small amount of propanoylferrocene was obtained (Table 7, entry 5). The reaction was performed also in a pyridinium based IL, i.e., 1-butylpyridinium bis(trifluoromethanesulfonyl) imide, bupyNTf₂. The results were not as good as in bmimNTf₂ (Table 7, entries 8 and 9). Attempts to recycle IL/catalyst confirmed that prolonged exposure to acidic medium is detrimental for FcH and/or the catalyst. No product at all was obtained with butanedioic or chloroethanoic anhydride and only traces of trifluoroacetylferrocene were detected. As to aromatic anhydrides, benzoic anhydride was scarcely reactive, since 24 h heating produced, at best, only 25% isolated benzoylferrocene.

2.7. Effect of microwave activation

To complete the exploration of reaction parameters, we decided to investigate the effect of microwaves, that should be readily absorbed by the ionic solvent. When microwave irradiation was used to heat the reaction mixture (Table 8), it was possible to drastically reduce reaction times, from hours to minutes. Different runs were performed, varying the initial concentration of ferrocene, the acetic anhydride excess, and the number of irradiation cycles. Addition of the catalyst in two portions did not improve the yield (Table 8, entry 3). Under best conditions, 5% molar catalyst yielded quantitatively acetylferrocene in 1.5 min (Table 8, entry 5). On the other hand, the same yields as with conventional heating were achieved in acetonitrile (Table 8, entries 6 and 7). It is worth mentioning that T_{bulk} in MeCN remained lower than in IL, despite the different irradiation power used (40 W in MeCN, 5 W in IL). This is due to the more efficient MW absorption by ionic species in comparison with the molecular solvent [22].

Excellent results were obtained by MW heating also with propanoic anhydride (Table 8, entries 8 and 9). In fact, fast quantitative conversion of ferrocene was accompanied by high yield of propanoylferrocene. The reaction mixture was also chromatographed and isolated yields were similar to GC ones. For example, from run of entry 9 propanoylferrocene was isolated in 84% yield, to-

gether with 13% 1,1'-dipropanoylferrocene. Total isolated products account for 97% of initial ferrocene, thus confirming that decomposition is due to prolonged heating. Also benzoylferrocene yield improved from 25% (conventional heating) to 42% with MW irradiation.

3. Conclusion

In conclusion, an extensive investigation of ferrocene acylation was performed. In our hands, imidazolium-based ionic liquids were superior to pyridinium based ones as solvents for ferrocene acylation, and scandium triflate as catalyst was better than yttrium or ytterbium triflates. A major improvement was realized using microwaves as heating source, where, in the best performance, quantitative GC and isolated yields of ferrocenylketones were reached within minutes. Thus, the results presented above clearly show that the protocol IL-MW-Sc(OTf)₃ is, at present, the most efficient in ferrocene acylation.

4. Experimental section

4.1. General

Mass spectra were recorded with a GC/MS Shimadzu CP 6000 instrument. GC analyses were performed with a Varian CP 3900, equipped with a Supelco SPB-1701 capillary column 30 m × 0.25 mm, coated with a 0.25 mm film of methylsilicone.

¹H NMR spectra were recorded with a Bruker AV 300 spectrometer, with CDCl₃ as solvent and using residual signal solvent as reference (7.28 ppm).

Commercial grade solvents were used. Ionic liquids were synthesized according to general methods [23], preparing bromides first and then exchanging the anion with the appropriate salt (Tf₂NLi, CF₃SO₃K, and KPF₆).

4.2. Procedure for conventionally heated acylation

In a typical experiment, 1 mmol FcH was weighed in a round-bottomed 10 mL flask, added with known amounts of solvent (either molecular or ionic) and acylating reagent. The resulting

mixture was heated in a thermostatted oil bath and, finally, the weighed amount of catalyst was introduced. The reaction course was followed by TLC. In the workup, different procedures were followed. For reactions performed in molecular solvents, the solvent was removed under vacuum and the residue chromatographed. For reactions performed in ILs, solvent extraction or distillation was used. Alternatively, the reaction mixture was directly chromatographed on a silica gel column.

4.2.1. Extraction

The reaction mixture was repeatedly extracted with diethyl ether, until colourless organic phase and acylferrocenes were purified by column chromatography.

4.2.2. Distillation

The reaction flask was introduced into a Kugelrohr distillation apparatus and distilled under reduced pressure. When volatile acids formed as by-products, pure acylferrocenes were obtained. With less volatile acids, an extraction with aqueous NaHCO_3 or a column chromatography yielded pure acylferrocenes.

Purity and identity of products was checked by GC/MS and ^1H NMR analyses and by comparison with authentic samples.

4.3. Procedure for microwave heated acylation

Microwave experiments were performed with use of a mono-mode microwave apparatus operating at 2.45 GHz with continuous irradiation power. In a typical experiment, FcH (1 mmol) was weighed in a vessel, added with known amounts of solvent, the acylating reagent (5 mmol) and, finally, the weighed amount of catalyst (0.05 mmol). The reaction vessel was placed in the single-mode cavity of the instrument and irradiated for the required time with power at 5 W (with ionic liquid) or 40 W (with acetonitrile) under simultaneous stirring and cooling by a stream of compressed air. The reaction was sampled by quantitative GC analysis after dilution in CH_2Cl_2 containing dodecane as internal standard. Blank experiments with ferrocene and Ac_2O in IL without $\text{Sc}(\text{OTf})_3$ gave no product with both conventional and MW heating.

Acknowledgments

Experimental contribution by undergraduate students Valentina Armuzza and Sara Lentini is acknowledged. Marcella Bonchio and Gianfranco Scorrano (ITM-CNR and Department of Chemical Sciences, Padova) are gratefully thanked for hospitality in MW experiments.

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